(Creation)2018 年 2 月 20 日

Magnetism of Metals (金属磁性)

HAMADA Noriaki (浜田典昭)
Osaka U. (大阪大学大学院 基礎工学研究科)
Tokyo U. of Science (東京理科大学理工学部)

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

Magnetic Impurity （磁性不純物）

3d Transition Metal （3d 遷移金属 ）

Magnetic Alloy （磁性合金）

（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）

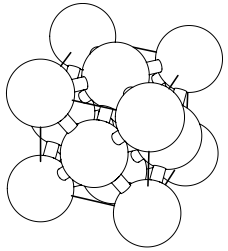
(4) J. R. Hook & H. E. Hall「Solid State Physics (2nd ed.)」(Wiley, 1991）

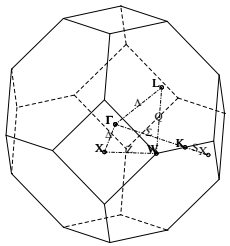
(S.I.)

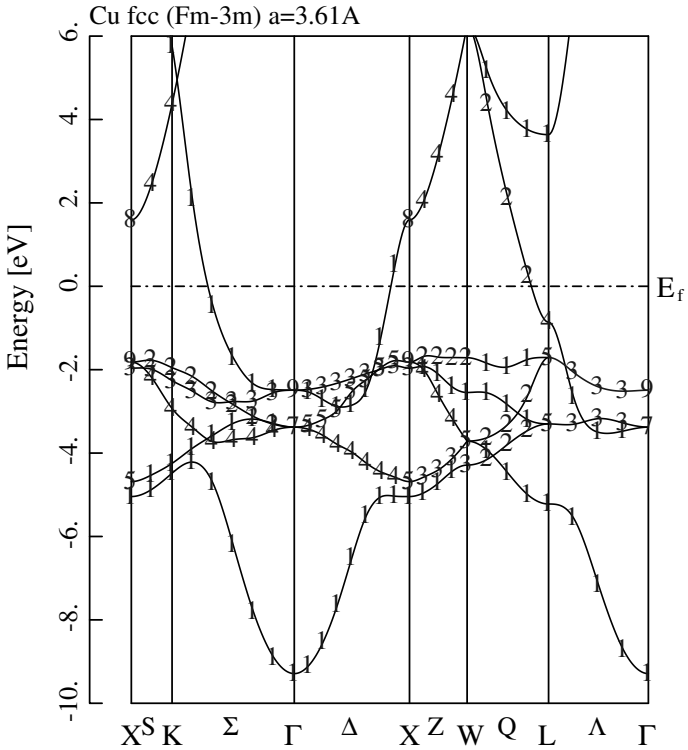
$$\boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M})$$

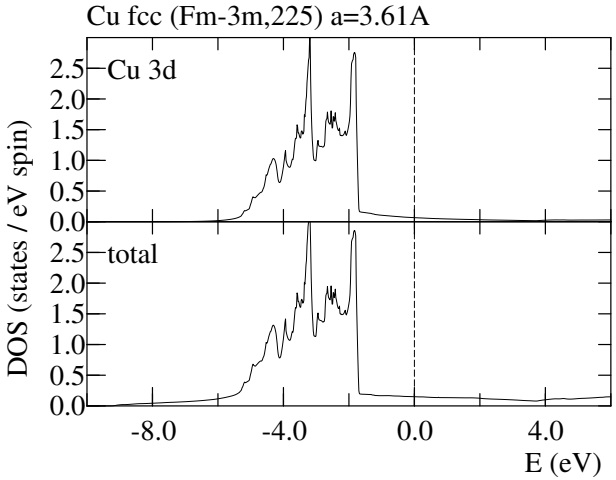
s, p band (∼ 15 eV) and d band (∼ 6 eV) for 3d transition metals

Cu

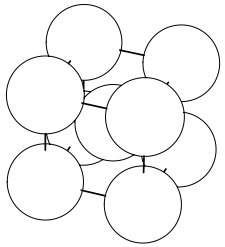


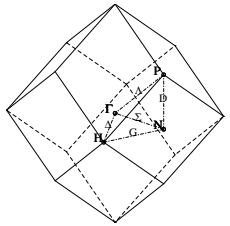


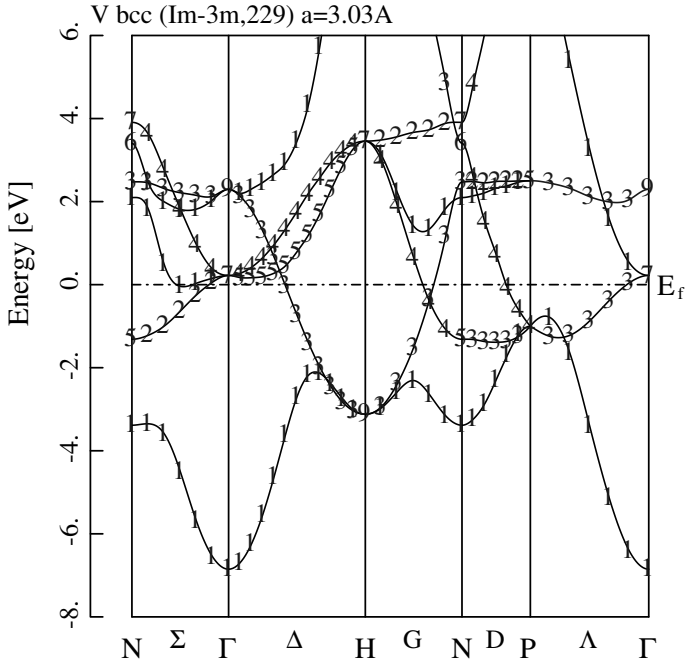


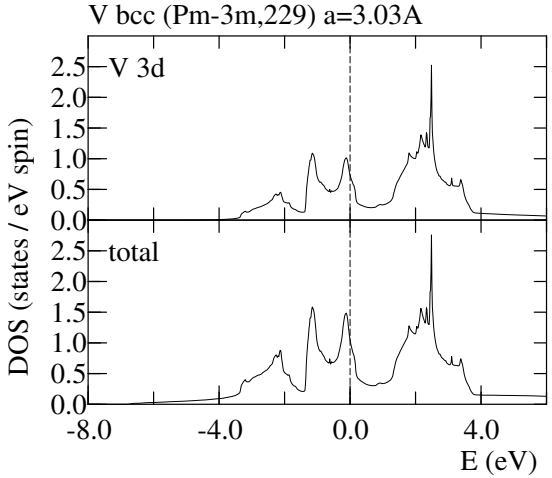


V



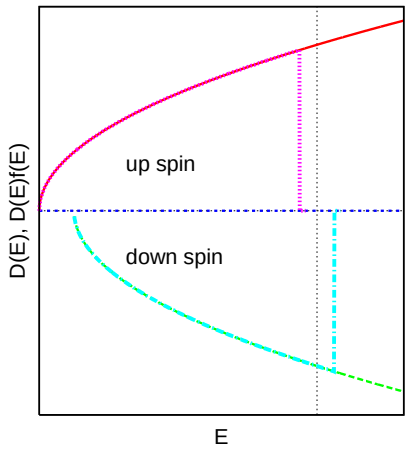






1 Conduction electron paramagnetism (常磁性)

Zeeman splitting : ($\pm\mu_{\mathrm{B}}B$)



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

$M = \mu_{\mathrm{B}}B \times D(E_{\mathrm{F}}) \times 2 \times \mu_{\mathrm{B}}$

Pauli paramagnetic susceptibility :

$$\chi_{\mathrm{P}} = \frac{\mu_0 M}{B} = 2\mu_0\mu_{\mathrm{B}}^2 D(E_{\mathrm{F}})$$

Temperature independent

	$10^6\ \chi_{\mathrm{P}}$	
Metal	Free el.	exp.
Li	0.80	2.0
Na	0.66	1.1
K	0.53	0.85
Rb	0.40	0.8
Cs	0.46	0.8
metal	Band cal.	exp.
Ti	5.29	7.4
V	2.80	5.3

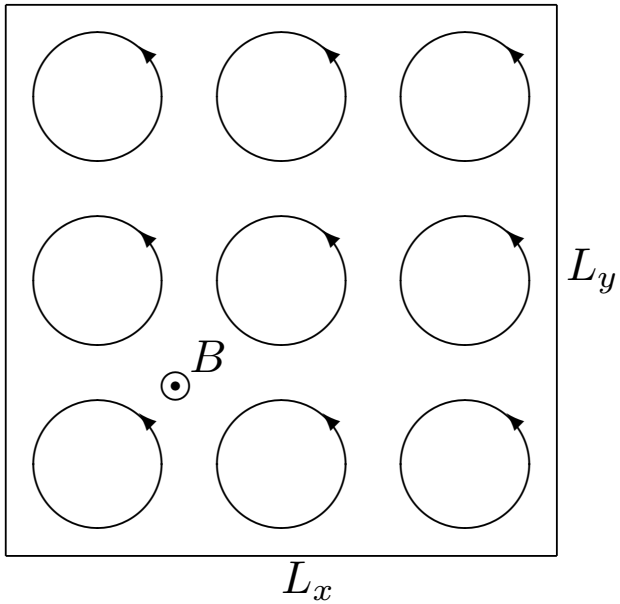
Deviation from the Free electron

Atomic potential

Electron-electron interaction

Electron-phonon interaction

2 Free electron under the uniform magnetic field



(Classical picture)

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

$\boxed{\omega_{\mathrm{c}} = \dfrac{v}{r} = \dfrac{eB}{m}}$: cyclotron frequency

v, r : arbitrary

When $B = 1$ T,

$\omega_{\mathrm{c}} \approx 1.8\times10^{11}$ rad·s^{-1}, $\hbar\omega_{\mathrm{c}} \approx 1.2$ meV

2.1 Landau level

(Quantum mechaical treatment)

Magnetic field: $\boldsymbol{B} = (0, 0, B) = \mathrm{rot}\boldsymbol{A}$

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

Free electron system:

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

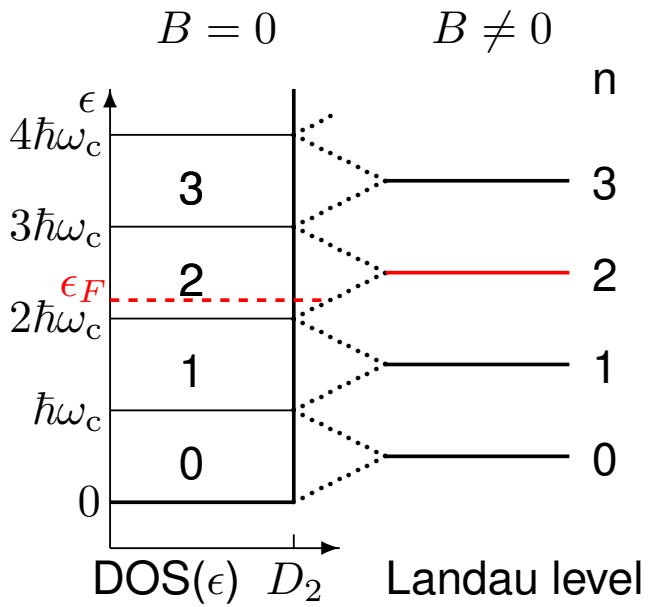
Eigenenergy:

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

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

n: Landau level index

2-D free-electron system



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

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: $l = \sqrt{\dfrac{\hbar}{eB}}$

$\sim$ 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 : $E_2(B)$ ($E = E_0 + E_2(B)$)

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

3 Landau diamagnetic susceptibility (Landau 反磁性)

($T \sim 300$K, $k_{\rm B}T \sim 30$meV, $B \sim 10^{-2}$T, $\hbar\omega_{\rm c} \sim 10^{-2}$meV, $\epsilon_{\rm F} \sim 1$eV, $n \sim 10^5$)

$k_{\rm B}T \gg \hbar\omega_{\rm c}$

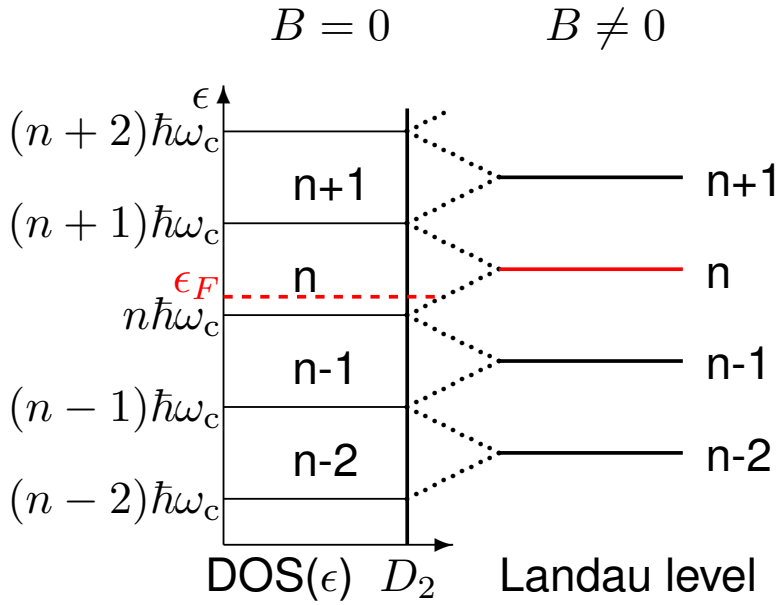
average over various Fermi energy : $n\hbar\omega_{\rm c} \le \epsilon_{\rm F} \le (n+1)\hbar\omega_{\rm c}$

$$\langle E_2(B)\rangle = \frac{1}{\hbar\omega_{\rm c}}\int_{n\hbar\omega_{\rm c}}^{(n+1)\hbar\omega_{\rm c}} {\rm d}\epsilon_{\rm F}\, E_2(B) = \frac{1}{3}\mu_{\rm B}^2 D(\epsilon_{\rm F})B^2$$

$$\begin{aligned} M(B) &= -\frac{{\rm d}\langle E_2(B)\rangle}{{\rm d}B} \\ \chi_{\rm L} &= \frac{\mu_0 M(B)}{B} \\ &= -\frac{2}{3}\mu_0\mu_{\rm B}^2 D(\epsilon_{\rm F}) \\ &= -\frac{1}{3}\chi_{\rm P} \end{aligned}$$

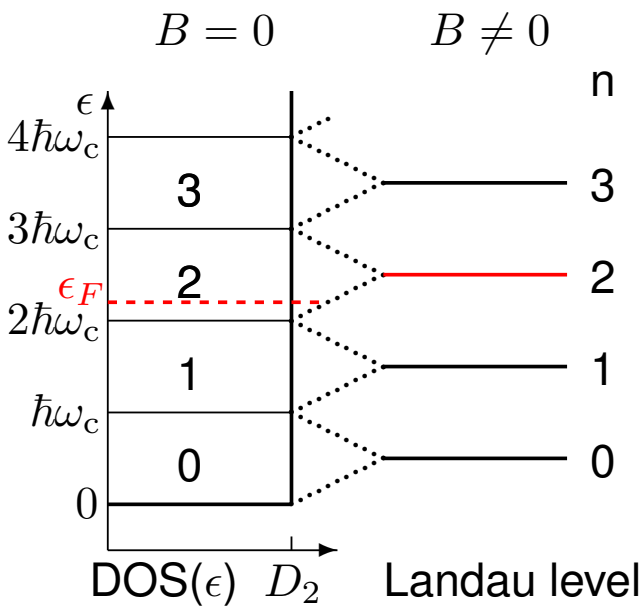
$\chi_{\rm L}$ Landau susceptibility

$\chi_{\rm P}$ Pauli susceptibility

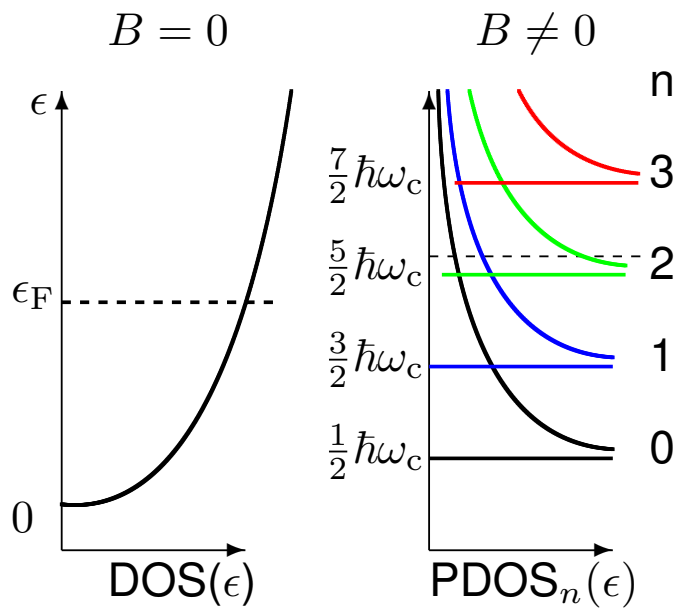


2-D free-electron system

2D vs. 3D

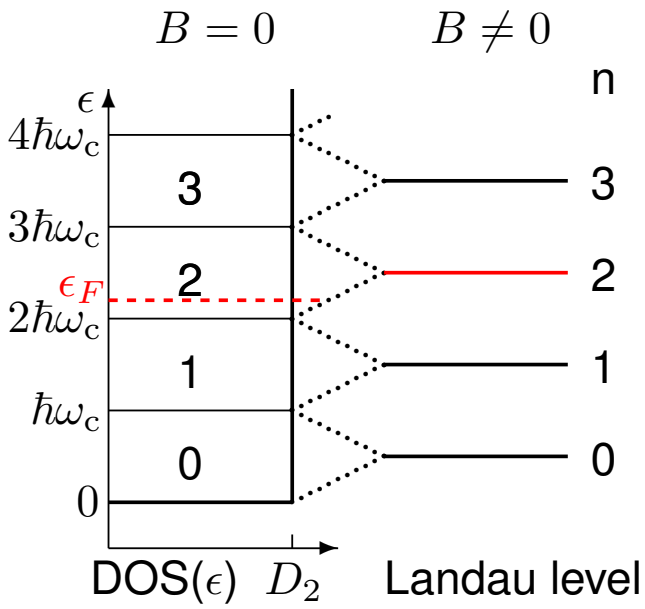


2-D free-electron system



3-D free-electron system

4 de Haas - van Alphen effect



2-D free-electron system

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 :

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

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

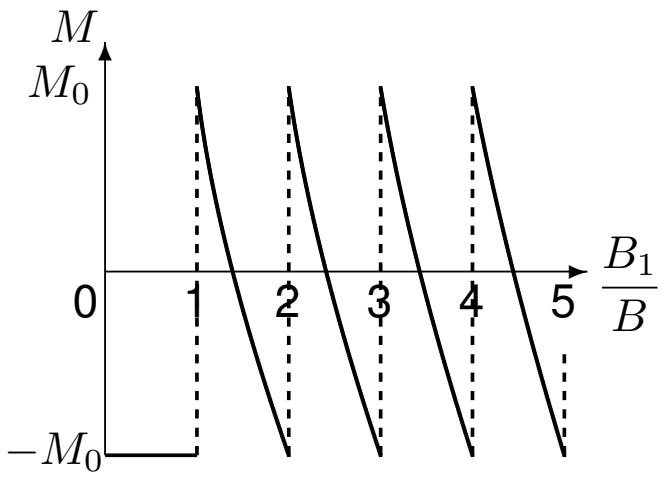
$$M(B) = -\frac{\partial E_2(B)}{\partial B} = -\mu_B\left[(\epsilon_F - n\hbar\omega_c)(n+1) - ((n+1)\hbar\omega_c - \epsilon_F)n\right] D_2$$

$$= -\mu_B \epsilon_F D_2 B\left[\left(\frac{1}{B} - \frac{n}{B_1}\right)(n+1) - \left(\frac{n+1}{B_1} - \frac{1}{B}\right)n\right]$$

de Haas - van Alphen effect

Magnetization oscillates as a function of B.

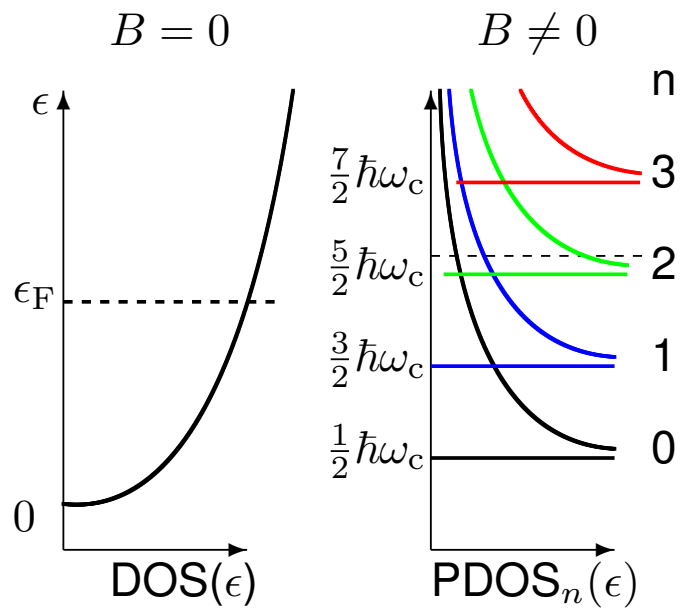
In the 2-D free-electron system,



$M_0 = \mu_{\mathrm{B}} \epsilon_{\mathrm{F}} D_2$

$\hbar\omega_{\mathrm{c}} = \epsilon_{\mathrm{F}}$ when $B = B_1$

In the 3-dimensional system,



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

$\Downarrow$

oscillation of $1/B$ plot

$\Rightarrow$ Fermi surface

(extremal orbit)

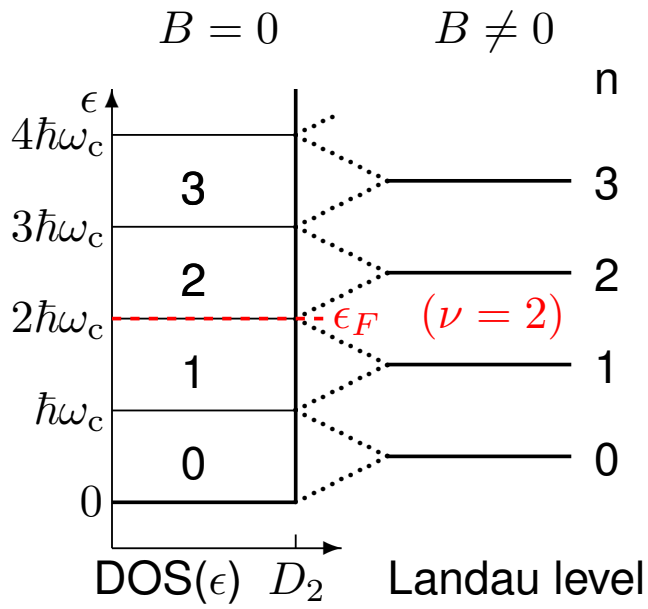
$T \sim 1$K, $k_{\mathrm{B}}T \sim 10^{-1}$meV, $B \sim 10$T, $\hbar\omega_{\mathrm{c}} \sim 10$meV, $\epsilon_{\mathrm{F}} \sim 1$eV, $n \sim 100$

5 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 $v_{\rm c} = \dfrac{E_x}{B}$, which causes the Hall current

$$J_y = e v_c N_{\rm e} = \frac{e N_{\rm e}}{B} E_x \ ,$$

where $N_{\rm e}$ is the total electron number per unit area. Namely, the Hall conductivity is $\boxed{\sigma_{yx} = \dfrac{e N_{\rm e}}{B}}$



2-D free-electron system

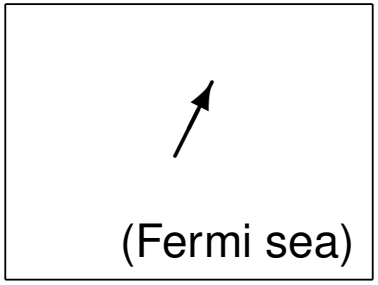
When $\dfrac{N_{\rm e}}{N(B)} = \nu \quad (\nu = 1, 2, \cdots)$, the sysmem becomes insulator. The condition gives $\dfrac{N_{\rm e} h}{eB} = \nu$; namely, $\boxed{\dfrac{e N_{\rm e}}{B} = \nu \dfrac{e^2}{h}}$.

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

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

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

6 Magnetic Impurity 1 (Kondo effect: $T \lesssim T_{\mathrm{K}}$)



(Example) Fe in Cu

At high temperatures

Susceptibility : Curie low

Local magnetic moment

$\Downarrow$

At low tempteratures

Susceptibility : $\rightarrow$ a constant

No local moment

Kondo singlet state

Kondo effect

6.1 Anderson Model

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

$$H = \sum_{\boldsymbol{k}\sigma} \epsilon_{\boldsymbol{k}\sigma}\, c_{\boldsymbol{k}\sigma}^\dagger c_{\boldsymbol{k}\sigma} + \sum_\sigma \epsilon_{\mathrm{d}} n_\sigma + U n_\uparrow n_\downarrow + \frac{1}{\sqrt{N_{\mathrm{A}}}} \sum_{\boldsymbol{k}\sigma} \left\{ V_{\boldsymbol{k}}\, c_{\boldsymbol{k}\sigma}^\dagger d_\sigma + V_{\boldsymbol{k}}^*\, d_\sigma^\dagger c_{\boldsymbol{k}\sigma} \right\}$$

For a "magnetic" impurity:

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

$$\Downarrow$$

Large U perturbation theory breaks down

at low temperatures.

($T \lesssim T_{\mathrm{K}}$)

6.2 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

$$H' = \frac{1}{\sqrt{N_{\mathrm{A}}}}\sum_{\boldsymbol{k}\sigma}\left\{V_{\boldsymbol{k}}c_{\boldsymbol{k}\sigma}^{\dagger}d_{\sigma} + V_{\boldsymbol{k}}^{*}d_{\sigma}^{\dagger}c_{\boldsymbol{k}\sigma}\right\}$$

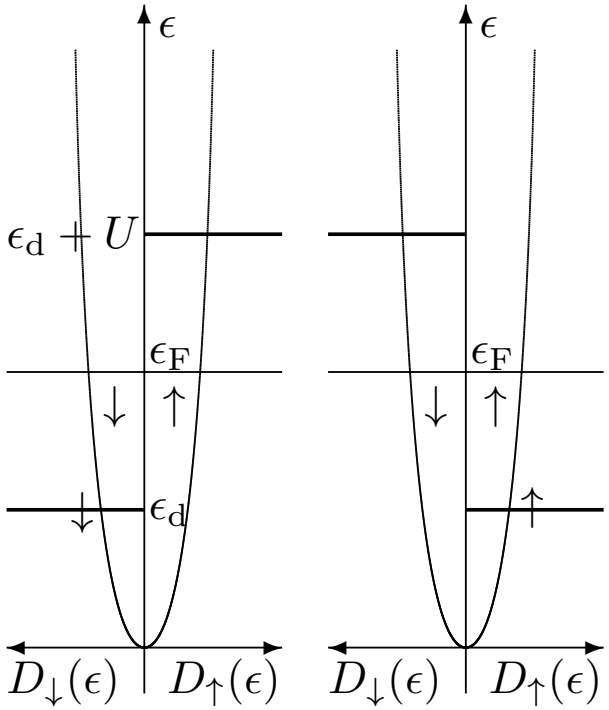
Approximations: $\boxed{\begin{array}{l} V_{\boldsymbol{k}\sigma} = V \quad (\ll U) \\ \epsilon_{\boldsymbol{k}\sigma} \sim \epsilon_{\mathrm{F}} = 0 \end{array}}$

$\Downarrow$ (2-nd order perturbation)

Effective Hamiltonian:

$$\begin{aligned} H_{\mathrm{eff}} =& \frac{1}{N_{\mathrm{A}}}\sum_{\boldsymbol{k}\boldsymbol{k}'\sigma}\frac{V^2}{2}\left(\frac{1}{-\epsilon_{\mathrm{d}}} - \frac{1}{\epsilon_{\mathrm{d}}+U}\right){c_{\boldsymbol{k}\sigma}}^{\dagger}c_{\boldsymbol{k}'\sigma} \\ &+\frac{1}{N_{\mathrm{A}}}\sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'}\frac{V^2}{2}\left(\frac{1}{-\epsilon_{\mathrm{d}}} + \frac{1}{\epsilon_{\mathrm{d}}+U}\right){c_{\boldsymbol{k}\sigma}}^{\dagger}\boldsymbol{\sigma}_{\sigma\sigma'}c_{\boldsymbol{k}'\sigma'}\cdot\boldsymbol{S} \end{aligned}$$

$\epsilon_{\mathrm{d}} < 0, \quad -\epsilon_{\mathrm{d}} \sim \epsilon_{\mathrm{d}} + U > 0$



Unperturbed system

The first term $= 0$, when $-\epsilon_{\rm d} = \epsilon_{\rm d} + U$,

The second term:

(spin-flip scattering of conduction electron)

$$H_{\rm K} = -\frac{J}{2N_{\rm A}} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} {c_{\boldsymbol{k}\sigma}}^{\dagger} \boldsymbol{\sigma}_{\sigma\sigma'} c_{\boldsymbol{k}'\sigma'} \cdot \boldsymbol{S}$$

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

Kondo model

Antiferromagnetic exchange interaction

Local spin $\boldsymbol{S}$ attracts antiparallel conduction spin $\boldsymbol{\sigma}$.

$\Rightarrow$ Kondo singlet at low temperatures ($T \lesssim T_{\rm K}$)

Kondo temperature : $T_{\rm K}$ (W: conduction band width)

Scaling (renormarization of J) theory gives

$$k_{\rm B} T_{\rm K} \sim W \exp \frac{1}{J D(\epsilon_{\rm F})}$$

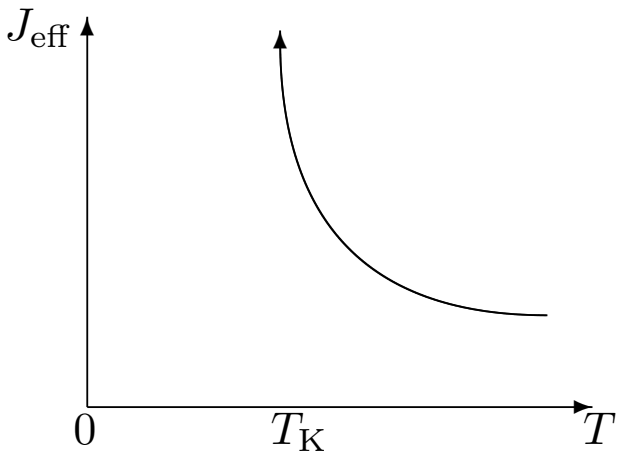
Scaling theory:

$|J_{\rm eff}| \to$ larger ($T \to$ lower)

$$J_{\rm eff} \to -\infty \quad (T \to T_{\rm K} + 0)$$

Kondo singlet state is created.

The large U perturbation expansion breaks down in $T \lesssim T_{\rm K}$.



6.3 Perturbation theory from $U = 0$

Unperturbed system: $U = 0$

No local magnetic moment

”Fermi liquid”

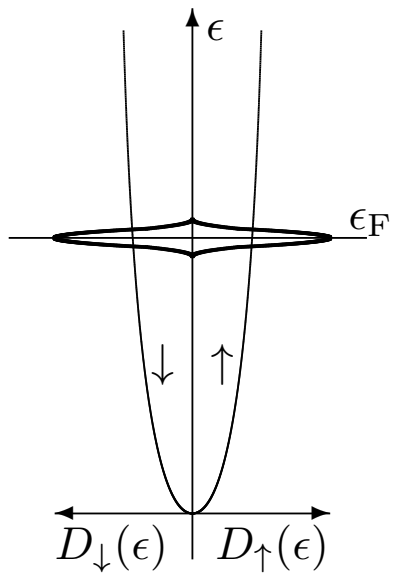
Perturbation: $H' = U n_\uparrow n_\downarrow$

$\downarrow$ (even if $U \to \infty$)

No local moment state is kept.

”Kondo singlet”

This is 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.

7 Magnetic Impurity 2 ($T \gg T_{\mathrm{K}}$)

Hartree-Fock approximation: ($\sigma = \uparrow, \ \downarrow$)

$$H_\sigma = \sum_{\boldsymbol{k}\sigma} \epsilon_{\boldsymbol{k}\sigma} c^\dagger_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \epsilon_{\mathrm{d}} n_\sigma + U \langle n_{-\sigma} \rangle n_\sigma$$
$$+ \frac{1}{\sqrt{N_{\mathrm{A}}}} \sum_{\boldsymbol{k}\sigma} \left\{ V_{\boldsymbol{k}} c^\dagger_{\boldsymbol{k}\sigma} d_\sigma + V^*_{\boldsymbol{k}} d^\dagger_\sigma c_{\boldsymbol{k}\sigma} \right\}$$

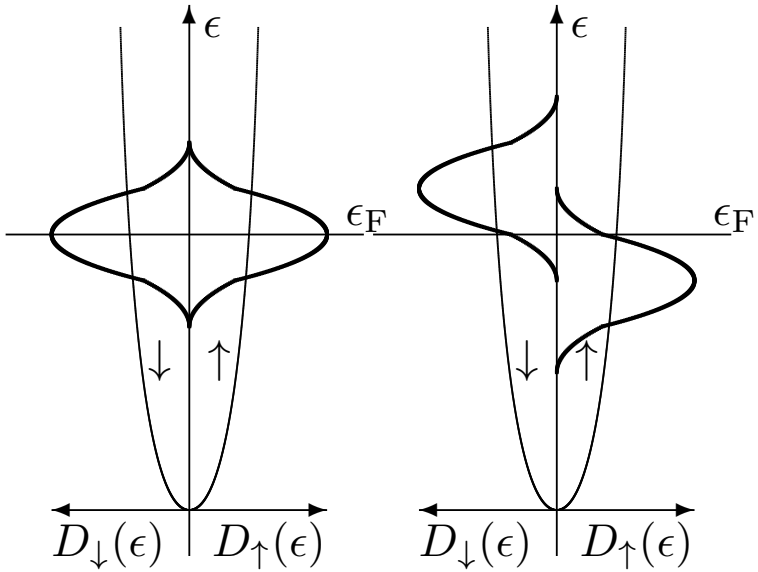
Self-consistent calculation for $\langle n_\uparrow \rangle$ and $\langle n_\downarrow \rangle$

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

7.1 Virtual bound state

Partial DOS of d state:

$$D_{\mathrm{d}\sigma}(\epsilon) = \frac{\Delta/\pi}{(\epsilon - \epsilon_{\mathrm{d}\sigma})^2 + \Delta^2}$$
$$\epsilon_{\mathrm{d}\sigma} = \epsilon_{\mathrm{d}} + U \langle n_{-\sigma} \rangle$$
$$\Delta \approx \pi \left\langle |V_{\boldsymbol{k}}|^2 \right\rangle D_{\mathrm{c}}(\epsilon_{\mathrm{F}})$$



No moment Local moment

7.2 Local magnetic moment

Susceptibility has a Curie term:

$$\chi(T) = \chi_0 + \frac{B}{T}; \quad B = \frac{N\mu^2}{3k_{\mathrm{B}}}$$

ex) Fe impurity in various 4d metals,

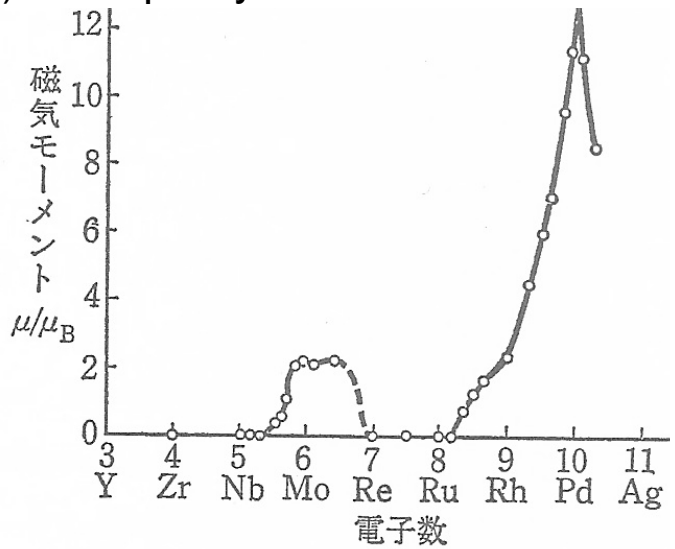


図 11-11 1% Fe を含む合金での Fe の
気モーメント (Clogston et al)

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

Virtual bound state

(parameters: E_{d}, U, Δ)

Starting with no magnetic moment,

$$D_{\mathrm{d}}(\epsilon_{\mathrm{F}}) \equiv D_{\mathrm{d}\uparrow}(\epsilon_{\mathrm{F}}) = D_{\mathrm{d}\downarrow}(\epsilon_{\mathrm{F}})$$

Appearance of local moment:

$$U D_{\mathrm{d}}(\epsilon_{\mathrm{F}}) > 1$$

$\Downarrow$ (now-a-days)

The DFT calculation is available.

8 3d transition metals

Local and non-local susceptibilities

Magnetic structure?

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

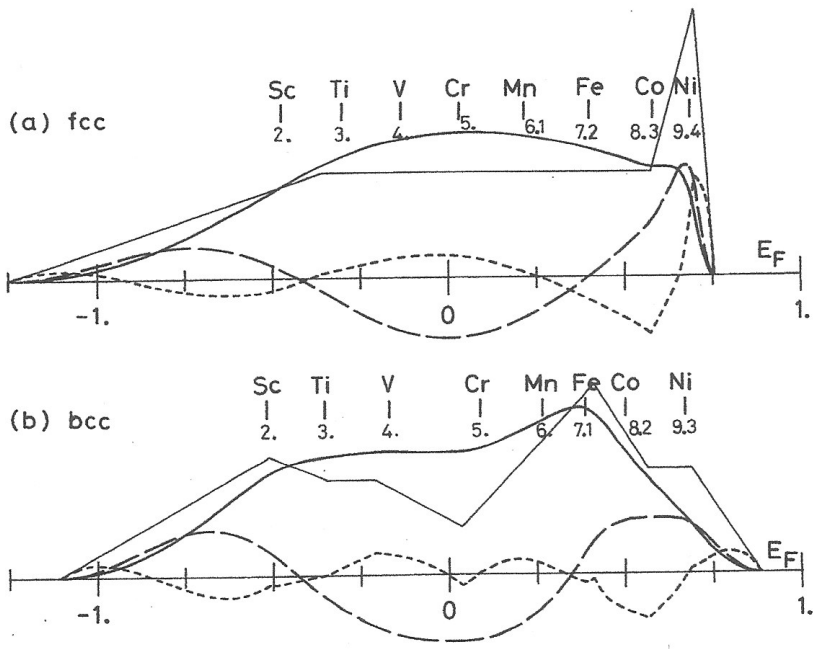
Local susceptibility: $\chi_{00} = \dfrac{M_0}{H_0}$

Nonlocal susceptibilities:

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

PDOS at the center:

$$D_0(\epsilon_{\rm F}) = \chi_{00} + \chi_{01} + \chi_{02}$$



—— $D_0(\epsilon_{\rm F})$,

—— $\chi_{00}(\epsilon_{\rm F})$, --- $\chi_{01}(\epsilon_{\rm F})$, ------ $\chi_{02}(\epsilon_{\rm F})$

$\chi_{01} > 0$ (AFM) for $n_{\rm d} \lesssim 3$ or $n_{\rm d} \gtrsim 7$

$\chi_{01} < 0$ (FM) for $3 \lesssim n_{\rm d} \lesssim 7$

The trend is similar for other lattices, although $n_{\rm d}$ is shifted.

9 Magnetic Alloys (磁性合金)

3d transition-metal alloys

Slater-Pauling curve

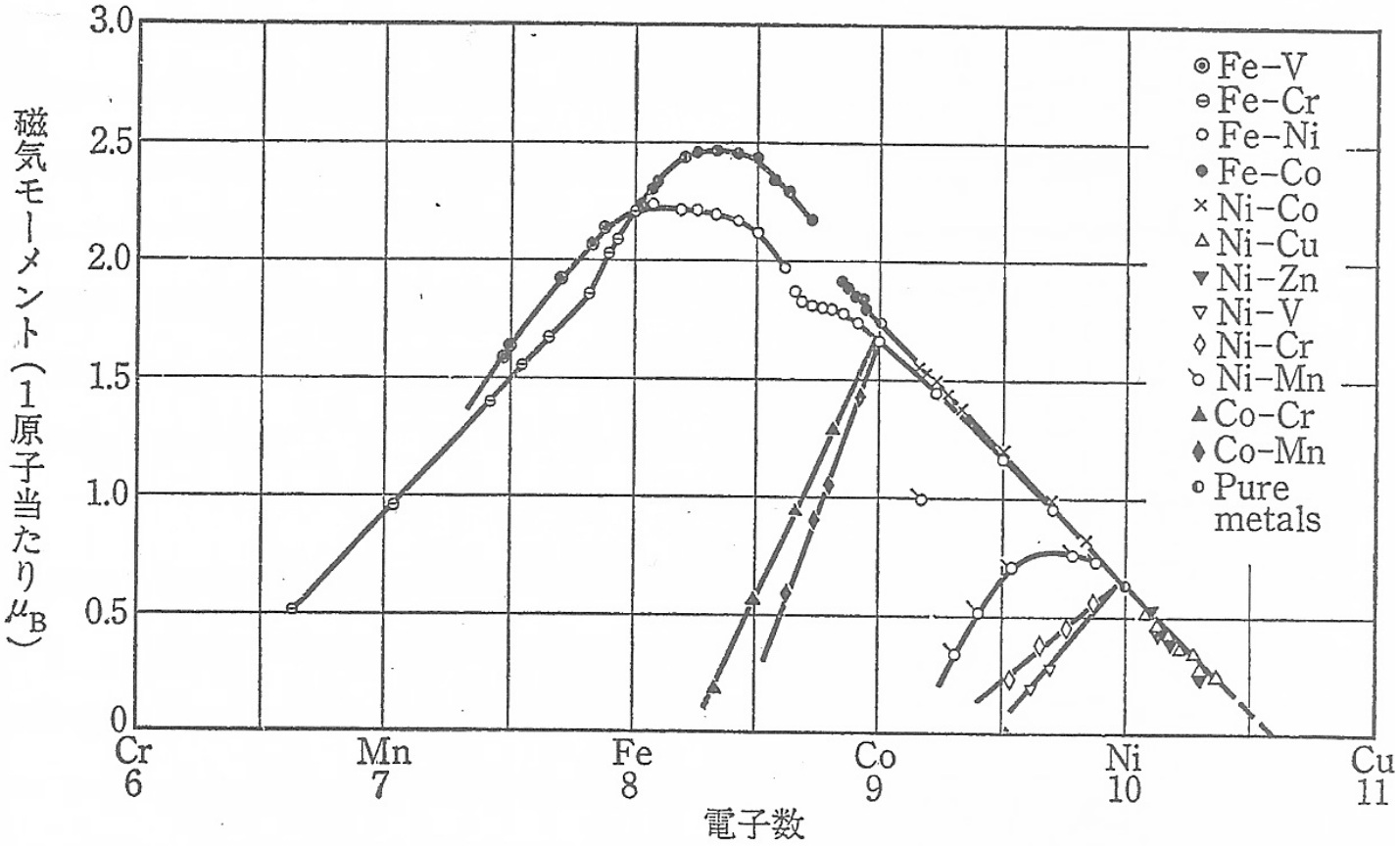


図 11-1 Slater-Pauling 曲線 (Bozorth)

9.1 Hubbard model

Hubbard Hamiltonian:

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

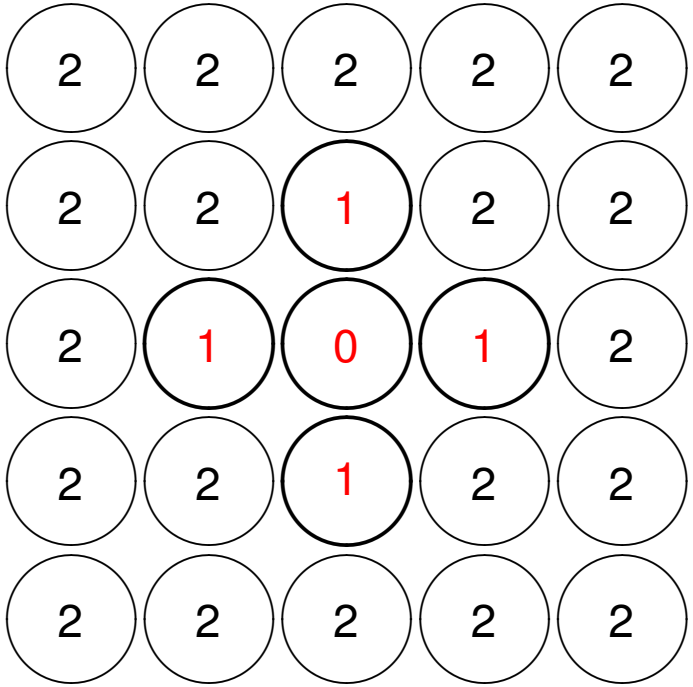
$$n_{i\sigma} = {a_{i\sigma}}^\dagger a_{i\sigma}$$

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

9.2 3d transition-metal alloys

Cluster CPA — 2: coherent potential —

9.2.1 NiFe alloy

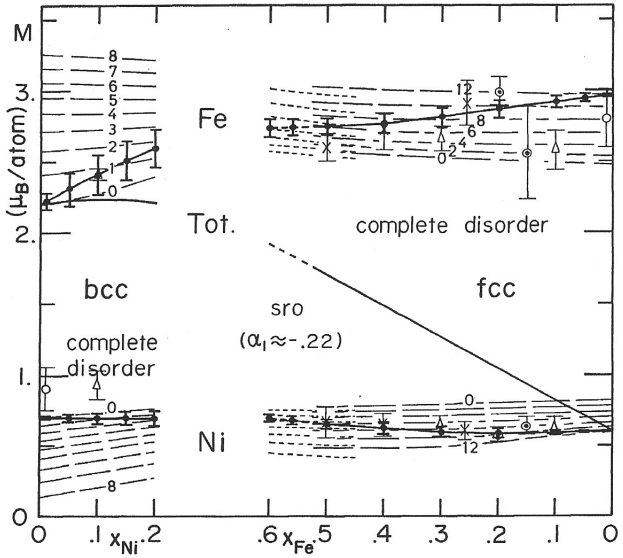
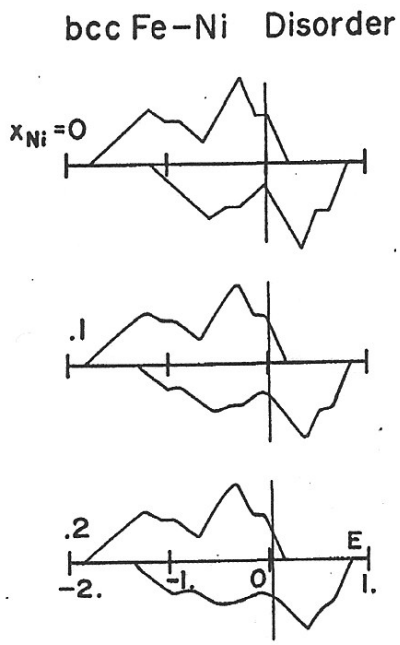
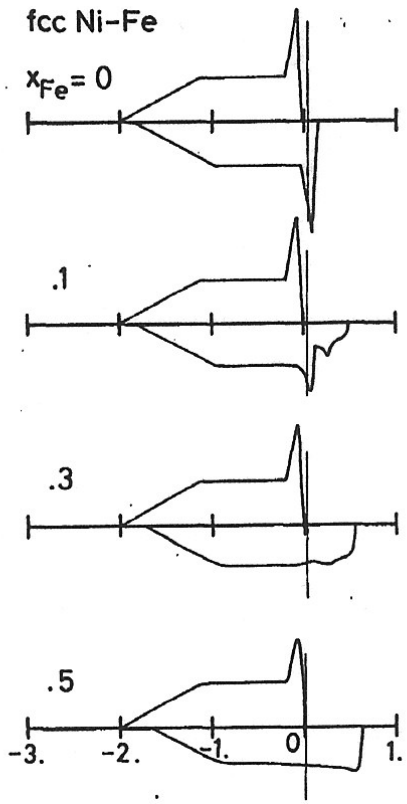


Fig. 4. The Ni and Fe atomic moments in fcc and bcc Ni–Fe. The dashed curves show the Ni and Fe moment for a given number of Ni nearest neighbors as is indicated in the figure. The full lines are the average Ni and Fe moment with the virtical bars representing the root mean square of the deviation of 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 ($\alpha_1 < 0$). ×,[8] △,[9,10] ○[11] and ⊙[12] show the experimental data by neutron diffraction.





- Fe: $2.2\mu_B \to \sim 3\mu_B$
- Ni: $0.6\mu_B$ constant

$\sim$

- Majority-spin band: fully filled?
- Charge neutrality

9.2.2 FeCo alloy

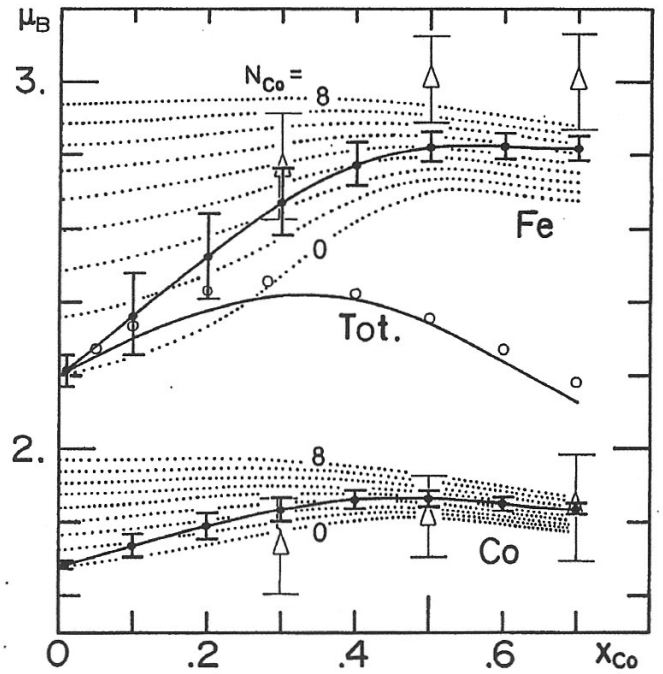


Fig. 12. The Fe and Co moments in bcc Fe–Co alloy with complete disorder. Triangles show the neutron diffuse scattering data for Fe and Co moments.[10] Circles display the experimental magnetization data.[13]

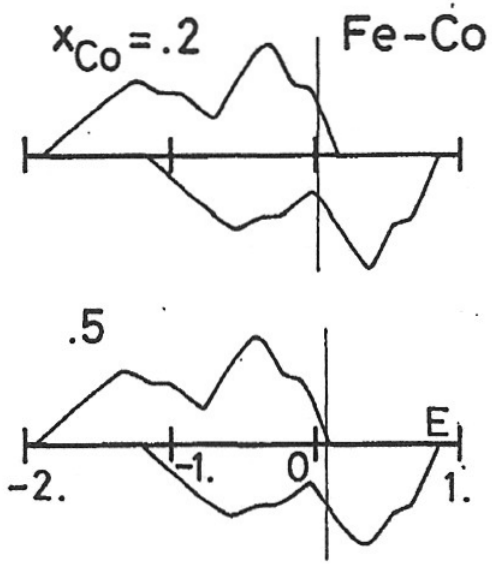


Fig. 9. The total DOS's in bcc Fe–Co.

- Fe: $2.2\mu_{\mathrm{B}} \rightarrow \sim 3\mu_{\mathrm{B}}$
- Co: $1.8\mu_{\mathrm{B}}$ constant

$\sim$

- Majority-spin band: fully filled?
- Charge neutrality

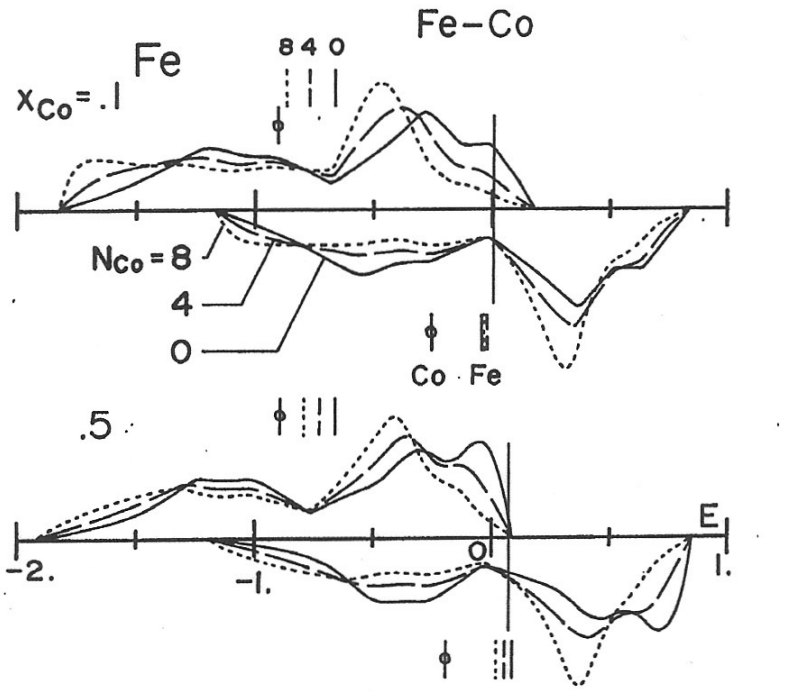


Fig. 10. The local DOS's and the atomic levels of Fe atom in bcc Fe–Co.

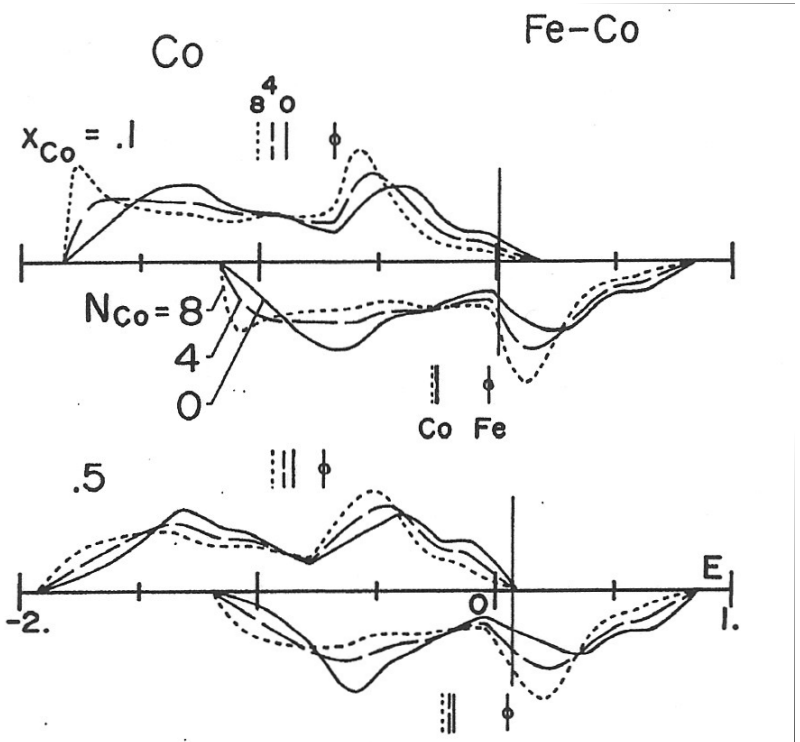


Fig. 11. The local DOS's and the atomic levels of Co atom in bcc Fe–Co.

Neighbor cobaltized Fe makes the Fe moment larger.

⇒ Large magnetization of NdFeB-magnet

9.2.3 FeV alloy

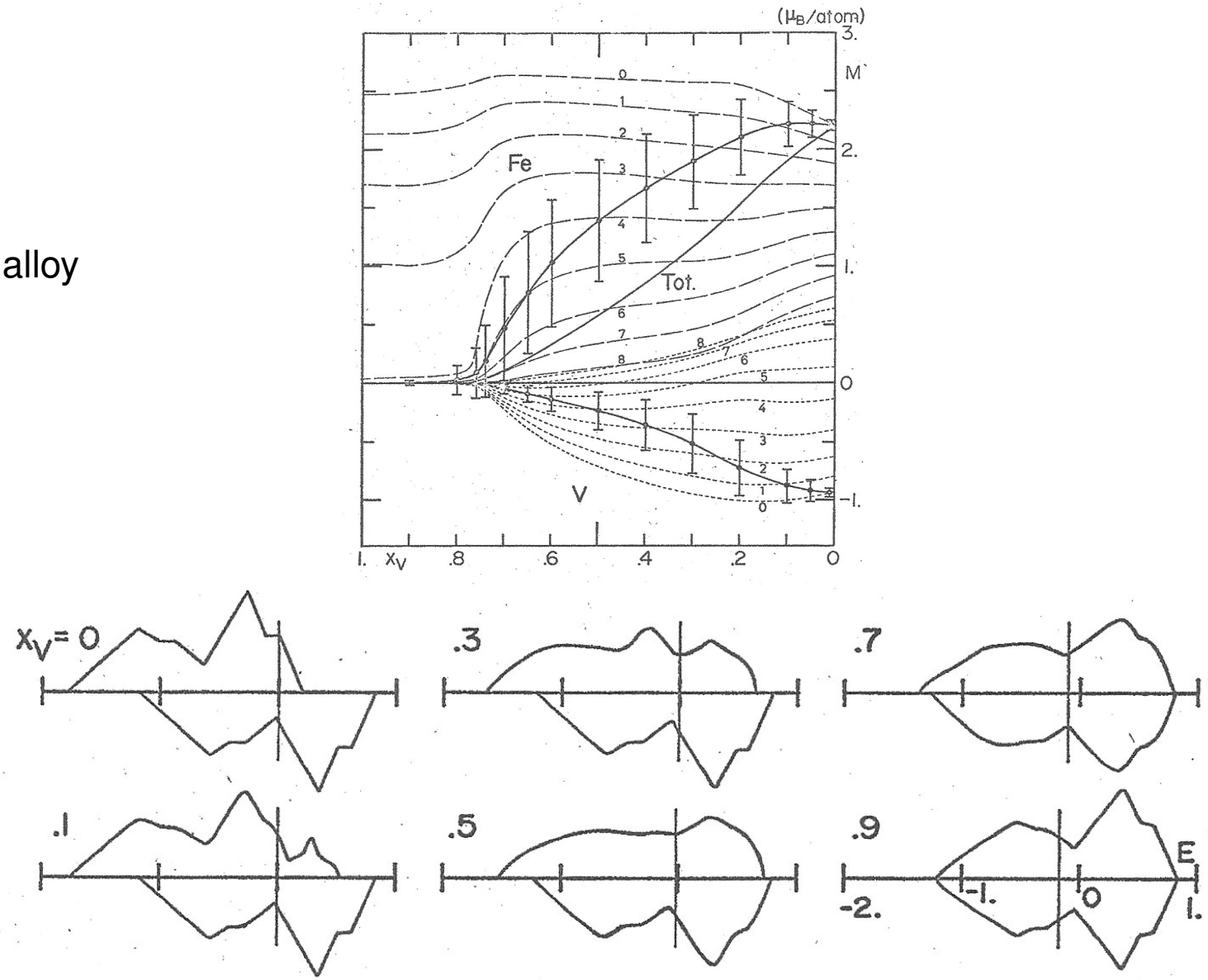


Fig. 3. The total density of states for each spin in various V concentrations. The vertical line near $E=0$ is the Fermi level.