2022.4.6 Lecture 1

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Syllabus

1. Phenomenology of magnetism. Magnetization process
2. Spin magnetic moments in solids
3. Mutual interaction between spins
4. Ordered states of spins. Phase transitions
5. Magnetism in insulators
6. Magnetism of itinerant electrons
7. Some advanced topics (?)

How the lecture will go on?

- The lecture notes (in Japanese, English) will be uploaded in the site
  https://kats.issp.u-tokyo.ac.jp/kats/magnetism/
  by the end of the lecture week.

- Attendance will be taken. That contributes to the achievement.

- Small amount of problems for your exercise at home will be given in the last of the lecture in every two weeks. Submission deadline of the solutions is two weeks later. In order to submit your answer, you need to register yourself from the web page that will be prepared by the next week.

- In the very last of the lecture in July, the problems for your report will be given. The deadline for the submission of the report will be notified then.

Contents Wed. 6th April 2022

Chapter 1 Basic Notions of Magnetism

1. Electromagnetic fields in the vacuum, and those with materials
2. Experimental methods to measure magnetization
3. Magnetism in classical pictures
4. Spins of electrons and their magnetic moment

Electromagnetic fields in the vacuum

$$\nabla \cdot \boldsymbol{E} = \frac{\rho}{\epsilon_0},$$

Maxwell equations for electromagnetic fields in the vacuum

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t},$$

Electromagnetic induction

$$\nabla \cdot \boldsymbol{B} = 0,$$

No magnetic monopole

$$\nabla \times \boldsymbol{B} = \mu_0 \left(\boldsymbol{j} + \epsilon_0 \frac{\partial \boldsymbol{E}}{\partial t} \right).$$

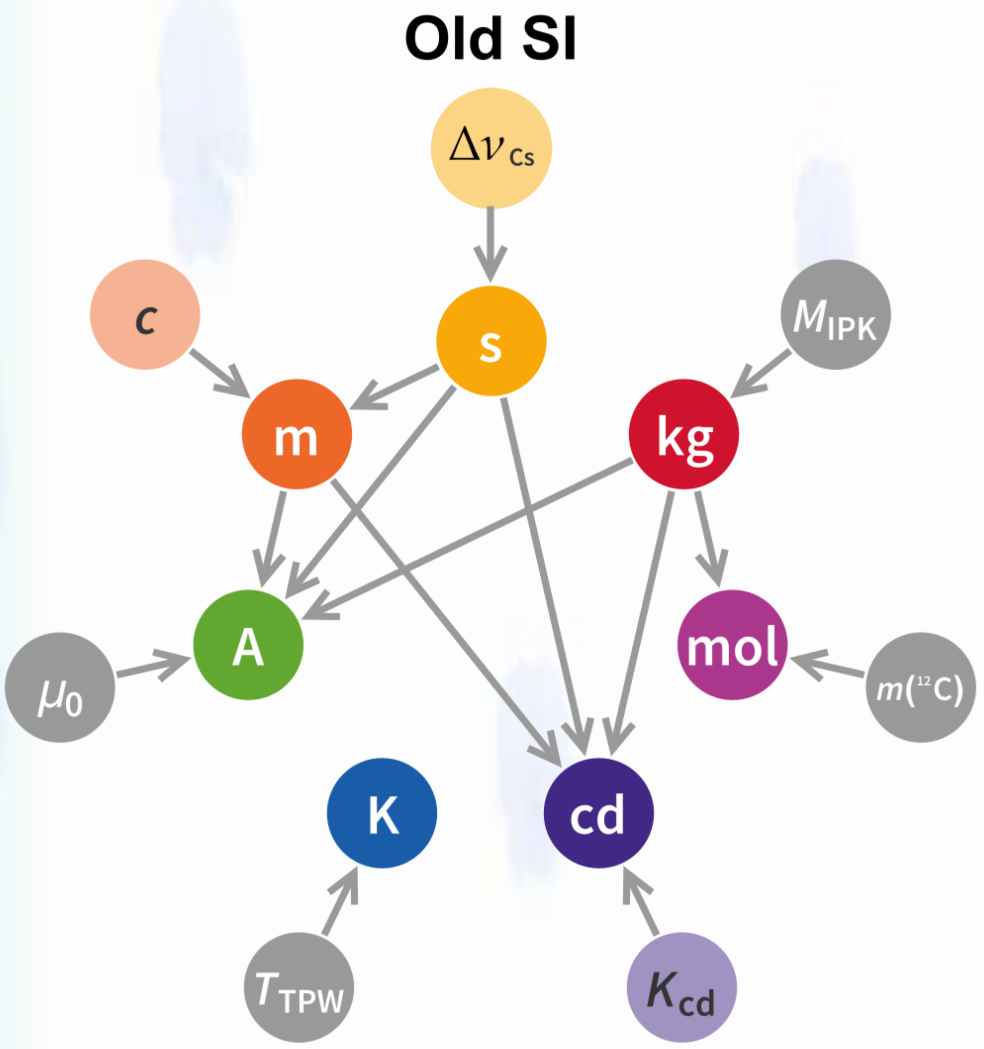
Electric current can create magnetic field

E: Electric field, ***B***: Magnetic flux density (Magnetic field)

Problem of "Unit"

No 4π factor appears in the above Maxwell equations: rationalized system of units

E-B formulation, E-H formulation : Difference in the unit of magnetization!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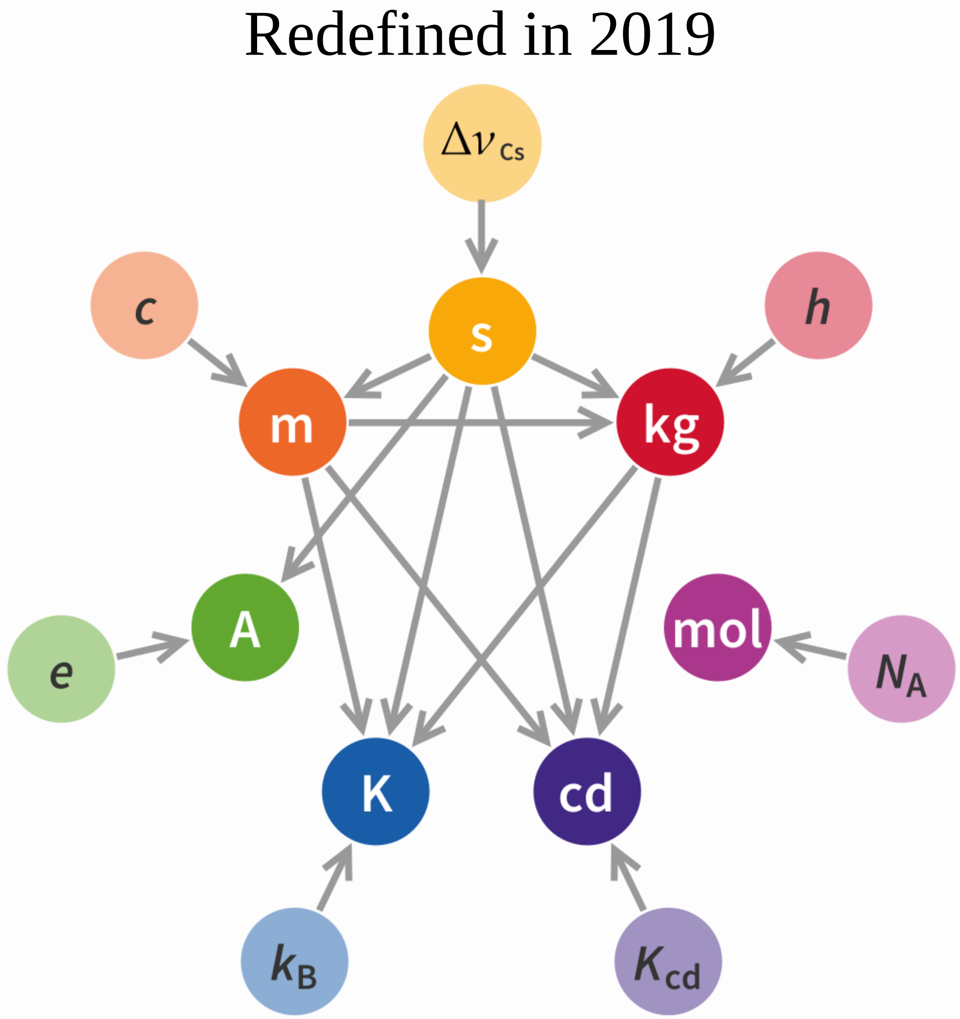
Redefined in 2019
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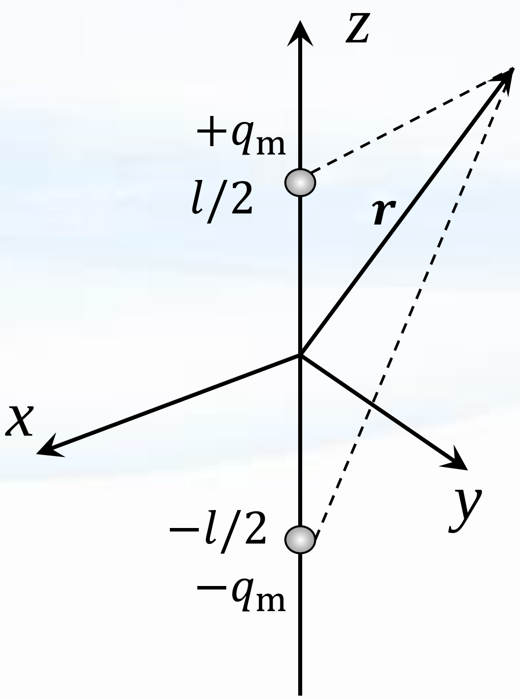
Magnetic dipole: a source of magnetic field

Two ways to introduce magnetic dipole:

1. Introduction of magnetic charge
2. Magnetic dipole as the shrink limit of circular current



Introduction of magnetic charge

There is no magnetic monopole but still we can consider pairs of fictitious magnetic charge with the total charge of zero.

$$\phi_{\mathrm{m}}(\boldsymbol{r}) = \frac{1}{4\pi\mu_0}\left(\frac{q_{\mathrm{m}}}{|\boldsymbol{r}-\boldsymbol{l}/2|} - \frac{q_{\mathrm{m}}}{|\boldsymbol{r}+\boldsymbol{l}/2|}\right)$$

Magnetic potential

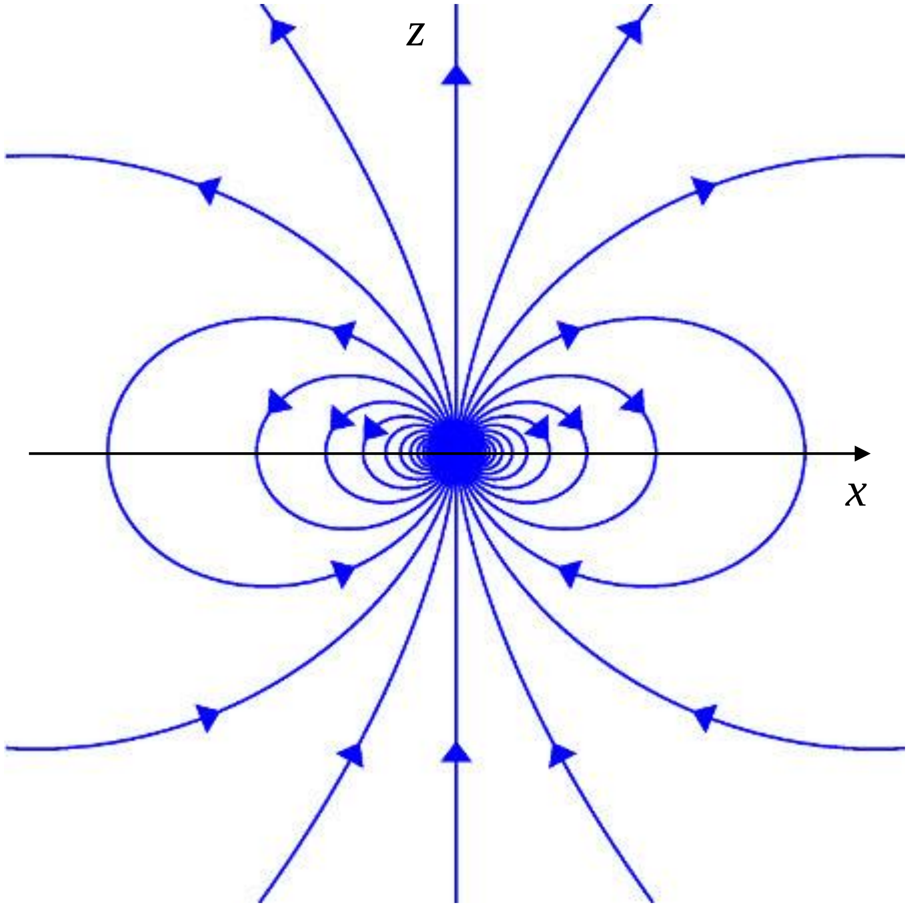
$$\boldsymbol{B} = -\frac{1}{4\pi\mu_0}\nabla\left(\frac{\boldsymbol{\mu}\cdot\boldsymbol{r}}{r^3}\right)$$

Dipole field

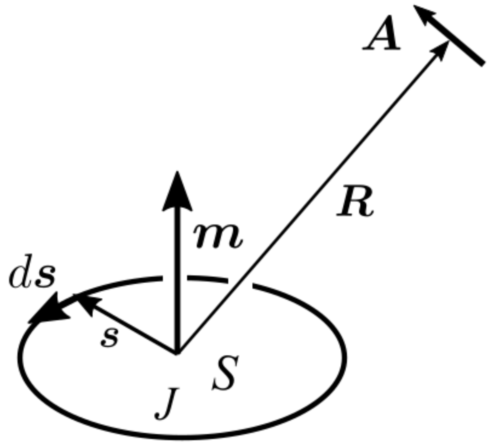
$$B_r = \frac{|\boldsymbol{\mu}|}{4\pi\mu_0}\frac{2\cos\theta}{r^3}, \quad B_\theta = \frac{|\boldsymbol{\mu}|}{4\pi\mu_0}\frac{\sin\theta}{r^3}$$

Expression in polar coordinate

Magnetic dipole: a source of magnetic field (2)



Magnetic dipole as the shrink limit of circular current



Vector potential

$$\boldsymbol{A} \simeq \frac{\mu_0 J}{4\pi}\frac{1}{R^3}\oint(\boldsymbol{R}\cdot\boldsymbol{s})d\boldsymbol{s}$$

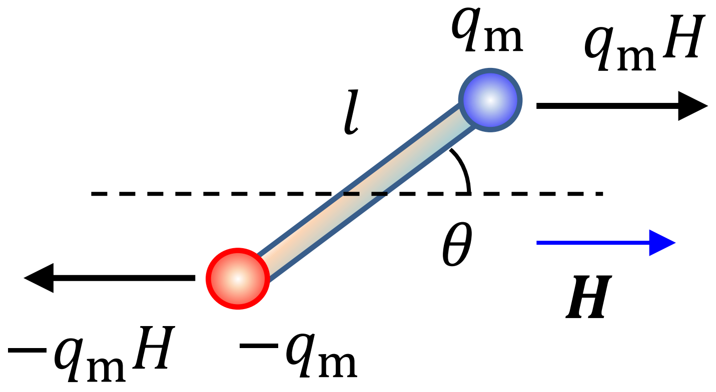
Magnetic moment (see the next)

$$\boldsymbol{\mu} = J\left(\frac{1}{2}\oint \boldsymbol{s}\times d\boldsymbol{s}\right)$$

Magnetic field: $\boldsymbol{B} = -\frac{\mu_0}{4\pi}\nabla\frac{\boldsymbol{\mu}\cdot\boldsymbol{r}}{r^3}$

A circular current can serve as a magnetic dipole.

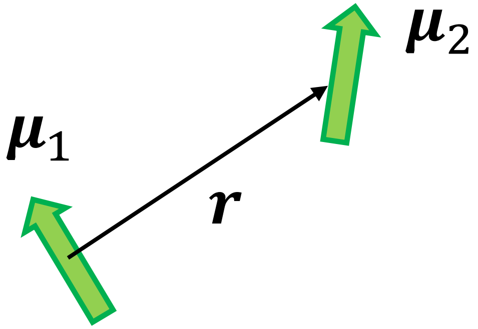
Magnetic moment



Couple of force moment: $L = -q_\mathrm{m} l H \sin\theta = -\frac{q_\mathrm{m} l}{\mu_0} B \sin\theta$

Magnetic moment $\mu \equiv \frac{q_\mathrm{m} l}{\mu_0}$

E-B formation



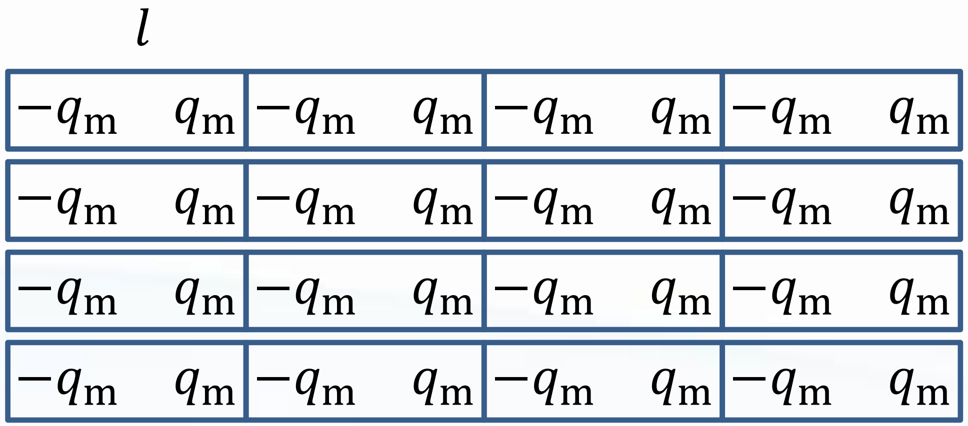
(a) Stable

(b) Unstable

Dipole-dipole interaction: the dipoles feel each other's fields.

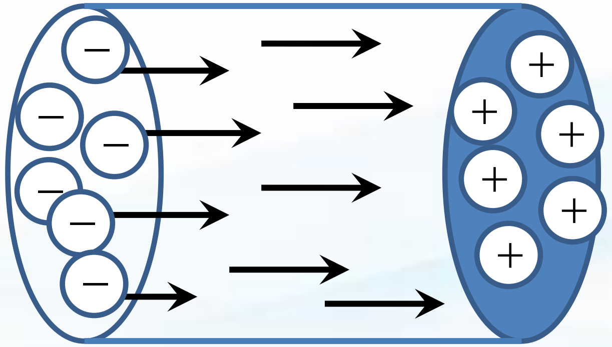
Potential: $U = \frac{1}{4\pi\mu_0 r^3}\left\{\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2 - \frac{3}{r^2}(\boldsymbol{\mu}_1\cdot\boldsymbol{r})(\boldsymbol{\mu}_2\cdot\boldsymbol{r})\right\}$

A naïve dipole model of magnetization of materials



Set of small magnets

Density of magnets: N



Magnetic charges appear at the ends of the material

Magnetization: $$\boldsymbol{M} = \sum_{\mathrm{unit vol.}} \boldsymbol{\mu} = N q_{\mathrm{m}} \boldsymbol{l}/\mu_0 \equiv \rho \boldsymbol{l}/\mu_0$$

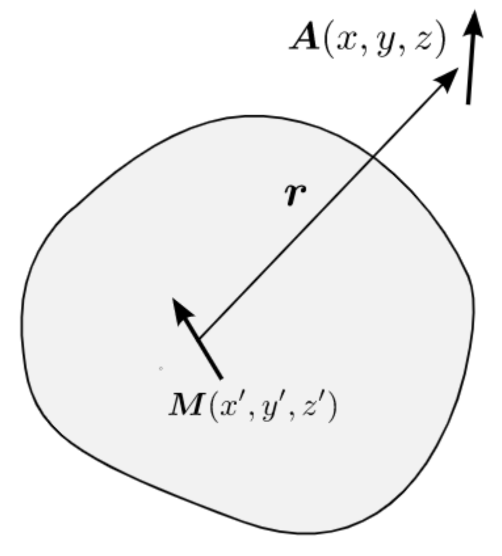
Surface density of magnetic charge $$\sigma = q_{\mathrm{m}} s = q_{\mathrm{m}} N l = \mu_0 |\boldsymbol{M}|$$

Expression with "equivalent current" in materials

Magnetic moments → vector potential

$$\boldsymbol{A} = \frac{\mu_0}{4\pi}\int_{\text{mat}} dv' \frac{\boldsymbol{M}' \times \boldsymbol{r}}{r^3} = -\frac{\mu_0}{4\pi}\int_{\text{mat}} dv' \left(\boldsymbol{M}' \times \nabla\frac{1}{r}\right)$$

$$= \frac{\mu_0}{4\pi}\int_{\text{mat}} dv' \left(\boldsymbol{M}' \times \nabla'\frac{1}{r}\right)$$



Partial integration: $$\boldsymbol{A} = \frac{\mu_0}{4\pi}\int_{\text{mat}} dv' \frac{\nabla' \times \boldsymbol{M}'}{r}$$

Equivalent current: $$\boldsymbol{j}_M \equiv \nabla \times \boldsymbol{M} \longrightarrow \boldsymbol{A} = \frac{\mu_0}{4\pi}\int dv' \frac{\boldsymbol{j}' + \boldsymbol{j}'_M}{r}$$

$$\nabla \times \boldsymbol{B} = \mu_0(\boldsymbol{j} + \boldsymbol{j}_M) = \mu_0\boldsymbol{j} + \mu_0\nabla \times \boldsymbol{M}$$

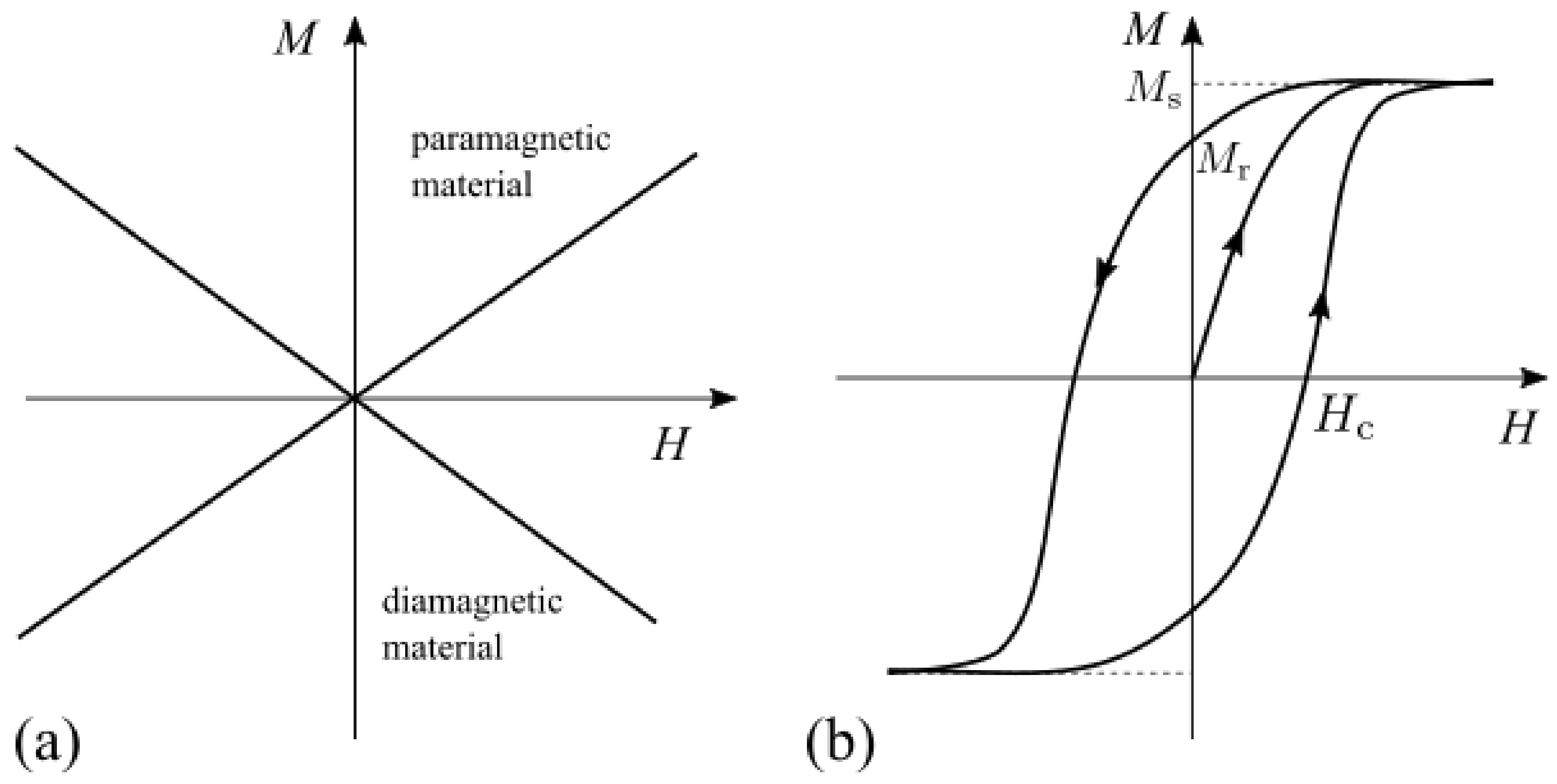
Introduction of magnetic field: $$\boldsymbol{H} \equiv \boldsymbol{B}/\mu_0 - \boldsymbol{M}$$

Maxwell equation with electric flux density

$$\nabla \times \boldsymbol{H} = \boldsymbol{j} + \frac{\partial \boldsymbol{D}}{\partial t}$$

M-H curve

M-H relation



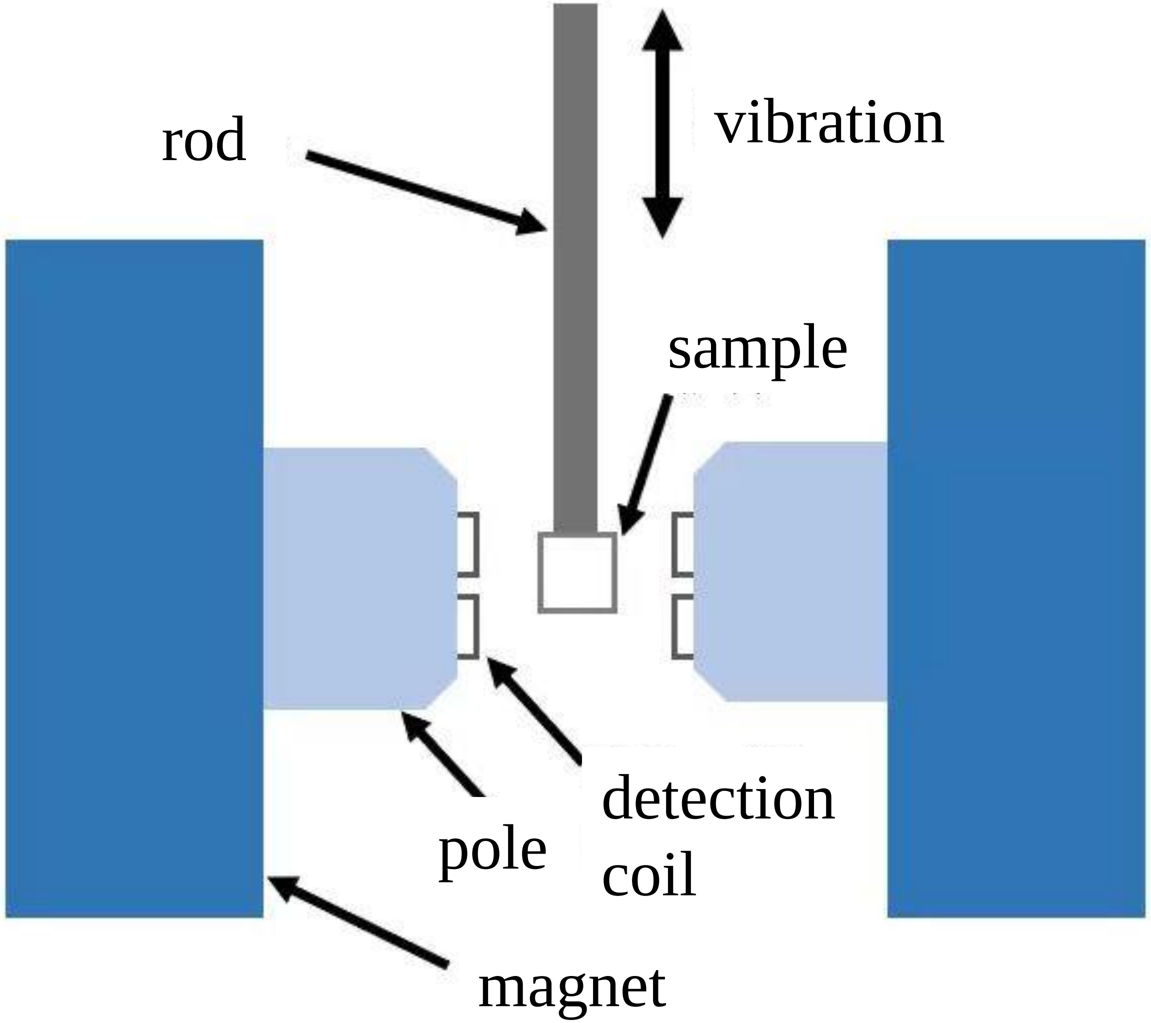
H_c: Coercive force,
M_r: Remanent magnetization,
M_s: Saturation magnetization

Linear: Paramagnetic materials, diamagnetic materials

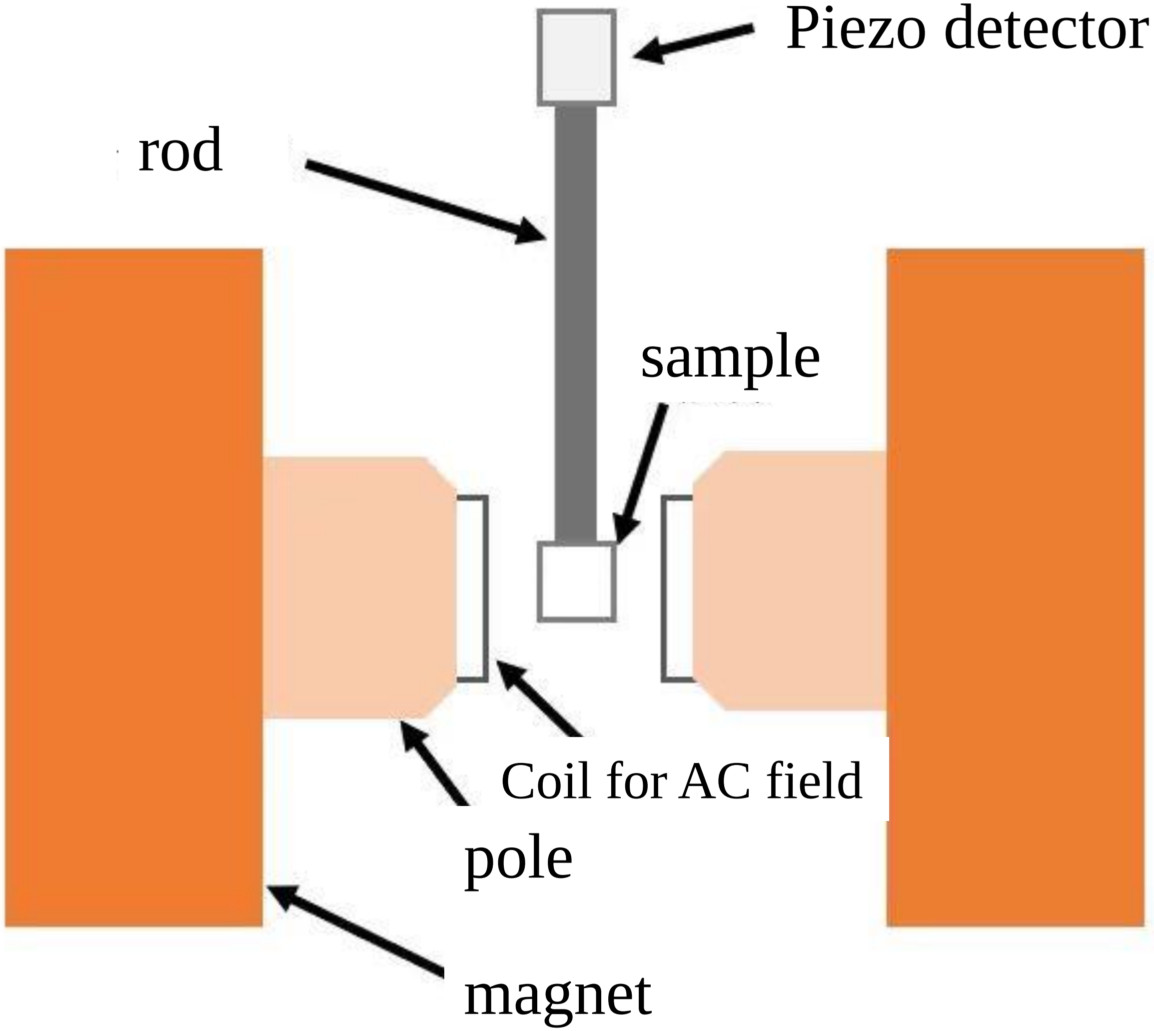
Strongly non-linear with hysteresis: Ferromagnetic materials, superconductors, …

Measurement of magnetization (1)

Vibrating sample magnetometer (VSM)

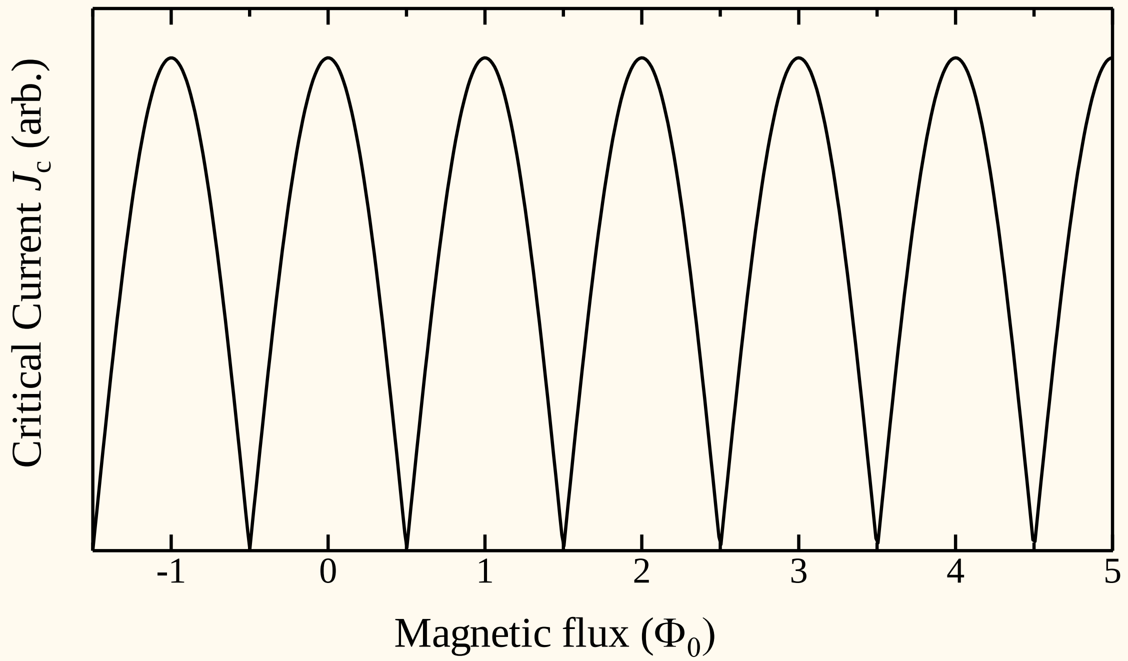


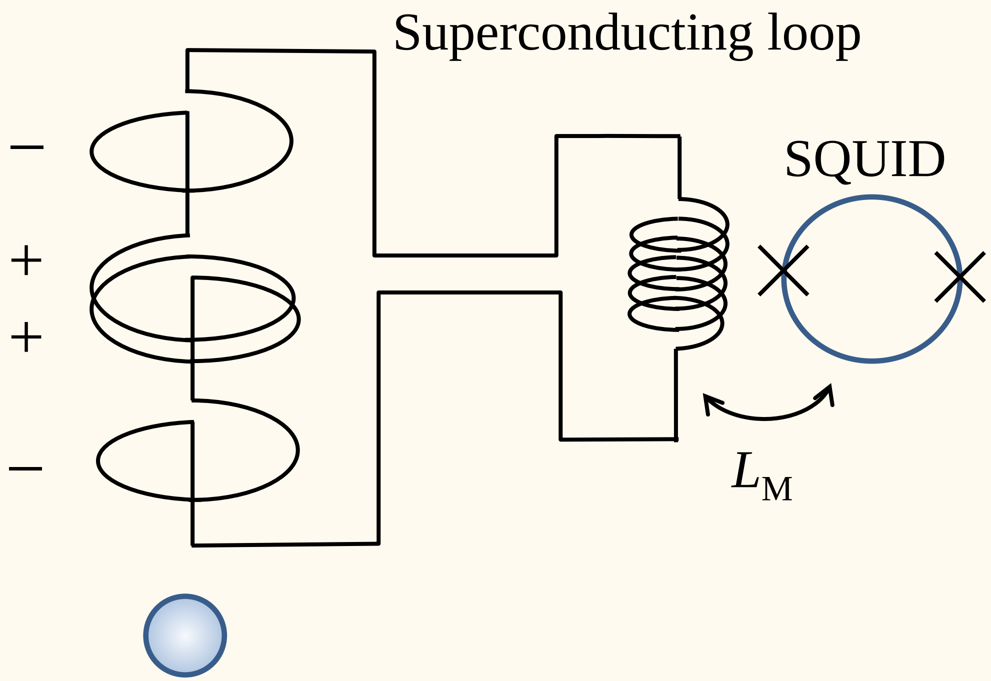
Alternating-gradient magnetometer (AGM)



Measurement of magnetization (2)

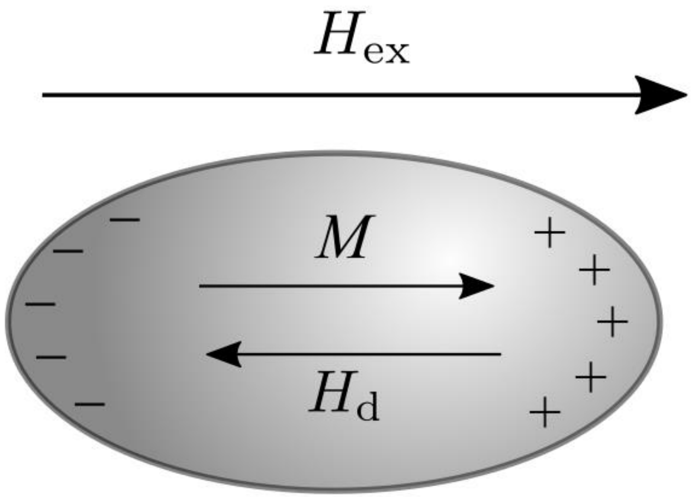
Superconducting quantum interference device (SQUID) magnetometer





$$\Phi_0 \equiv h/2e \approx 2.07 \times 10^{-15} \ \text{Wb}$$

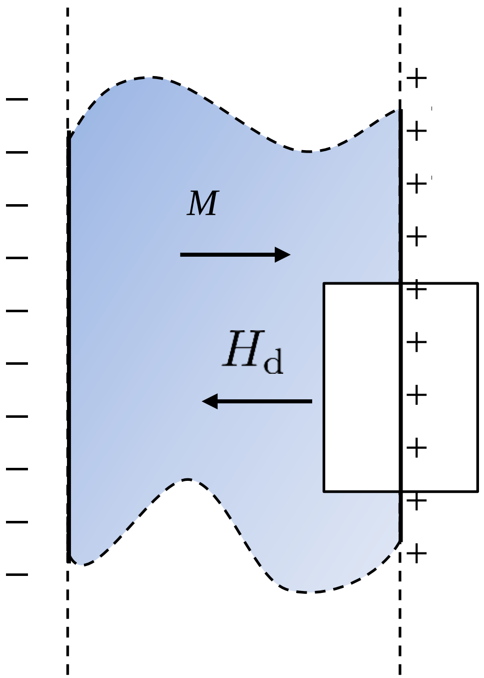
Effect of demagnetizing field



Magnetization causes creation of magnetic charges on the surface, which produces demagnetizing field inside.

$$H_{\mathrm{d}} = N\frac{M}{\mu_0}$$

N : demagnetizing factor (depends only on shape)



In the case of infinite plate

$$\int_{\mathrm{surface}} H_{\mathrm{n}} ds = H_{\mathrm{d}} = \frac{M}{\mu_0}$$

$$\therefore N = 1$$

Example: Permalloy (Py)

Coercive force: 0.025 Oe
Saturation magnetization field: 3860 Oe

Classical treatment of magnetism

Paramagnetic moment

Model: set of molecules with independent magnetic moment μ in the magnetic field with flux density B along z-axis

Moment magnetic energy: $$U = -\boldsymbol{\mu} \cdot \boldsymbol{B} = -\mu B \cos\theta$$

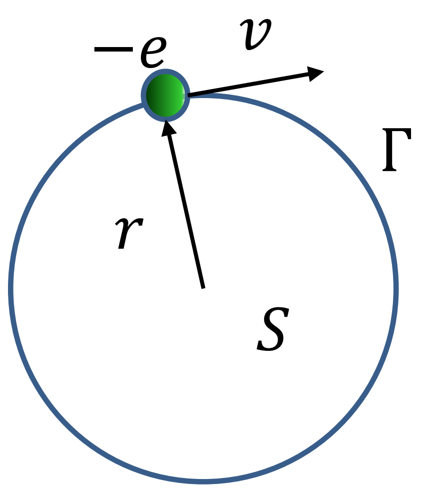
Average on classical distribution:

$$\begin{aligned}
\langle \mu_z \rangle &= \int \exp\left(-\frac{U}{k_{\mathrm{B}}T}\right) \mu_z d\Omega \Big/ \int \exp\left(-\frac{U}{k_{\mathrm{B}}T}\right) d\Omega \\
&= \int \exp\left(\frac{\mu B \cos\theta}{k_{\mathrm{B}}T}\right) \mu \cos\theta d\Omega \Big/ \int \exp\left(\frac{\mu B \cos\theta}{k_{\mathrm{B}}T}\right) d\Omega \\
&= k_{\mathrm{B}}T \frac{\partial}{\partial B} \log\left[2\pi \int_0^{\pi} \exp\left(\frac{\mu B \cos\theta}{k_{\mathrm{B}}T}\right) \sin\theta d\theta\right] = \mu\left[\coth\left(\frac{\mu B}{k_{\mathrm{B}}T}\right) - \frac{k_{\mathrm{B}}T}{\mu B}\right]
\end{aligned}$$

High temperature approximation: $$\mu B \ll k_{\mathrm{B}}T$$

Curie law: $$\frac{\langle \mu_z \rangle}{B} \sim \frac{\mu^2}{3k_{\mathrm{B}}} \frac{1}{T}$$

Classical paramagnetism



$$\oint_\Gamma \boldsymbol{E}\cdot d\boldsymbol{l} = -\frac{\partial}{\partial t}\int_S \boldsymbol{B}\cdot d\boldsymbol{\sigma}$$ Maxwell equation

$$2\pi r E = -\frac{\partial}{\partial t}\left(B\pi r^2\right) \qquad \therefore E = -\frac{r}{2}\frac{dB}{dt}$$

$$\frac{dL}{dt} = r\times(-eE) = e\frac{r^2}{2}\frac{dB}{dt}$$

Magnetic flux 0 $\rightarrow B$

Angular momentum $0 \rightarrow L = e\frac{r^2}{2}B$

$$\mu = SJ = \pi r^2\frac{ev}{2\pi r} = \pi r^2\frac{L}{mr}\frac{e}{\pi r} = \frac{e}{2m}e\frac{r^2}{2}B$$

$$\mu = -\frac{e^2}{4m}\left\langle x^2+y^2\right\rangle_{\text{av}} B$$

Breakdown of classical magnetism

Hamiltonian $$\mathcal{H} = \frac{1}{2m}(\boldsymbol{p} + e\boldsymbol{A})^2 - e\phi$$

Symmetric gauge: $$\boldsymbol{A} = (\boldsymbol{B} \times \boldsymbol{r})/2$$

$$\mathcal{H} = \frac{\boldsymbol{p}^2}{2m} + \frac{e}{2m}(\boldsymbol{r} \times \boldsymbol{p}) \cdot \boldsymbol{B} + \frac{e^2}{8m}(\boldsymbol{B} \times \boldsymbol{r})^2$$

Dipole moment: $$\mu_{\mathrm{m}} = -\frac{\partial \mathcal{H}}{\partial B} = -\frac{e}{2m}(\boldsymbol{r} \times \boldsymbol{p}) - \frac{e^2}{4m}(\boldsymbol{r} \times (\boldsymbol{B} \times \boldsymbol{r}))$$

paramagnetic diamagnetic

N-electron system $$\mathcal{H}_N = \sum_{n=1}^{N} \left[\frac{1}{2m}\left(\boldsymbol{p}_n + e\boldsymbol{A}(\boldsymbol{r}_n)\right)^2 - e\phi(\boldsymbol{r}_n)\right] + V(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$$

Breakdown of classical magnetism (2)

Partition function: $Z = \prod_{n=1}^{N} \int \frac{d\boldsymbol{r}_n d\boldsymbol{p}_n}{h^3} e^{-\mathcal{H}/k_{\mathrm{B}}T}$

$$\boldsymbol{\pi}_n = \boldsymbol{p}_n + e\boldsymbol{A}(\boldsymbol{r})$$

$$Z = \prod_{n=1}^{N} \int \frac{d\boldsymbol{r}_n d\boldsymbol{\pi}_n}{h^3} e^{-\mathcal{H}'/k_{\mathrm{B}}T},$$

$$\mathcal{H}' = \sum_{n=1}^{N} \left[\frac{\boldsymbol{\pi}_n^2}{2m} - e\phi(\boldsymbol{r}_n) \right] + V(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$$

Cancellation of paramagnetic and diamagnetic term $\langle \boldsymbol{\mu}_{\mathrm{m}} \rangle = -\frac{1}{N}\frac{\partial F}{\partial \boldsymbol{B}} = \frac{1}{N k_{\mathrm{B}} T}\frac{\partial \ln Z}{\partial \boldsymbol{B}} = \langle \boldsymbol{\mu}_{\mathrm{para}} \rangle + \langle \boldsymbol{\mu}_{\mathrm{dia}} \rangle = 0$

Bohr- van Leeuwen theorem

Electron spin from Dirac equation

Dirac equation and electron spin magnetic moment

Energy-momentum relation in Newtonian mechanics

$$E = \frac{p^2}{2m}$$

Quantum mechanical replacement to obtain Schroedinger equation:

$$E \to i\hbar\frac{\partial}{\partial t}, \quad p \to -i\hbar\frac{\partial}{\partial x}$$

Energy-momentum relation in relativity

$$E^2 = (pc)^2 + (mc^2)^2 \qquad (1)$$

However simple replacement is impossible: the wave equation must be the first-order in time

$$E = \sum_{k=1,2,3} \alpha_k p_k c + \beta mc^2 \qquad (2)$$

How to compromise (2) with (1) ?

These conditions require α_k and β to be 4×4 matrices.

$$\begin{cases} \alpha_k^2 = 1, \quad \beta^2 = 1, \\ \alpha_k\alpha_j + \alpha_j\alpha_k = 0 \ (k \neq j), \\ \alpha_k\beta + \beta\alpha_k = 0 \end{cases}$$

Pauli representation

Wave equation

$$i\hbar\frac{\partial\psi}{\partial t} = \left[-i\hbar c\sum_{k=x,y,z}\alpha_k\frac{\partial}{\partial x_k} + \beta mc^2\right]\boldsymbol{\psi}$$

$$\equiv \mathcal{H}_{\mathrm{D}}\boldsymbol{\psi}, \quad \mathcal{H}_{\mathrm{D}} = c\boldsymbol{\alpha}\boldsymbol{p} + mc^2\beta$$

Dirac hamiltonian

Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\sigma_i\sigma_j = -\sigma_j\sigma_i = i\sigma_k, \quad \sigma_x^2 = \sigma_y^2 = \sigma_z^2 = I$$

Pauli representation

$$\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

Spin angular momentum

$$\mathcal{H} = \mathcal{H}_{\mathrm{D}} + V(\boldsymbol{r})$$

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} \qquad \underline{[\boldsymbol{L}, \mathcal{H}] = i\boldsymbol{\alpha} \times \boldsymbol{p}} \qquad \boldsymbol{\alpha} = \begin{pmatrix} \alpha_x \\ \alpha_y \\ \alpha_z \end{pmatrix}$$

L does not commute with Hamiltonian, is thus, not a constant of motion.

4×4 Pauli matrices: $\sigma_k^{(4)} = \begin{pmatrix} \sigma_k & 0 \\ 0 & \sigma_k \end{pmatrix}$ $\qquad \underline{[\boldsymbol{\sigma}, \mathcal{H}] = -2i\boldsymbol{\alpha} \times \boldsymbol{p}/\hbar}$

Then $\boldsymbol{J} = \boldsymbol{L} + \frac{\hbar}{2}\boldsymbol{\sigma} \equiv \boldsymbol{L} + \boldsymbol{s}$ $\qquad [\boldsymbol{J}, \mathcal{H}] = 0$

Spin angular momentum: $\boldsymbol{s} \equiv (\hbar/2)\boldsymbol{\sigma}$

Magnetic moment of electron spin

Dirac eq. with electromagnetic field $$i\hbar\frac{\partial\psi}{\partial t}=[c\boldsymbol{\alpha}(\boldsymbol{p}+e\boldsymbol{A})+\beta m-e\phi]\,\psi$$

$$\left[\left(i\hbar\frac{\partial}{\partial t}+e\phi\right)-c\sum_{j=x,y,z}\alpha_j\left(-i\hbar\frac{\partial}{\partial r_j}+eA_j\right)-\beta mc^2\right]\psi=0$$

Operation from left: $$i\hbar\frac{\partial}{\partial t}+e\phi+c\sum_{j=x,y,z}\alpha_j\left(-i\hbar\frac{\partial}{\partial r_j}+eA_j\right)+\beta mc^2$$

We obtain

$$\left[\left(i\hbar\frac{\partial}{\partial t}+e\phi\right)^2-c^2(\boldsymbol{p}+e\boldsymbol{A})^2-m^2c^4+ic\hbar e(\boldsymbol{\alpha}\cdot\boldsymbol{E})+i\hbar c^2e(\alpha_x\alpha_yB_z+\alpha_y\alpha_zB_x+\alpha_z\alpha_xB_y)\right]\psi=0$$

Because $$\alpha_x\alpha_y=i\sigma_z^{(4)},\quad \alpha_y\alpha_z=i\sigma_x^{(4)},\quad \alpha_z\alpha_x=i\sigma_y^{(4)}$$

$$\left[\left(i\hbar\frac{\partial}{\partial t}+e\phi\right)^2-c^2(\boldsymbol{p}+e\boldsymbol{A})^2-m^2c^4+ic\hbar e(\boldsymbol{\alpha}\cdot\boldsymbol{E})-\hbar c^2e\boldsymbol{\sigma}\cdot\boldsymbol{B}\right]\psi=0$$

Magnetic moment of electron spin (2)

Stationary solution: $\psi(\boldsymbol{r},t)=\exp(-i\epsilon t/\hbar)\varphi(\boldsymbol{r})$

$$\left[(\epsilon+e\phi)^2-c^2(\boldsymbol{p}+e\boldsymbol{A})^2-m^2c^4+ic\hbar e(\boldsymbol{\alpha}\cdot\boldsymbol{E})-\hbar c^2 e\boldsymbol{\sigma}\cdot\boldsymbol{B}\right]\varphi=0$$

$$\phi=0,\ \ \boldsymbol{E}=0$$

Low energy expansion

$$\epsilon=mc^2+\delta$$

We take first order in $\dfrac{\delta}{mc^2}$

$$\left[\frac{1}{2m}(\boldsymbol{p}+e\boldsymbol{A})^2+\frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{B}\right]\varphi=\delta\varphi$$

Bohr magneton $\mu_{\mathrm{B}}\equiv\dfrac{e\hbar}{2m}\approx 9.274\times 10^{-24}\ \mathrm{JT}^{-1}$

$$\frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{B}=\mu_{\mathrm{B}}\boldsymbol{\sigma}\cdot\boldsymbol{B}=\frac{2}{\hbar}\mu_{\mathrm{B}}\boldsymbol{s}\cdot\boldsymbol{B}$$

Therefore the magnetic moment is $-2\mu_{\mathrm{B}}\boldsymbol{s}/\hbar$

Summary

1. Introduction of magnetic moment
2. Measurement of magnetization
3. Magnetism in classical interpretation and its breakdown
4. Introduction of electron spin along Dirac equation

2022.4.13 Lecture 2

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Review

Chapter1 Basic Notions of Magnetism

Classical pictures of magnetic moments in materials:

- Magnetic charges
- Circular currents

Experimental methods to measure magnetization

Paramagnetic and diamagnetic terms in classical magnetization

Breakdown of classical magnetism: cancellation of paramagnetic and diamagnetic terms (Bohr-van Lewuuen theorem)

Introduction of spin angular momentum by relativistic quantum mechanics

Agenda

1. Spin-orbit interaction
2. Magnetism in quantum theory

Chapter 2 Magnetism in localized systems

1. Spherical potential
2. Larmor precession
3. Magnetism of inert gas
4. LS multiplex ground state of open shell ions and Hund's rule

Magnetic moment of electron spin

Dirac eq. with electromagnetic field $i\hbar\frac{\partial\psi}{\partial t} = [c\boldsymbol{\alpha}(\boldsymbol{p}+e\boldsymbol{A})+\beta m - e\phi]\,\psi$

$$\left[\left(i\hbar\frac{\partial}{\partial t}+e\phi\right)-c\sum_{j=x,y,z}\alpha_j\left(-i\hbar\frac{\partial}{\partial r_j}+eA_j\right)-\beta mc^2\right]\psi=0$$

Operation from left: $i\hbar\frac{\partial}{\partial t}+e\phi+c\sum_{j=x,y,z}\alpha_j\left(-i\hbar\frac{\partial}{\partial r_j}+eA_j\right)+\beta mc^2$

We obtain

$$\left[\left(i\hbar\frac{\partial}{\partial t}+e\phi\right)^2-c^2(\boldsymbol{p}+e\boldsymbol{A})^2-m^2c^4+ic\hbar e(\boldsymbol{\alpha}\cdot\boldsymbol{E})+i\hbar c^2e(\alpha_x\alpha_yB_z+\alpha_y\alpha_zB_x+\alpha_z\alpha_xB_y)\right]\psi=0$$

Because $\alpha_x\alpha_y=i\sigma_z^{(4)},\quad \alpha_y\alpha_z=i\sigma_x^{(4)},\quad \alpha_z\alpha_x=i\sigma_y^{(4)}$

$$\left[\left(i\hbar\frac{\partial}{\partial t}+e\phi\right)^2-c^2(\boldsymbol{p}+e\boldsymbol{A})^2-m^2c^4+ic\hbar e(\boldsymbol{\alpha}\cdot\boldsymbol{E})-\hbar c^2e\boldsymbol{\sigma}\cdot\boldsymbol{B}\right]\psi=0$$

Magnetic moment of electron spin (2)

Stationary solution: $\psi(\boldsymbol{r},t) = \exp(-i\epsilon t/\hbar)\varphi(\boldsymbol{r})$

$$\left[(\epsilon + e\phi)^2 - c^2(\boldsymbol{p} + e\boldsymbol{A})^2 - m^2c^4 + ic\hbar e(\boldsymbol{\alpha}\cdot\boldsymbol{E}) - \hbar c^2 e\boldsymbol{\sigma}\cdot\boldsymbol{B}\right]\varphi = 0$$

$$\phi = 0,\ \ \boldsymbol{E} = 0$$

Low energy expansion

$$\epsilon = mc^2 + \delta$$

We take first order in $\dfrac{\delta}{mc^2}$

$$\left[\frac{1}{2m}(\boldsymbol{p} + e\boldsymbol{A})^2 + \frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{B}\right]\varphi = \delta\varphi$$

Bohr magneton $\mu_{\mathrm{B}} \equiv \dfrac{e\hbar}{2m} \approx 9.274\times 10^{-24}\ \mathrm{JT}^{-1}$

$$\frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{B} = \mu_{\mathrm{B}}\boldsymbol{\sigma}\cdot\boldsymbol{B} = 2\mu_{\mathrm{B}}\boldsymbol{s}\cdot\boldsymbol{B}$$

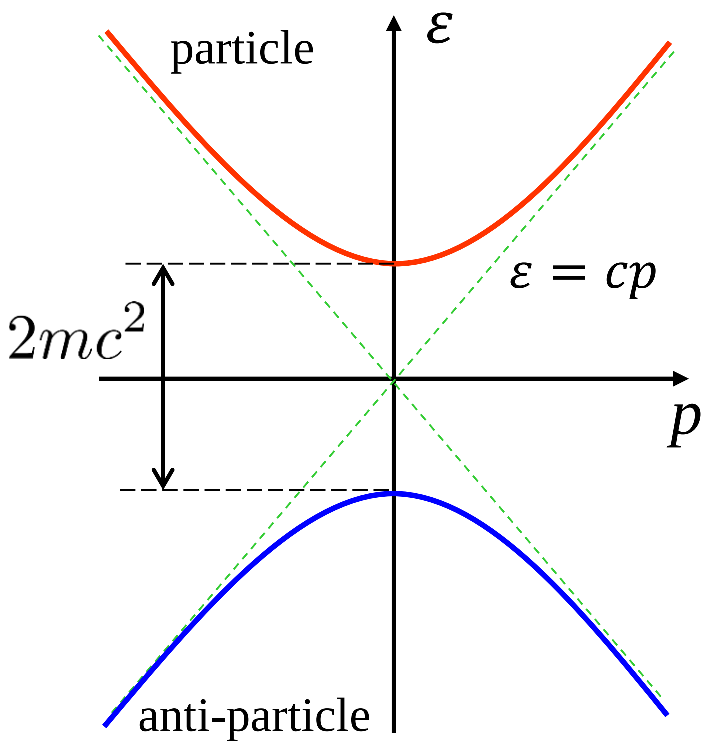
Therefore the magnetic moment is $-2\mu_{\mathrm{B}}\boldsymbol{s}$

Two-component separation approximation

Stationary Dirac equation $[c\boldsymbol{\alpha p} + mc^2\beta]\varphi = \epsilon\varphi$

Pauli representation $\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$ 4 × 4 matrices

When the particle sits still: $\epsilon = \pm mc^2$



+ corresponds to I, – corresponds to $-I$ in β

→ upper two laws: particle, lower two: anti-particle (?)

Finite momentum p requires correction.

$\tan 2\theta = \dfrac{p}{mc}$ $\quad \psi_\uparrow = e^{i(kz-\omega t)} \begin{pmatrix} \cos\theta \\ 0 \\ \sin\theta \\ 0 \end{pmatrix}$ Leak to lower laws

Spin-orbit interaction

Stationary equation $$(c\boldsymbol{\alpha}\cdot\boldsymbol{p}+\beta mc^2+V)\varphi=\epsilon\varphi$$

Two-component approximation $$\varphi=\begin{pmatrix}\varphi_{\mathrm{A}}\\ \varphi_{\mathrm{B}}\end{pmatrix}$$

Simultaneous equations $$\begin{cases}\boldsymbol{\sigma}\cdot\boldsymbol{p}\varphi_{\mathrm{B}}=c^{-1}(\delta-V)\varphi_{\mathrm{A}},\\ \boldsymbol{\sigma}\cdot\boldsymbol{p}\varphi_{\mathrm{A}}=c^{-1}(\delta-V+2mc^2)\varphi_{\mathrm{B}}.\end{cases}$$ $$\delta=\epsilon-mc^2$$

Erase of φ_{B} $$c^{-2}\boldsymbol{\sigma}\cdot\boldsymbol{p}(\delta-V+2mc^2)^{-1}\boldsymbol{\sigma}\cdot\boldsymbol{p}\varphi_{\mathrm{A}}=(\delta-V)\varphi_{\mathrm{A}}$$

Low velocity ($p\ll mc$) expansion $$c^2(\delta-V+2mc^2)^{-1}\approx\frac{1}{2m}\left[1-\frac{\delta-V}{2mc^2}+\cdots\right]$$

Normalization condition $$\langle\varphi|\varphi\rangle=\langle\varphi_{\mathrm{A}}|\varphi_{\mathrm{A}}\rangle+\langle\varphi_{\mathrm{B}}|\varphi_{\mathrm{B}}\rangle=1$$

Spin-orbit interaction (2)

Introduction of magnetic field $\boldsymbol{p} \to \boldsymbol{p} + e\boldsymbol{A}$

Correction due to leakage $$\langle \varphi_\mathrm{B} | \varphi_\mathrm{B} \rangle = \left\langle \varphi_\mathrm{A} \middle| \left[\frac{p^2 + e\hbar \boldsymbol{\sigma} \cdot \boldsymbol{B}}{4m^2c^2} \right] \middle| \varphi_\mathrm{A} \right\rangle = O\left(\frac{v^2}{c^2} \right)$$

Corrected two-component wavefunction $$\varphi_a = \left(1 + \frac{p^2 + e\hbar \boldsymbol{\sigma} \cdot \boldsymbol{B}}{8m^2c^2} \right) \varphi_\mathrm{A}$$

Pauli two-component approximation

Zeeman Spin-orbit interaction

$$\left[\frac{p^2}{2m} + V + \boxed{\frac{e\hbar}{2m} \boldsymbol{\sigma} \cdot \boldsymbol{B}} - \boxed{\frac{e\hbar \boldsymbol{\sigma} \cdot \boldsymbol{p} \times \boldsymbol{E}}{4m^2c^2}} - \frac{e\hbar^2}{8m^2c^2} \nabla \cdot \boldsymbol{E} \right.$$
$$\left. - \frac{p^4}{8m^3c^2} - \frac{e\hbar p^2}{4m^3c^2} \boldsymbol{\sigma} \cdot \boldsymbol{B} - \frac{(e\hbar B)^2}{8m^3c^2} \right] \varphi_a = \delta \varphi_a$$

Quantum Mechanical Treatment of Magnetism

$$\mathcal{H} = \sum_n \left[\frac{1}{2m} (\boldsymbol{p}_n + e\boldsymbol{A}(\boldsymbol{r}_n))^2 + U(\boldsymbol{r}_n) + g\mu_{\mathrm{B}} \boldsymbol{s}_n \cdot \boldsymbol{B} \right] + V(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots)$$

Nucleus potential g-factor

Symmetric gauge $\boldsymbol{A}(\boldsymbol{r}_n) = (\boldsymbol{B} \times \boldsymbol{r}_n)/2$

$$\mathcal{H} = \sum_n \left[\frac{\boldsymbol{p}_n^2}{2m} + U(\boldsymbol{r}_n) \right] + V(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots) \quad \cdots\cdots \quad \mathcal{H}_0$$

$\hbar \boldsymbol{l}_n \equiv \boldsymbol{r}_n \times \boldsymbol{p}_n$

$$+ \mu_{\mathrm{B}} \sum_n (\boldsymbol{l}_n + g\boldsymbol{s}_n) \cdot \boldsymbol{B} \quad \cdots\cdots \quad \mathcal{H}_1$$

$$+ \frac{e^2}{8m} \sum_n \{ r_n^2 B^2 - (\boldsymbol{B} \cdot \boldsymbol{r}_n)^2 \} \quad \cdots\cdots \quad \mathcal{H}_2$$

Magnetic moment

Commutation relations

$$\begin{cases} [r_{n\alpha}, p_{n\beta}] = r_{n\alpha}p_{n\beta} - p_{n\beta}r_{n\alpha} = i\hbar\delta_{\alpha\beta} \quad (\alpha, \beta = x, y, z) \\ [s_{n\alpha}, s_{n\beta}] = is_{n\gamma} \quad (\alpha, \beta, \gamma = x, y, z \text{ (cyclic)}) \\ [l_{n\alpha}, l_{n\beta}] = il_{n\gamma} \quad (\alpha, \beta, \gamma = x, y, z \text{ (cyclic)}) \end{cases}$$

Magnetic moment

$$\mu = -\frac{\partial \mathcal{H}}{\partial \boldsymbol{B}} = -\mu_{\mathrm{B}} \sum_n (\boldsymbol{l}_n + g\boldsymbol{s}_n) - \frac{e^2}{4m} \sum_n \{r_n^2 \boldsymbol{B} - \boldsymbol{r}_n(\boldsymbol{r}_n \cdot \boldsymbol{B})\}$$

$$= -\mu_{\mathrm{B}} \sum_n (\boldsymbol{l}_n + g\boldsymbol{s}_n) - \frac{e^2}{4m} \sum_n (\boldsymbol{r}_n \times (\boldsymbol{B} \times \boldsymbol{r}_n))\}$$

Paramagnetic Diamagnetic

This expression does not have drastic changes other than spin magnetic moment.
However …

Comment: Spins of nucleons

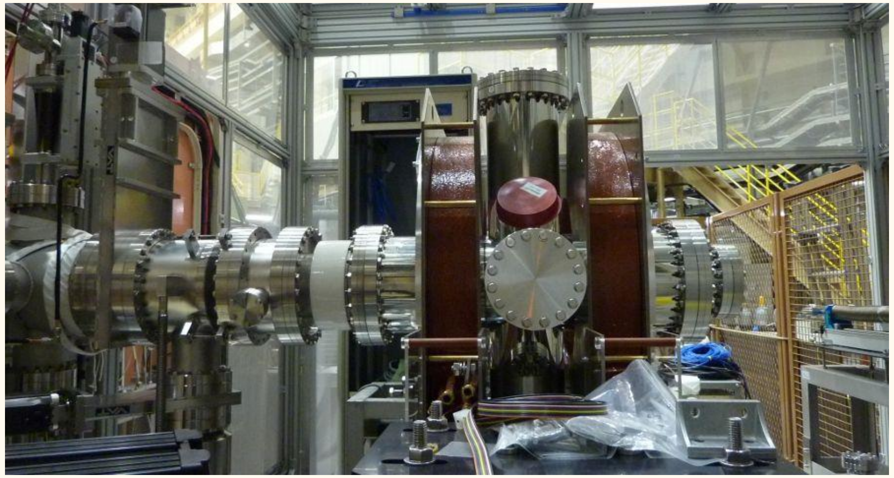
Protons, Neutrons, Muons have spins.

MRI

NMR

J-PARC

Neutron diffraction



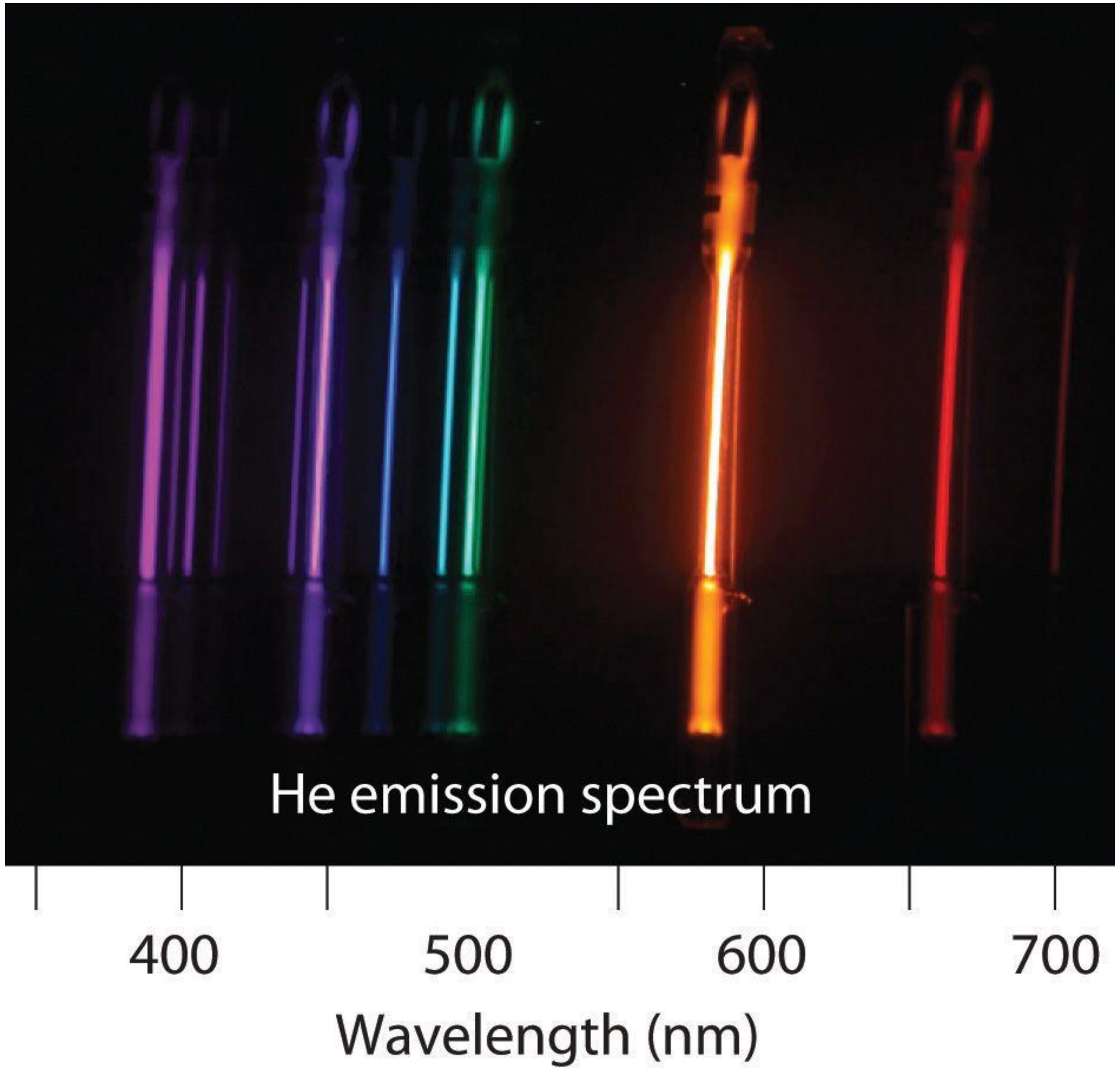
KEK

μSR

Chapter 2

Magnetism of Localized Electrons

Star birth



Second quantization

$|\boldsymbol{n}\rangle = |n_1, n_2, \cdots\rangle$ Number representation
(index the state with number of particles occupying basis states)

$|0\rangle$ Vacuum

$a_j^\dagger |0\rangle = |1_j\rangle$ Creation operator of *j*-th state
(Hermitian conjugate: annihilation operator)

Fermion:
anti-commutation relation

$$[a_i, a_j]_+ = [a_i^\dagger, a_i^\dagger]_+ = 0, \quad [a_i, a_j^\dagger]_+ = \delta_{ij}$$

number operator $\hat{n}_j \equiv a_j^\dagger a_j \qquad \hat{n}_j |\boldsymbol{n}\rangle = n_j |\boldsymbol{n}\rangle$

Boson: commutation relation

$$[b_i, b_j] = [b_i^\dagger, b_i^\dagger] = 0, \quad [b_i, b_j^\dagger] = \delta_{ij}$$

$$|n_j\rangle = \frac{1}{\sqrt{n_j!}} (a_j^\dagger)^{n_j} |0\rangle$$

Operators in second quantization representation

Multiparticle operator $\mathcal{F}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots) = \sum_i f(\boldsymbol{r}_i)$

Slater determinant $|\psi_{1,2,\ldots}\rangle$

$$\langle\psi_{m_1,m_2,\cdots}|\,\mathcal{F}\,|\psi_{n_1,n_2,\cdots}\rangle = \sum_i \langle\psi_{m_1,m_2,\cdots}|\,f(\boldsymbol{r}_i)\,|\psi_{n_1,n_2,\cdots}\rangle$$

Second quantization

$$F = \sum_{mn} \langle m|f|n\rangle\, a_m^\dagger a_n$$

Particle statistics

$$\langle m|f|n\rangle = \int d\boldsymbol{r}\phi_m^*(\boldsymbol{r})f(\boldsymbol{r})\psi_n(\boldsymbol{r})$$

Annihilation and creation operator (anti-)commutation relations

$$\langle\psi_{m_1,m_2,\cdots}|\,\mathcal{F}\,|\psi_{n_1,n_2,\cdots}\rangle = \langle\boldsymbol{m}|F|\boldsymbol{n}\rangle$$

$$G = \frac{1}{2}\sum_{klmn} \langle kl|g|mn\rangle\, a_k^\dagger a_l^\dagger a_n a_m$$

Electrons in a central force potential

$$\mathcal{H}_{\mathrm{L}} = \mathcal{H}_{\mathrm{L0}} + \mathcal{H}_{\mathrm{C}} + \mathcal{H}_{\mathrm{SOI}} + \mathcal{H}_{\mathrm{CF}}$$

Localized system

crystal field

spin-orbit interaction

mutual Coulomb interaction

single-electron (non-interaction)

$$\mathcal{H}_{\mathrm{L0}} = \sum_j \left[\frac{\boldsymbol{p}_j^2}{2m} + V_{\mathrm{sp}}(r_j) \right]$$

Electrons in a central force (spherical) potential

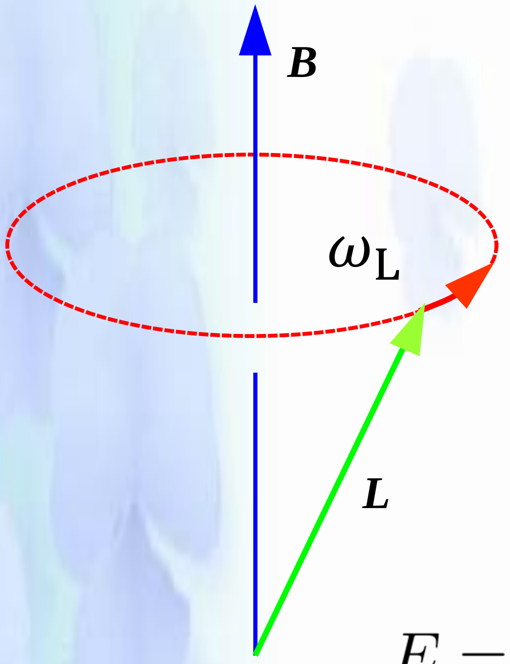
Eigenfunction in polar coordinate: (r, θ, φ)

$$\psi_{nlm}(\boldsymbol{r}) = R_{nl}(r) Y_{lm}(\theta, \varphi)$$

Radial wavefunction $R_{nl}(r) = b_{nl}\rho^l e^{-\rho/2} L_{n+1}^{2l+1}(\rho), \quad \rho \equiv \frac{2}{n}\frac{r}{a_0}$

Eigen energy $\epsilon_{nl} = -\frac{R_\infty}{n^2}, \quad R_\infty = \frac{me^4}{8\epsilon_0 h^3 c}$

$$\mathcal{H}_{\mathrm{L0}} = \sum_{nl} \epsilon_{nl} \sum_{m\sigma} a_{nlm\sigma}^\dagger a_{nlm\sigma}$$



Coulomb potential $V_{\mathrm{sp}}(r_j) = -\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_j}$

Total orbital angular momentum $\hbar \boldsymbol{L} = \hbar \sum_i \boldsymbol{l}_i$

$$\mathcal{H}_1 = \mu_\mathrm{B} \boldsymbol{L} \cdot \boldsymbol{B} = \mu_\mathrm{B} L_z B$$

Directional quantization $L_z = M : -L,\ -L+1, \cdots, L-1,\ L$

$$E = E_0 + \mu_\mathrm{B} M B \equiv E_0 + \hbar \omega_\mathrm{L} M, \quad \boxed{\omega_\mathrm{L} \equiv \frac{\mu_\mathrm{B} B}{\hbar} = \frac{eB}{2m} \ (\text{Larmor frequency})}$$

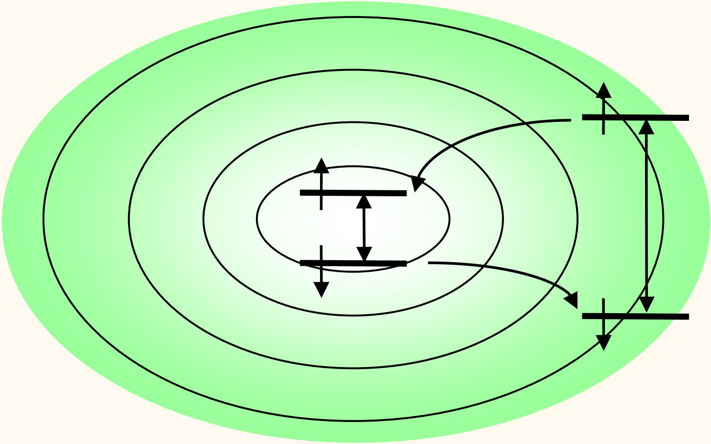
Heisenberg equation $\frac{\mathrm{d}\boldsymbol{L}}{\mathrm{d}t} = \frac{1}{i\hbar}[\boldsymbol{L}, \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2]$

Larmor precession $L_x(t) = L_0 \cos(\omega_\mathrm{L} t + \theta_0), \quad L_y(t) = L_0 \sin(\omega_\mathrm{L} t + \theta_0)$

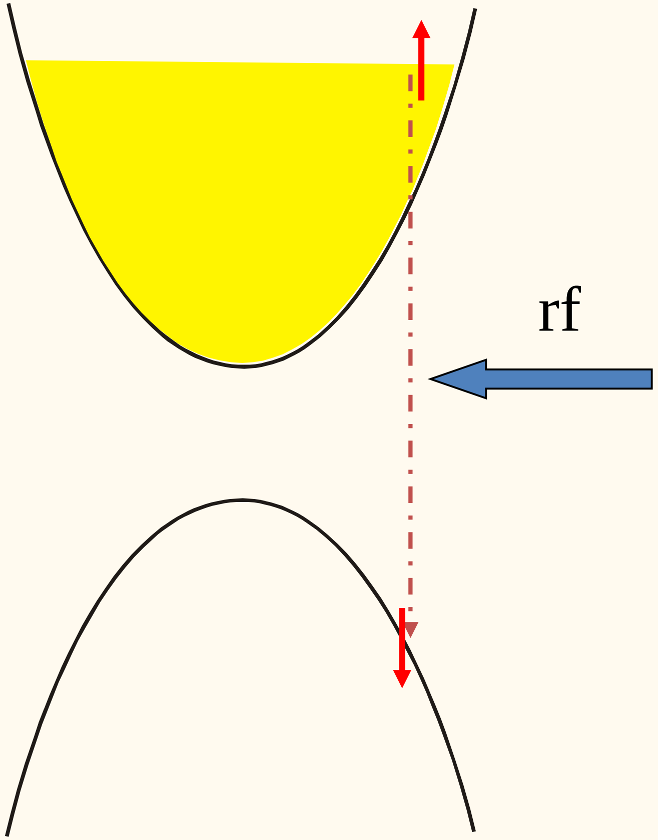
In the case of spin: g-factor $\omega_\mathrm{L} = g\frac{eB}{2m} \approx \frac{eB}{m}$

Magnetism of inert gases

Star birth



Magnetic trap



Evaporation cooling

Total angular momentum

$$\boldsymbol{L} = \sum_j \boldsymbol{l}_j = \sum_\sigma \sum_{mm'} \langle m | \boldsymbol{l} | m' \rangle_{nl} \, a^\dagger_{m\sigma} a_{m'\sigma},$$

$$\boldsymbol{S} = \sum_j \boldsymbol{s}_j = \sum_m \sum_{\sigma\sigma'} \left(\frac{\sigma}{2} \right)_{\sigma\sigma'} a^\dagger_{m\sigma} a_{m\sigma'},$$

$$\boldsymbol{J} = \sum_j \boldsymbol{j}_j = \boldsymbol{L} + \boldsymbol{S}$$

Magnetism of inert gases

Inert gases: Closed shell structure $L = S = 0$ due to quantization!

Residual is the dielectric term: $$\boldsymbol{\mu}_{\mathrm{dia}} = -\frac{e^2}{4m}\sum_n [\boldsymbol{r}_n \times (\boldsymbol{B} \times \boldsymbol{r}_n)]$$

$$= -\frac{e}{2}\sum_n [\boldsymbol{r}_n \times (\boldsymbol{\omega}_{\mathrm{L}} \times \boldsymbol{r}_n)] = -\frac{\mu_{\mathrm{B}}}{\hbar}\sum_n [\boldsymbol{r}_n \times (m\boldsymbol{v}_n)]$$

Larmor rotation angular momentum

Z	Element	Susceptibility
2	He	-1.9×10^{-6}
10	Ne	-7.2×10^{-6}
18	Ar	-19.4×10^{-6}
36	Kr	-28×10^{-6}
54	Xe	-43×10^{-6}

$$\mu_{\mathrm{d}} = -\frac{e^2}{4m}\left\langle x^2 + y^2 \right\rangle B = -\frac{e^2}{6m}\left\langle r^2 \right\rangle B$$

$$\chi = -\frac{N_{\mathrm{A}} Z e^2 \left\langle r^2 \right\rangle}{6m}$$ Moll susceptibility

$$\frac{\left\langle r^2 \right\rangle}{a_{\mathrm{B}}^2} \sim ??$$

PERIODIC TABLE OF ELEMENTS

1	Atomic Number
H	Symbol
Hydrogen	Name
Nonmetal	Chemical Group Block

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen Nonmetal																	2 He Helium Noble Gas
3 Li Lithium Alkali Metal	4 Be Beryllium Alkaline Earth Metal											5 B Boron Metalloid	6 C Carbon Nonmetal	7 N Nitrogen Nonmetal	8 O Oxygen Nonmetal	9 F Fluorine Halogen	10 Ne Neon Noble Gas
11 Na Sodium Alkali Metal	12 Mg Magnesium Alkaline Earth Metal											13 Al Aluminum Post-Transition Metal	14 Si Silicon Metalloid	15 P Phosphorus Nonmetal	16 S Sulfur Nonmetal	17 Cl Chlorine Halogen	18 Ar Argon Noble Gas
19 K Potassium Alkali Metal	20 Ca Calcium Alkaline Earth Metal	21 Sc Scandium Transition Metal	22 Ti Titanium Transition Metal	23 V Vanadium Transition Metal	24 Cr Chromium Transition Metal	25 Mn Manganese Transition Metal	26 Fe Iron Transition Metal	27 Co Cobalt Transition Metal	28 Ni Nickel Transition Metal	29 Cu Copper Transition Metal	30 Zn Zinc Transition Metal	31 Ga Gallium Post-Transition Metal	32 Ge Germanium Metalloid	33 As Arsenic Metalloid	34 Se Selenium Nonmetal	35 Br Bromine Halogen	36 Kr Krypton Noble Gas
37 Rb Rubidium Alkali Metal	38 Sr Strontium Alkaline Earth Metal	39 Y Yttrium Transition Metal	40 Zr Zirconium Transition Metal	41 Nb Niobium Transition Metal	42 Mo Molybdenum Transition Metal	43 Tc Technetium Transition Metal	44 Ru Ruthenium Transition Metal	45 Rh Rhodium Transition Metal	46 Pd Palladium Transition Metal	47 Ag Silver Transition Metal	48 Cd Cadmium Transition Metal	49 In Indium Post-Transition Metal	50 Sn Tin Post-Transition Metal	51 Sb Antimony Metalloid	52 Te Tellurium Metalloid	53 I Iodine Halogen	54 Xe Xenon Noble Gas
55 Cs Cesium Alkali Metal	56 Ba Barium Alkaline Earth Metal	*	72 Hf Hafnium Transition Metal	73 Ta Tantalum Transition Metal	74 W Tungsten Transition Metal	75 Re Rhenium Transition Metal	76 Os Osmium Transition Metal	77 Ir Iridium Transition Metal	78 Pt Platinum Transition Metal	79 Au Gold Transition Metal	80 Hg Mercury Transition Metal	81 Tl Thallium Post-Transition Metal	82 Pb Lead Post-Transition Metal	83 Bi Bismuth Post-Transition Metal	84 Po Polonium Metalloid	85 At Astatine Halogen	86 Rn Radon Noble Gas
87 Fr Francium Alkali Metal	88 Ra Radium Alkaline Earth Metal	**	104 Rf Rutherfordium Transition Metal	105 Db Dubnium Transition Metal	106 Sg Seaborgium Transition Metal	107 Bh Bohrium Transition Metal	108 Hs Hassium Transition Metal	109 Mt Meitnerium Transition Metal	110 Ds Darmstadtium Transition Metal	111 Rg Roentgenium Transition Metal	112 Cn Copernicium Transition Metal	113 Nh Nihonium Post-Transition Metal	114 Fl Flerovium Post-Transition Metal	115 Mc Moscovium Post-Transition Metal	116 Lv Livermorium Post-Transition Metal	117 Ts Tennessine Halogen	118 Og Oganesson Noble Gas
		*	57 La Lanthanum Lanthanide	58 Ce Cerium Lanthanide	59 Pr Praseodymium Lanthanide	60 Nd Neodymium Lanthanide	61 Pm Promethium Lanthanide	62 Sm Samarium Lanthanide	63 Eu Europium Lanthanide	64 Gd Gadolinium Lanthanide	65 Tb Terbium Lanthanide	66 Dy Dysprosium Lanthanide	67 Ho Holmium Lanthanide	68 Er Erbium Lanthanide	69 Tm Thulium Lanthanide	70 Yb Ytterbium Lanthanide	71 Lu Lutetium Lanthanide
		**	89 Ac Actinium Actinide	90 Th Thorium Actinide	91 Pa Protactinium Actinide	92 U Uranium Actinide	93 Np Neptunium Actinide	94 Pu Plutonium Actinide	95 Am Americium Actinide	96 Cm Curium Actinide	97 Bk Berkelium Actinide	98 Cf Californium Actinide	99 Es Einsteinium Actinide	100 Fm Fermium Actinide	101 Md Mendelevium Actinide	102 No Nobelium Actinide	103 Lr Lawrencium Actinide

Electronic states in magnetic ions

Open shell electronic states

Angular momentum *l* orbit $m = -l, -l+1, \cdots, l$

State of many electrons: indexed with *L* and *S* : state (*L*, *S*) degenerated in the absence of coulomb term

(*L*, *S*) term degenerated (2*L*+1)(2*S*+1) : LS multiplex

Which state is the ground state?

$$\mathcal{H}_{\rm C} = \frac{1}{2}\sum_{m_1,\cdots,m_4}\sum_{\sigma_1\sigma_2}\left\langle m_1 m_2 \left| \frac{e^2}{4\pi\epsilon_0 r} \right| m_3 m_4 \right\rangle a^\dagger_{m_1\sigma_1} a^\dagger_{m_2\sigma_2} a_{m_3\sigma_3} a_{m_4\sigma_4}$$

$$\left\langle m_1 m_2 \left| \frac{e^2}{4\pi\epsilon_0 r} \right| m_3 m_4 \right\rangle = \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 u^*_{m_1}(\boldsymbol{r}_1) u^*_{m_2}(\boldsymbol{r}_2) \frac{e^2}{4\pi\epsilon_0|\boldsymbol{r}_1 - \boldsymbol{r}_2|} u_{m_3}(\boldsymbol{r}_2) u_{m_4}(\boldsymbol{r}_1)$$

Dominating terms

$$m_1 = m_2 = m_3 = m_4$$

$$\left\langle m_1 m_1 \middle| \frac{e^2}{4\pi\epsilon_0 r} \middle| m_1 m_1 \right\rangle a^\dagger_{m_1\uparrow} a^\dagger_{m_1\downarrow} a_{m_1\uparrow} a_{m_1\downarrow} = U_0 \sum_m \hat{n}_{m\uparrow}\hat{n}_{m\downarrow} \quad (\hat{n}_{m\sigma} = a^\dagger_{m\sigma} a_{m\sigma})$$

Coulomb repulsion in the same orbit

$$m_1 = m_4 \neq m_2 = m_3$$

$$\frac{1}{2}\sum_{m_1 \neq m_2} U(m_1, m_2)\hat{n}_{m1}\hat{n}_{m2} \quad \left(\hat{n}_m = \sum_\sigma n_{m\sigma}\right)$$

Coulomb repulsion between different orbits

$$m_1 = m_3 \neq m_2 = m_4$$

Exchange term

$$\frac{1}{2}\sum_{m_1 \neq m_2}\sum_{\sigma_1\sigma_2} J(m_1, m_2) a^\dagger_{m_1\sigma_1} a^\dagger_{m_2\sigma_2} a_{m_1\sigma_2} a_{m_2\sigma_1}$$

$$= -\frac{1}{2}\sum_{m_1 \neq m_2} J(m_1, m_2)\left(\frac{1}{2}\hat{n}_{m_1}\hat{n}_{m_2} + 2\boldsymbol{s}_{m_1}\cdot\boldsymbol{s}_{m_2}\right)$$

Exchange integral

Spin operator $$\boldsymbol{s}_m = \sum_{\sigma_1\sigma_2} \left(\frac{\boldsymbol{\sigma}}{2}\right)_{\sigma_1\sigma_2} a^\dagger_{m\sigma_1} a_{m\sigma_2}$$

Exchange integral $J(m_1, m_2)$

$$\begin{aligned}
J(m_1, m_2) &= \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 u^*_{m_1}(\boldsymbol{r}_1) u_{m_2} \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{r}_1 - \boldsymbol{r}_2|} u_{m_1}(\boldsymbol{r}_2) u^*_{m_2}(\boldsymbol{r}_2) \\
&= \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 u^*_{m_1}(\boldsymbol{r}_1) u_{m_2} \left[\int d\boldsymbol{q} \frac{e^2}{\epsilon_0 q^2} e^{i\boldsymbol{q}\cdot(\boldsymbol{r}_1 - \boldsymbol{r}_2)}\right] u_{m_1}(\boldsymbol{r}_2) u^*_{m_2}(\boldsymbol{r}_2) \\
&= \int d\boldsymbol{q} \frac{e^2}{\epsilon_0 q^2} \left| \int d\boldsymbol{r}_1 u^*_{m_1}(\boldsymbol{r}_1) u_{m_2}(\boldsymbol{r}_1) e^{i\boldsymbol{q}\cdot\boldsymbol{r}_1} \right|^2 > 0
\end{aligned}$$

Hund's rule

Hund's rule

The ground LS multiplex is determined by the following

1. It should have maximum S.
2. Under the condition 1., it should have maximum L.

3d transition metal ions

Element	Configuration	Ion	Configuration	L	S
Sc	$3d^1 4s^2$				
Ti	$3d^2 4s^2$	Ti^{3+}, V^{4+}	$3d^1$	2	1/2
V	$3d^3 4s^2$	V^{3+}	$3d^2$	3	1
Cr	$3d^5 4s^1$	Cr^{3+}, V^{2+}	$3d^3$	3	3/2
Mn	$3d^5 4s^2$	Mn^{3+}, Cr^{2+}	$3d^4$	2	2
Fe	$3d^6 4s^2$	Fe^{3+}, Mn^{2+}	$3d^5$	0	5/2
Co	$3d^7 4s^2$	Co^{3+}, Fe^{2+}	$3d^6$	2	2
Ni	$3d^8 4s^2$	Co^{2+}	$3d^7$	3	3/2
Cu	$3d^{10} 4s^1$	Ni^{2+}	$3d^8$	3	1
Zn	$3d^{10} 4s^2$	Cu^{2+}	$3d^9$	2	1/2

Summary

1. Spin-orbit interaction
2. Magnetism in quantum theory

Chapter 2 Magnetism in localized systems

1. Spherical potential
2. Larmor precession
3. Magnetism of inert gas
4. LS multiplex ground state of open shell ions and Hund's rule

Lecture on

2022.4.20 Lecture 3

10:25 – 11:55

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Review

1. Spin-orbit interaction
2. Magnetism in quantum theory

Chapter 2 Magnetism in localized systems

1. Spherical potential
2. Larmor precession
3. Magnetism of inert gas
4. LS multiplex ground state of open shell ions and Hund’s rule

Agenda

Electronic states in magnetic ions

- LS coupling approach
- j-j coupling approach

Paramagnetism by magnetic ions in insulators

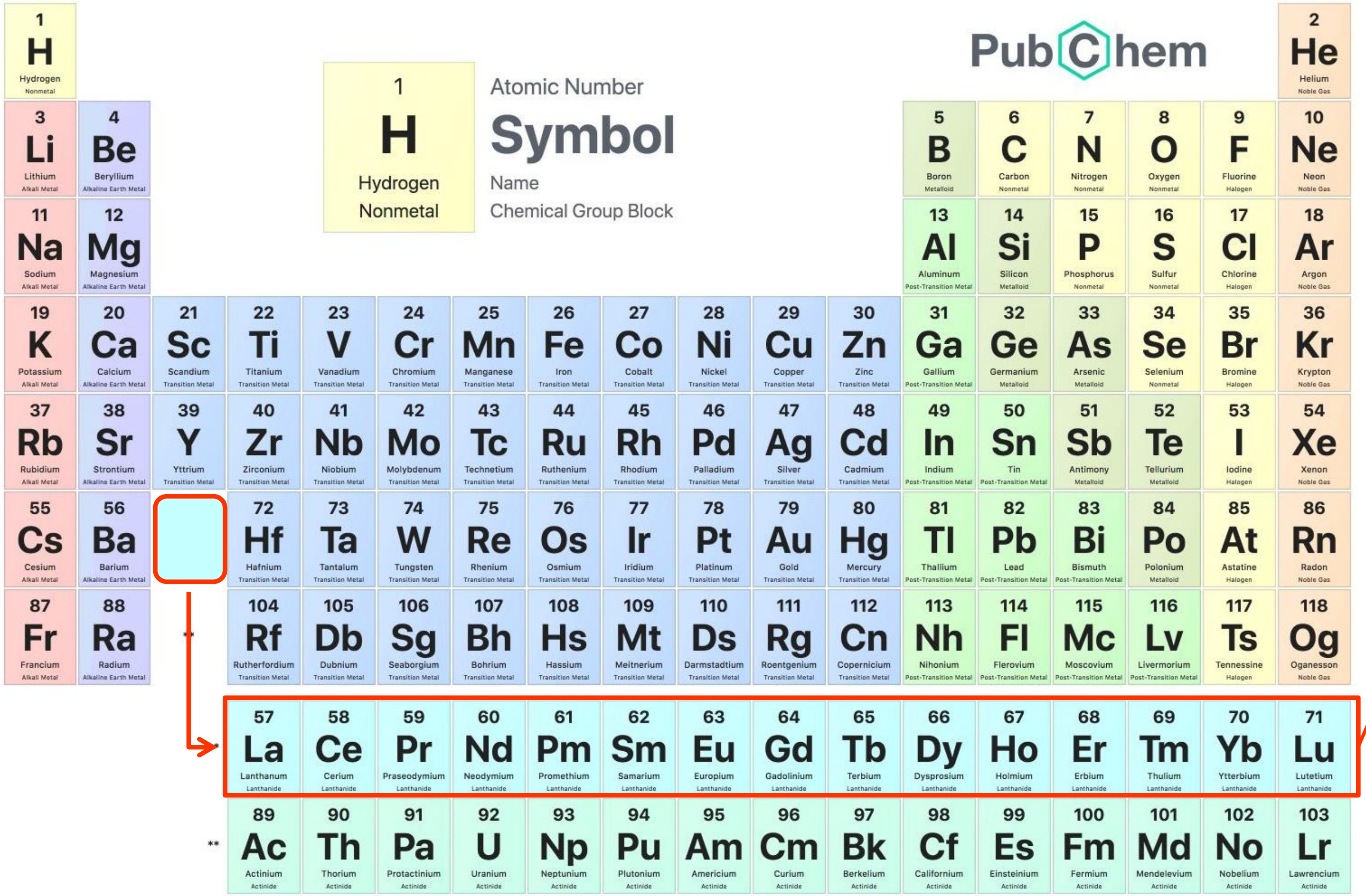
- Curie law
- Breakdown of LS coupling approach in 3*d* transition metals

Ligand field approach

- Octahedron potential

Electronic states in magnetic ions (continued)

Periodic table of elements



Sm

$$4s^2 4p^6 (4f)^6 5s^2 5p^6 6s^2$$

Electronic states in magnetic ions (continued)

Ex) Lanthanoid:

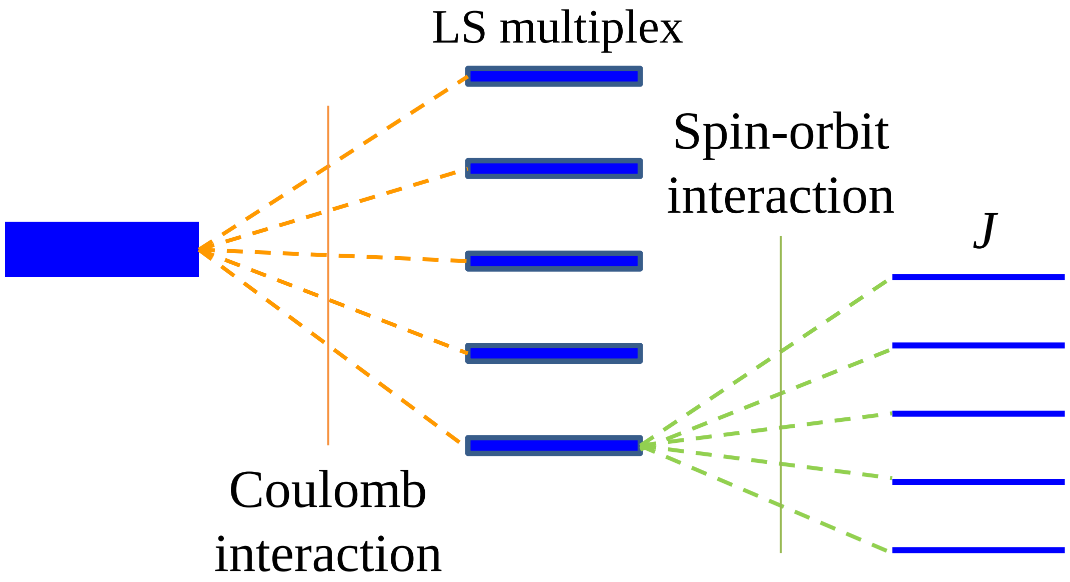
	57 La Lanthanum Lanthanide	58 Ce Cerium Lanthanide	59 Pr Praseodymium Lanthanide	60 Nd Neodymium Lanthanide	61 Pm Promethium Lanthanide	62 Sm Samarium Lanthanide	63 Eu Europium Lanthanide	64 Gd Gadolinium Lanthanide	65 Tb Terbium Lanthanide	66 Dy Dysprosium Lanthanide	67 Ho Holmium Lanthanide	68 Er Erbium Lanthanide	69 Tm Thulium Lanthanide	70 Yb Ytterbium Lanthanide	71 Lu Lutetium Lanthanide
Number of 4*f* electrons:	0	1	3	4	5	6	7	7	9	10	11	12	13	14	15
Number of 4*f* electrons (3+ion):	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

$$\mathcal{H}_{\mathrm{L}} = \underline{\mathcal{H}_{\mathrm{L0}} + \mathcal{H}_{\mathrm{C}}} + \mathcal{H}_{\mathrm{SOI}} + \mathcal{H}_{\mathrm{CF}}$$

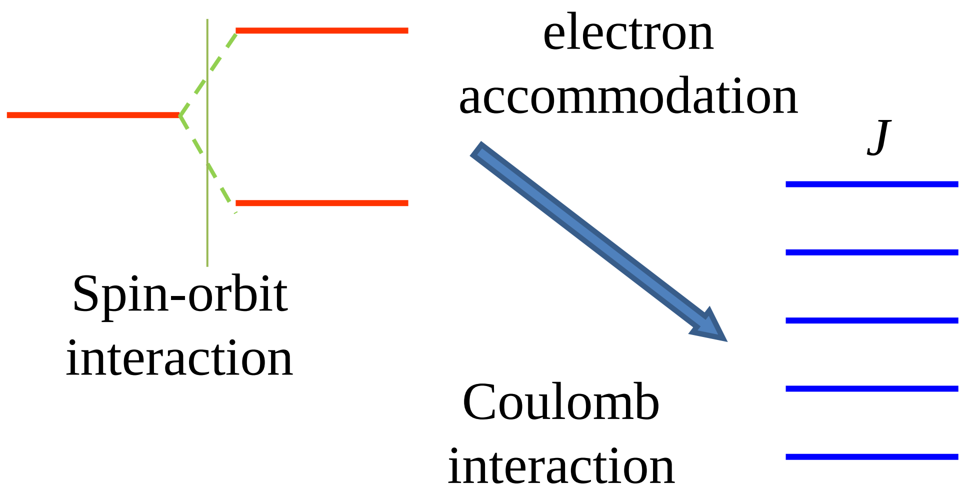
Lifting of degeneracy to LS multiplex

Hund's rule to find the ground LS multiplex

LS coupling (Russell-Saunders)



j-j coupling



Spin-orbit splitting of multiplex in single-electron problem

Spin-orbit term in the Pauli approximation: $$-\frac{e\hbar\boldsymbol{\sigma}\cdot\boldsymbol{p}\times\boldsymbol{E}}{4m^2c^2} = -\frac{e^2\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\boldsymbol{p}\times\nabla V) = \frac{e^2\hbar}{2m^2c^2}\zeta(r)\boldsymbol{s}\cdot\boldsymbol{l} \equiv \xi(r)\boldsymbol{l}\cdot\boldsymbol{s}$$

Coulomb potential: $V(r) = -\dfrac{Ze^2}{4\pi\epsilon_0 r}$ then $\xi(r) = \dfrac{Ze^2}{2m^2c^2}\dfrac{1}{(4\pi\epsilon_0)r^3}$

The expression tells that the SOI is more important for larger Z and orbitals closer to the nucleus.

Lanthanoid: (effect of spin-orbit interaction) > (that of crystal field)

Spin-orbit single electron hamiltonian: $$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\rm so} = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}) + \xi(r)\boldsymbol{l}\cdot\boldsymbol{s}$$

$[\mathcal{H},\boldsymbol{l}]\neq 0 \quad [\mathcal{H},\boldsymbol{s}]\neq 0$ $\quad$ $\boldsymbol{l},\boldsymbol{s}$: not constants of motion

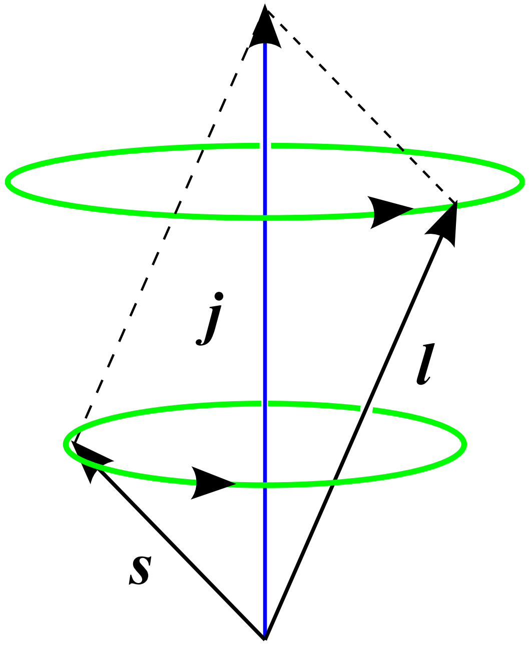
$$[\boldsymbol{l}\cdot\boldsymbol{s},\hat{l}_z] = i\hbar(-l_y s_x + l_x s_y), \quad [\boldsymbol{l}\cdot\boldsymbol{s},\hat{s}_z] = i\hbar(-l_x s_y + l_y s_x) = -[\boldsymbol{l}\cdot\boldsymbol{s},\hat{l}_z]$$

Total angular momentum

$$\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s} \longrightarrow [\mathcal{H}, \boldsymbol{j}] = 0$$

j is a constant of motion

$$\boldsymbol{l}\cdot\boldsymbol{s} = (\boldsymbol{l}+\boldsymbol{s})\cdot\boldsymbol{s} - \boldsymbol{s}^2 = \underbrace{\boldsymbol{j}\cdot\boldsymbol{s}}_{\text{Zeeman-like term}} - \boldsymbol{s}^2 \qquad [\mathcal{H}, \boldsymbol{s}^2] = 0$$



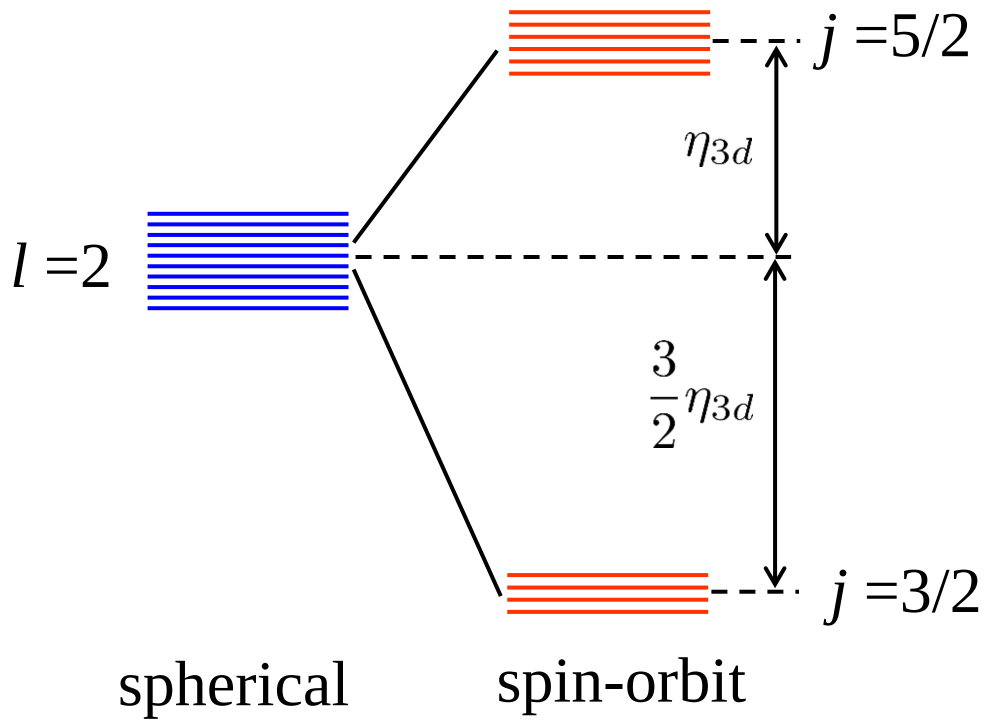
l*, *s : Precession around ***j***

$$2\boldsymbol{l}\cdot\boldsymbol{s} = (\boldsymbol{l}+\boldsymbol{s})^2 - \boldsymbol{l}^2 - \boldsymbol{s}^2 = \boldsymbol{j}^2 - \boldsymbol{l}^2 - \boldsymbol{s}^2$$

Eigenvalue of $\boldsymbol{l}\cdot\boldsymbol{s}$

$$[j(j+1) - l(l+1) - s(s+1)]/2 = \frac{1}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]$$

Spin-orbit splitting of multiplex in single-electron problem (2)



Energy eigenvalues:

$$\epsilon_{nlj} = \epsilon_{nl} + \frac{\eta_{nl}}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]$$

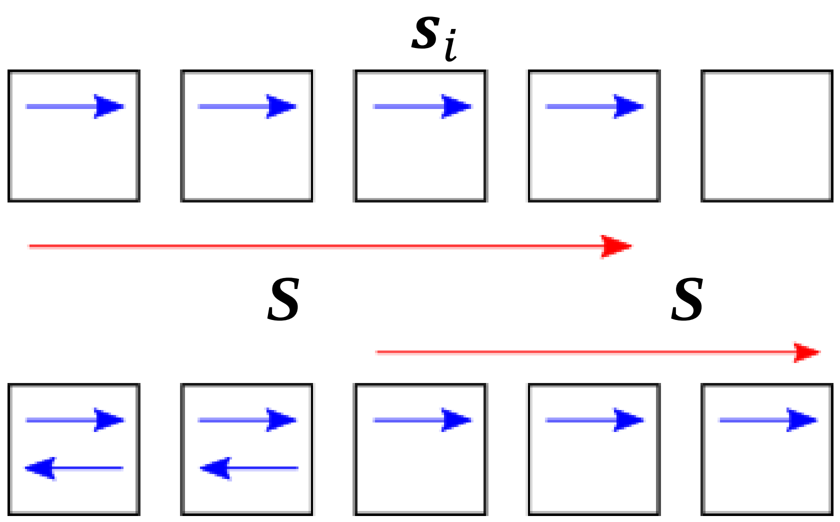
$$\eta_{nl} = \int_0^\infty \xi(r) R_{nl}(r)^2 r^2 dt$$

j can take values: $|l \pm 1/2|$

Spin-orbit interaction in the ground state of LS multiplex

Multi-electron hamiltonian: $\mathcal{H}_{\rm SOI} = \sum_i \xi(r_i)\boldsymbol{l}_i \cdot \boldsymbol{s}_i \rightarrow \sum_i \xi_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i \rightarrow \xi \sum_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i$

LS-coupling approach



Hund's rule $\longrightarrow$ LS multiplex ground state
$(2L+1)(2S+1)$ degeneracy

$[\mathcal{H}, \boldsymbol{L}] \neq 0 \quad [\mathcal{H}, \boldsymbol{S}] \neq 0$

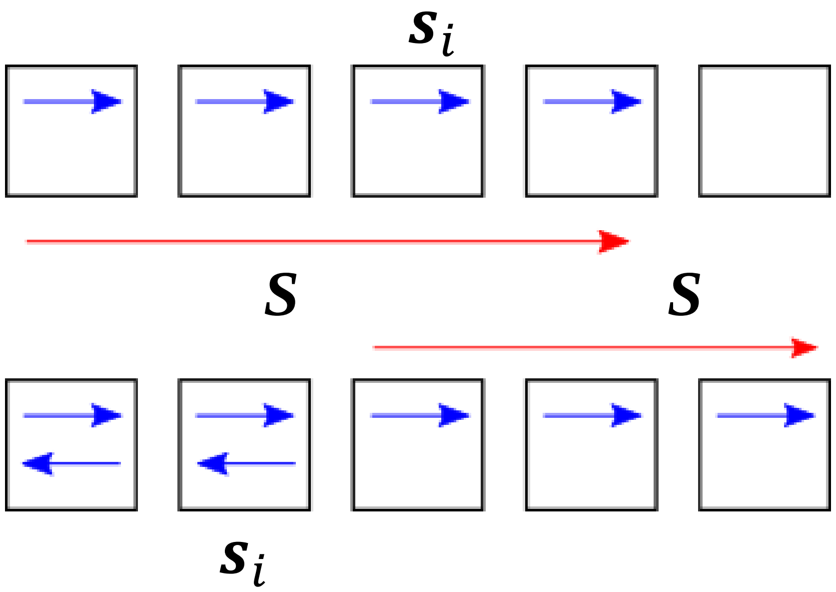
$\boldsymbol{L}$, $\boldsymbol{S}$ are not constant of motion.

$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$: a constant of motion

$$\boldsymbol{s}_i = \frac{1}{n}\boldsymbol{S} = \frac{1}{2S}\boldsymbol{S} \quad (n \leq 2l+1)$$

$$\mathcal{H}_{\rm SOI} = \xi \sum_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i = \xi \left(\sum_i \boldsymbol{l}_i\right) \cdot \boldsymbol{s} = \frac{\xi}{2S}\boldsymbol{L} \cdot \boldsymbol{S} \equiv \lambda \boldsymbol{L} \cdot \boldsymbol{S}$$

Spin-orbit interaction in the ground state of LS multiplex



$n > 2l + 1$

Summation on all m_l: $\sum l_i = 0$

Residual part: $\boldsymbol{s}_i$ and $\boldsymbol{S}$ are inverted

$$\mathcal{H}_{\mathrm{SOI}} = \xi \left[\left(\sum_{i=1}^{2l+1} \boldsymbol{l}_i \right) \cdot \boldsymbol{s} - \left(\sum_{i=2l+2}^{n} \boldsymbol{l}_i \right) \cdot \boldsymbol{s} \right]$$

$$= -\frac{\xi}{2S} \boldsymbol{L} \cdot \boldsymbol{S} = -\lambda \boldsymbol{L} \cdot \boldsymbol{S}$$

$$J = |L - S|, |L - S| + 1, \cdots, L + S$$

$$\boldsymbol{L} \cdot \boldsymbol{S} = \frac{1}{2}(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2) = \frac{1}{2}[J(J+1) - L(L+1) - S(S+1)]$$

Ground state

$n \leq 2l + 1 \qquad J = |L - S|$

$n > 2l + 1 \qquad J = L + S$

Electron configuration of Lanthanoid ions

Elements (Lanthanoid)	Electronic Configuration atom R	Electronic Configuration ion R^{3+}	L	S	J	Ground state multiplex	g_j
La	$5d6s^2$		0	0	0	$^1S_0$	0
Ce	$4f5d6s^2$	$4f^1$	3	1/2	5/2	$^2F_{5/2}$	6/7
Pr	$4f^36s^2$	$4f^2$	5	1	4	$^3H_4$	4/5
Nd	$4f^46s^2$	$4f^3$	6	3/2	9/2	$^4I_{9/2}$	8/11
Pm	$4f^56s^2$	$4f^4$	6	2	4	$^5I_4$	1/5
Sm	$4f^66s^2$	$4f^5$	5	5/2	5/2	$^6H_{5/2}$	2/7
Eu	$4f^76s^2$	$4f^6$	3	3	0	$^7F_0$	0
Gd	$4f^75d6s^2$	$4f^7$	0	7/2	7/2	$^8S_{7/2}$	2
Tb	$4f^96s^2$	$4f^8$	3	3	6	$^7F_6$	3/2
Dy	$4f^{10}6s^2$	$4f^9$	5	5/2	15/2	$^6H_{15/2}$	4/3
Ho	$4f^{11}6s^2$	$4f^{10}$	6	2	8	$^5I_8$	5/4
Er	$4f^{12}6s^2$	$4f^{11}$	6	3/2	15/2	$^4I_{15/2}$	6/5
Tm	$4f^{13}6s^2$	$4f^{12}$	5	1	6	$^3H_6$	7/6
Yb	$4f^{14}6s^2$	$4f^{13}$	3	1/2	7/2	$^2F_{7/2}$	8/7
Lu	$4f^{14}5d6s^2$	$4f^{14}$	0	0	0	$^1S_0$	0

Spectroscopic symbol of multi-electron state

$$(L, S, J)$$
$$\downarrow$$
$$^{2S+1}L_J$$

$2S+1$: number
L: symbol
J: number

Eigenfunction and second quantization representation

Eigenfunction for (J, M): $$|J, M\rangle = \sum_{M_l M_s} \underbrace{\langle L, M_l; S, M_s | J, M\rangle}_{\text{Clebsch-Gordan coefficient}} |L, M_l; S, M_s\rangle$$

Second quantization representation: $$\mathcal{H}_{\mathrm{SOI}} = \sum_{mm'\sigma\sigma'} \lambda_{nl}(m\sigma, m'\sigma') a^\dagger_{m\sigma} a_{m'\sigma'},$$

$$\lambda_{nl}(m\sigma, m'\sigma') \equiv \frac{Z_{\mathrm{eff}} e^2 \hbar^2 \langle r^3 \rangle}{2m^2 c^2 (4\pi\epsilon_0)} \langle m | \boldsymbol{l} | m' \rangle_{nl} \cdot \left(\frac{\boldsymbol{\sigma}}{2} \right)_{\sigma\sigma'}$$

Effective Coulomb potential: $$V(r) = -\frac{Z_{\mathrm{eff}} e^2}{4\pi\epsilon_0 r}$$

Clebsch-Gordan calculator on Wolfram alpha

https://www.wolframalpha.com/input/?i=Clebsch-Gordan+calculator

j-j coupling (short comment)

$(4f)^2$ Pr^{3+} $l=2 \quad j = 3 \pm \frac{1}{2} = \underline{\frac{5}{2}}, \ \frac{7}{2}$

Ground state

$J_{\max} = \frac{5}{2} + \frac{3}{2} = 4$: same as LS coupling

$$|J, M\rangle = |4, +4\rangle = a^\dagger_{+5/2} a^\dagger_{+3/2} |0\rangle$$

$$a^\dagger_{j_z} = \sum_{m,s} \langle 3, m; 1/2, s | 5/2, j_z \rangle \, a^\dagger_{ms} = \sqrt{\frac{7+2j_z}{14}} a^\dagger_{j_z+1/2\downarrow} - \sqrt{\frac{7-2j_z}{14}} a^\dagger_{j_z-\uparrow}$$

Paramagnetism by magnetic ions in insulators

Free local moment and Curie law

Due to the g-factor, the magnetization is not parallel with the total momentum, hence the magnetization is not a constant of motion.

$$\mathcal{H}_1 = \mu_\mathrm{B}(\boldsymbol{L} + g\boldsymbol{S}) \cdot \boldsymbol{B} \qquad \mathcal{H}_1 = g_J \mu_\mathrm{B} \boldsymbol{J} \cdot \boldsymbol{B}$$

$$g_J \boldsymbol{J} = \boldsymbol{L} + g\boldsymbol{S}, \quad \boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$

Average gives effective g-factor: $$g_J = \frac{1+g}{2} - \frac{g-1}{2}\frac{L(L+1) - S(S+1)}{J(J+1)}$$ Lande g-factor

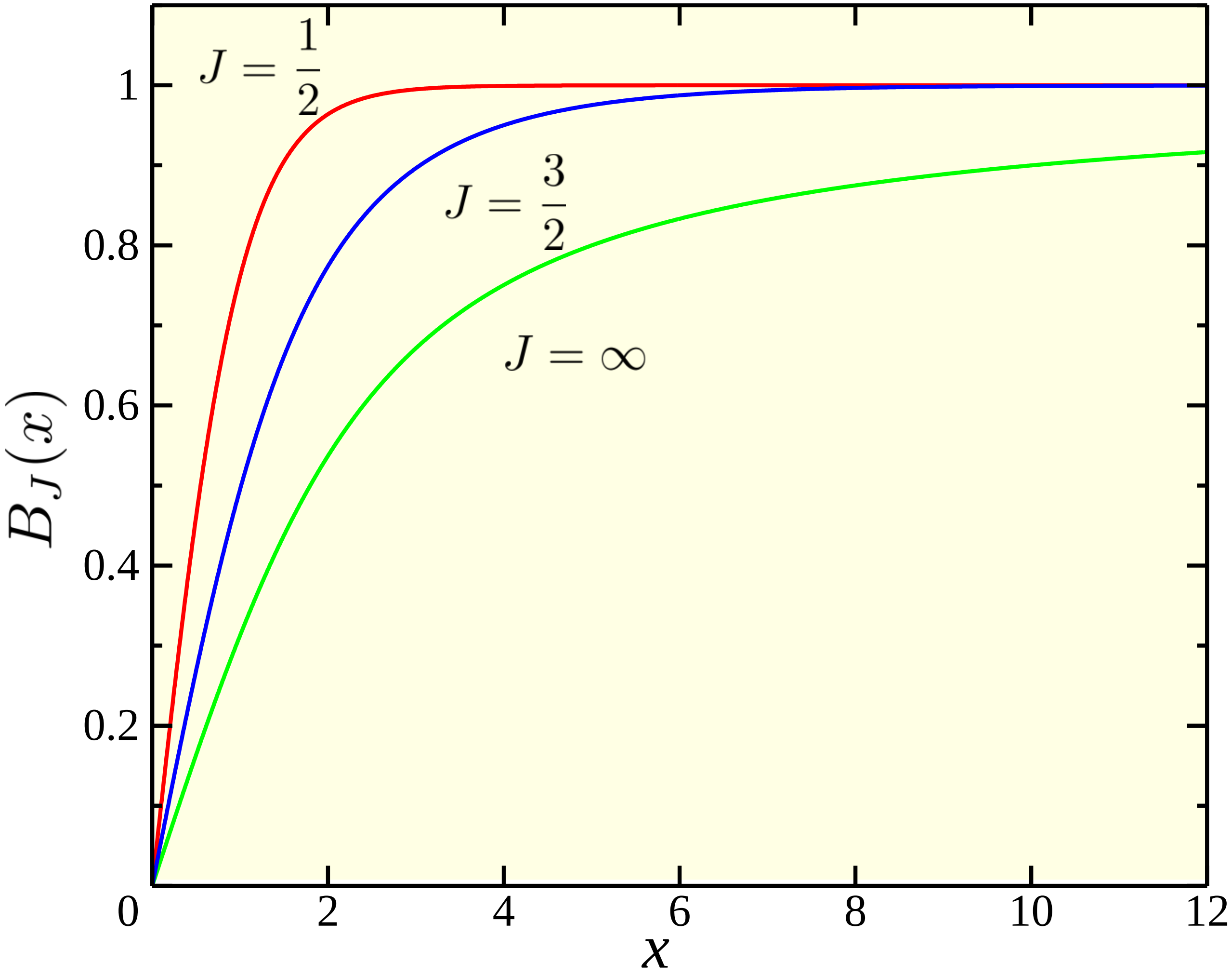
Expectation value of magnetization:

$$M = \langle -g_j \mu_\mathrm{B} J_z \rangle = -\frac{\mathbf{Tr}[g_j \mu_\mathrm{B} J_z \exp(-g_j \mu_\mathrm{B} J_z B / k_\mathrm{B} T)]}{\mathrm{Tr}[\exp(-g_j \mu_\mathrm{B} J_z B / k_\mathrm{B} T)]}$$

$$= k_\mathrm{B} T \frac{\partial}{\partial B} \log \left[\mathrm{Tr} \left(\exp \frac{-g_j \mu_\mathrm{B} J_z B}{k_\mathrm{B} T} \right) \right]$$

Partition function: $$\mathrm{Tr} \left(\exp \frac{-g_j \mu_\mathrm{B} J_z B}{k_\mathrm{B} T} \right) = \frac{\sinh \left[\frac{1}{2k_\mathrm{B} T} g_J \mu_\mathrm{B} \left(J + \frac{1}{2} \right) B \right]}{\sinh(g_J \mu_\mathrm{B} B / 2k_\mathrm{B} T)}$$

Free moment and Curie law



$$M = g_J \mu_B J B_J\left(\frac{g_J \mu_B J B}{k_B T}\right)$$

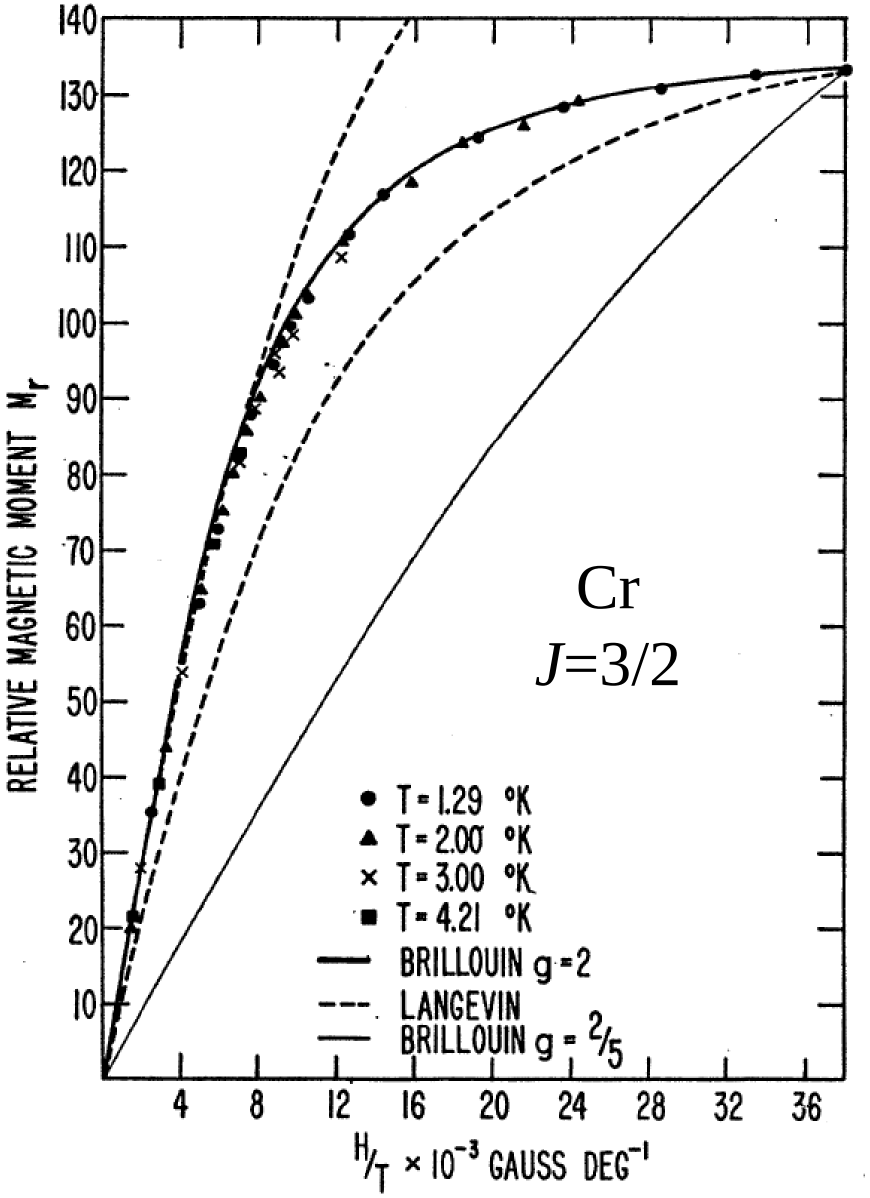
$$B_J(x) = \frac{2J+1}{2J}\coth\frac{2J+1}{2J}x - \frac{1}{2J}\coth\frac{x}{2J}$$

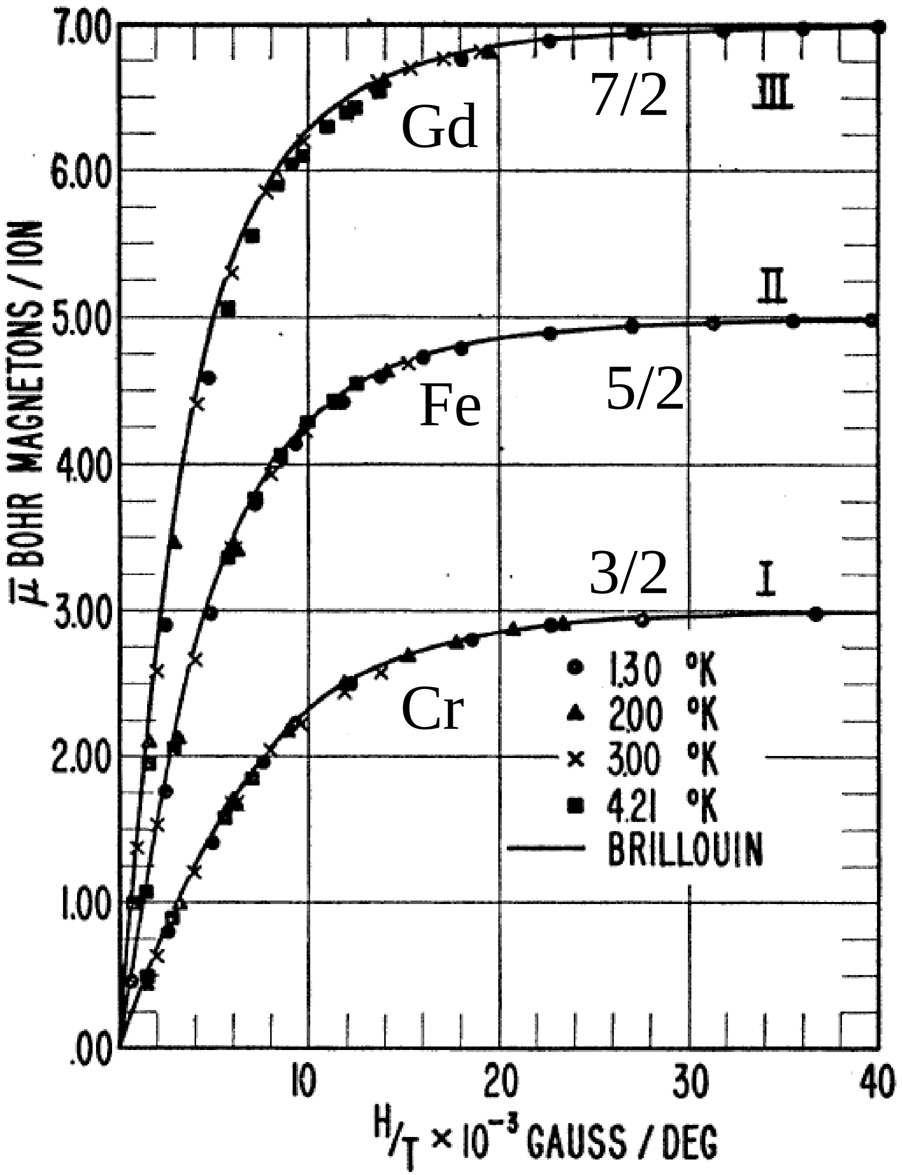
Brillouin function

$$x \ll 1 \rightarrow B_J(x) \sim (J+1)x/3J$$

$$\chi = \frac{dM}{dB} = (g_J\mu_B)^2\frac{J(J+1)}{3k_B T}$$

Examples of experiments





II

$FeNH_4(SO_4)_2 \cdot 12H_2O$

Iron Ammonium Alum

W. E. Henry, PR**88**, 556, 1952

LS coupling approach for Lanthanoid (rare earth)

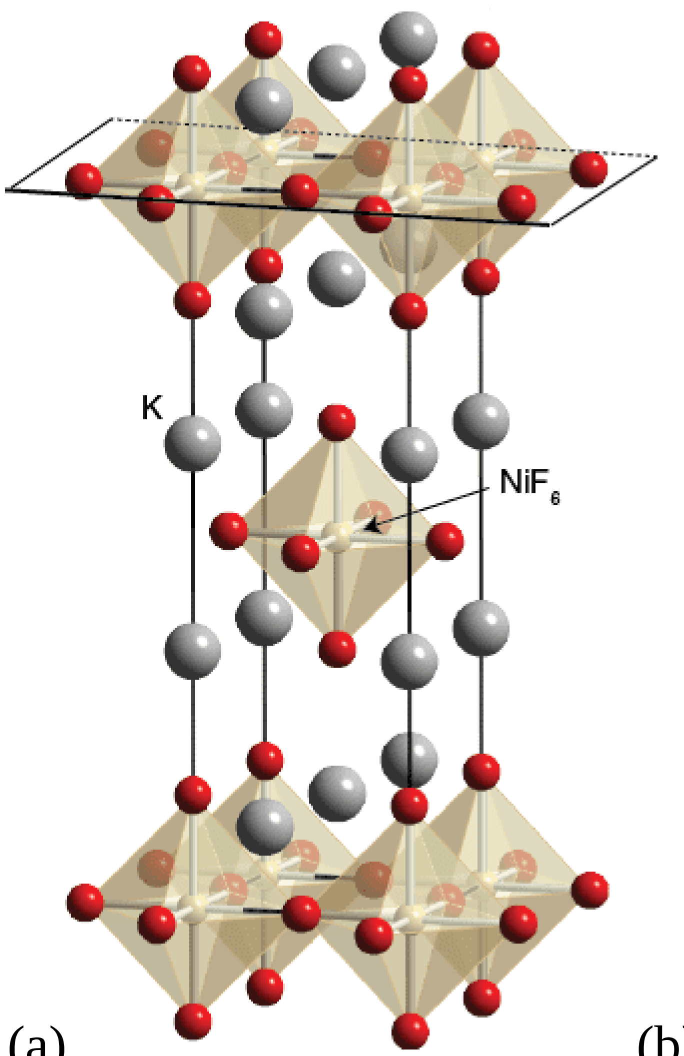
Configuration		ion	p (exp.)	$g_J[J(J+1)]^{1/2}$	$2[S(S+1)]^{1/2}$
$4f^1$	$^2F_{5/2}$	Ce^{3+}	2.5	2.54	2.56
$4f^2$	$^3H_4$	Pr^{3+}	3.6	3.58	3.62
$4f^3$	$^4I_{9/2}$	Nd^{3+}	3.8	3.62	3.68
$4f^5$	$^6H_{5/2}$	Sm^{3+}	1.5	0.84	1.53
$4f^6$	$^7F_0$	Eu^{3+}	3.6	0.00	3.40
$4f^7$	$^8S_{7/2}$	Gd^{3+}	7.9	7.94	7.94
$4f^8$	$^7F_0$	Tb^{3+}	9.7	9.72	9.7
$4f^9$	$^6H_{15/2}$	Dy^{3+}	10.5	10.65	10.6
$4f^{10}$	$^5I_8$	Ho^{3+}	10.5	10.61	10.6
$4f^{11}$	$^4I_{15/2}$	Er^{3+}	9.4	9.58	9.6
$4f^{12}$	$^3H_6$	Tm^{3+}	7.2	7.56	7.6
$4f^{13}$	$^2F_{7/2}$	Yb^{3+}	4.5	4.54	4.5

3d transition metals

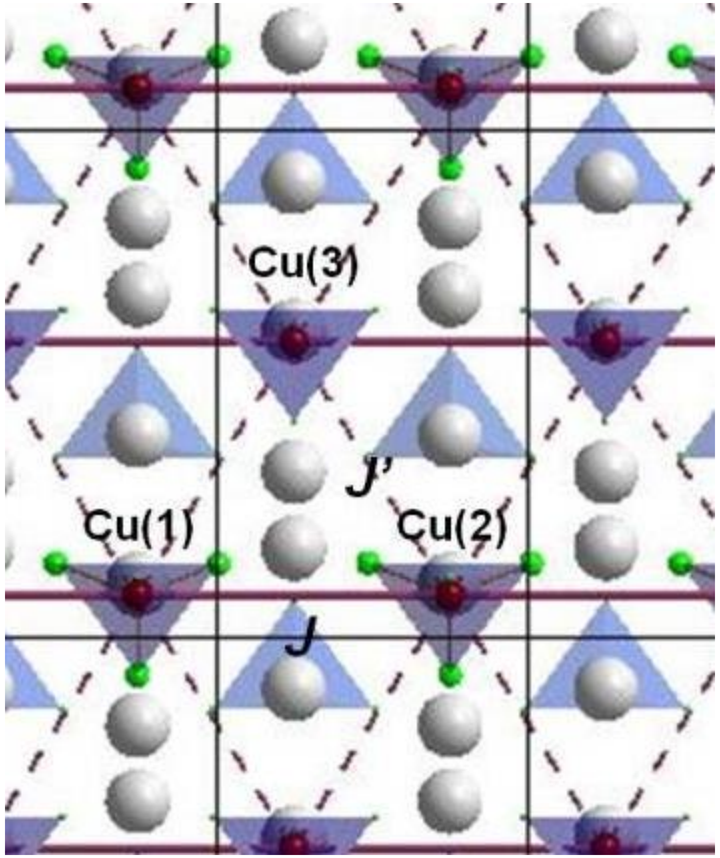
Configuration		ion	p (exp.)	$g_J[J(J+1)]^{1/2}$	$2[S(S+1)]^{1/2}$
$3d^1$	$^2D_{3/2}$	V^{4+}	1.8	1.55	1.73
$3d^2$	$^3F_2$	V^{3+}	2.8	1.63	2.83
$3d^3$	$^4F_{3/2}$	V^{2+}	3.8	0.77	3.87
		Cr^{3+}	3.7	0.77	3.87
		Mn^{4+}	4.0	0.77	3.87
$3d^4$	$^5D_0$	Cr^{2+}	4.8	0	4.90
		Mn^{3+}	5.0	0	4.90
$3d^5$	$^6S_{5/2}$	Mn^{2+}	5.9	5.92	5.92
		Fe^{3+}	5.9	5.92	5.92
$3d^6$	$^5D_4$	Fe^{2+}	5.4	6.7	4.90
$3d^7$	$^4F_{9/2}$	Co^{2+}	4.8	6.63	3.87
$3d^8$	$^3F_4$	Ni^{2+}	3.2	5.59	2.83
$3d^9$	$^2D_{5/2}$	Cu^{2+}	1.9	3.55	1.73

The discrepancy tells that we need to take the effect of crystal field into account before going into the spin-orbit interaction.

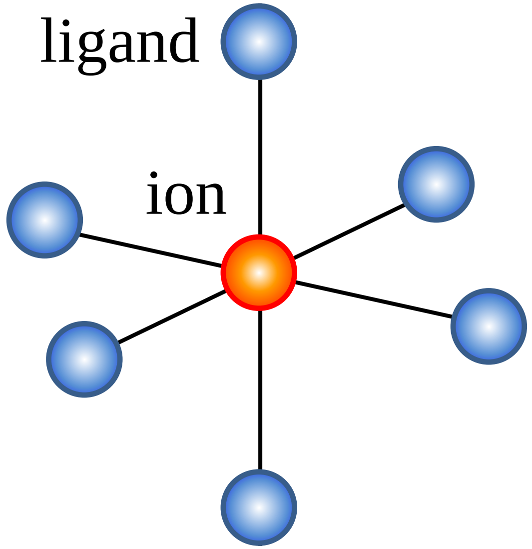
Magnetic ions in insulating crystals: ligands configuration



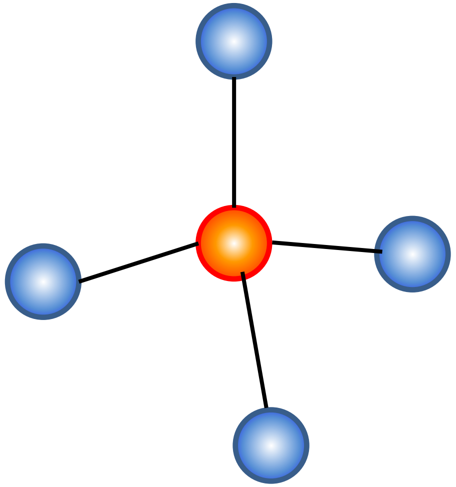
(a) K_2NiF_4



(b) Cs_2CuCl_4



(c) Octahedron coordination



(d) Tetrahedral coordination

Effect of ligand field

Color centers in insulators

Ruby red in Al_2O_3

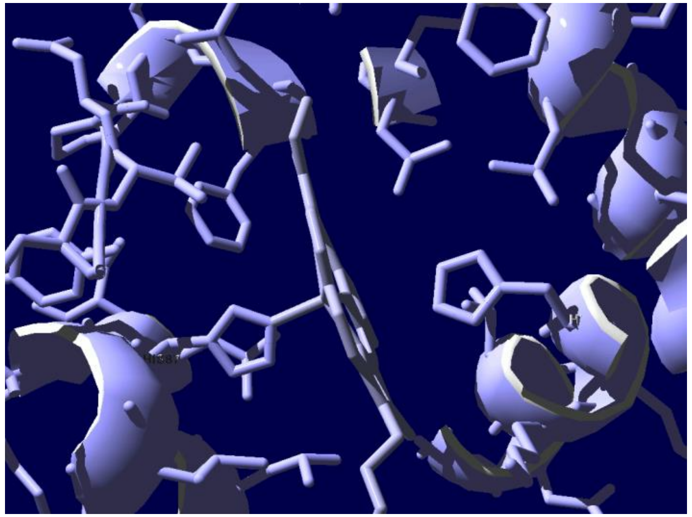
Al^{3+}

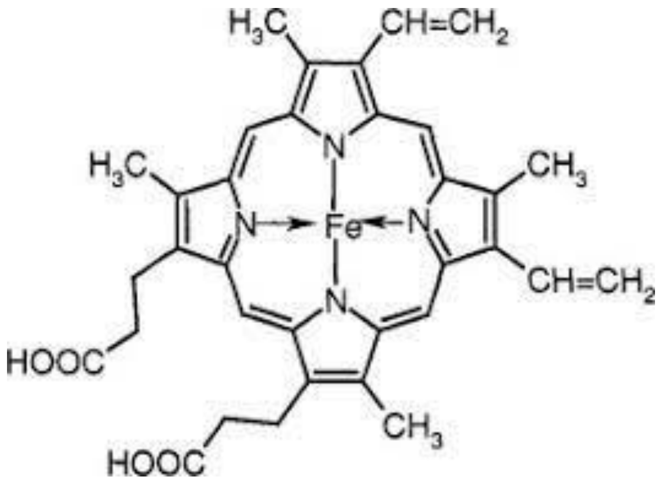
Emerald green in Al_2O_3

Cr^{3+}

Sapphire blue in Al_2O_3

Fe^{2+}



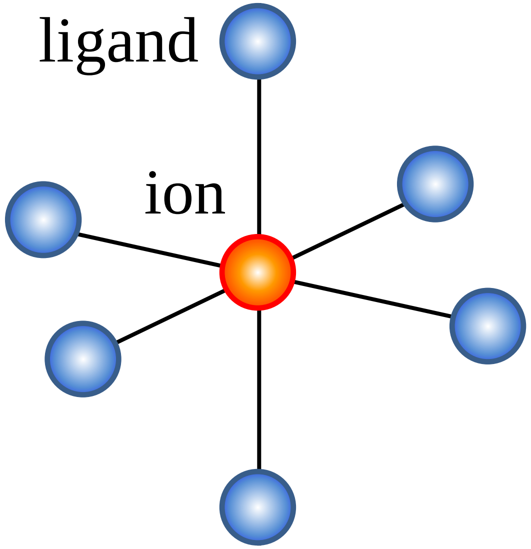


Hemoglobin: Fe

Octahedron ligand field

$$v_{\mathrm{c}}(\boldsymbol{r}) = \sum_i \frac{Z_i e^2}{|\boldsymbol{r} - \boldsymbol{R}_i|} = \sum_i \frac{Ze^2}{\sqrt{r^2 + R^2 - 2Rr\cos\omega_i}}$$

Unit: CGS



$$\boldsymbol{R}_i = (R, \theta_i, \varphi_i) \qquad (\pm R, 0, 0), (0, \pm R, 0), (0, 0, \pm R)$$

$$(\pi/2, 0),\ (\pi/2, \pi/2),\ (0, 0),\ (\pi/2, \pi),\ (\pi/2, 3\pi/2),\ (\pi, 0)$$

$\frac{r}{R} \ll 1$ Expansion: $$v_{\mathrm{c}}(\boldsymbol{r}) = \sum_i \frac{Ze^2}{R} \sum_{k=0}^{\infty} \left(\frac{r}{R}\right)^k P_k(\cos\omega_i)$$

Legendre function: $$P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n}[(x^2 - 1)]$$

$$P_k(\cos\omega_i) = \frac{4\pi}{2k+1} \sum_{m=-k}^{k} Y_{km}(\theta, \varphi) Y^*_{km}(\theta_i, \varphi_i)$$

Octahedron ligand field (potential)

Define $$T_{km} \equiv \sqrt{\frac{4\pi}{2k+1}} \frac{Ze^2}{R^{k+1}} \sum_i Y_{km}(\theta_i, \varphi_i), \quad C_{km} \equiv \sqrt{\frac{4\pi}{2k+1}} Y_{km}(\theta, \varphi)$$

then we write $$v_c(\boldsymbol{r}) = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} r^k T_{km} C_{km}(\theta, \varphi)$$

$$\begin{cases} T_{km} = 0 & \text{for } m\text{: odd} \\ T_{k0} = \sqrt{\frac{2}{2k+1}} \frac{Ze^2}{R^{k+1}} \left[\Theta_{k0}(0) + 4\Theta_{k0}\left(\frac{\pi}{2}\right) + \Theta_{k0}(\pi)\right], & \\ T_{km} = \sqrt{\frac{8}{2k+1}} \frac{Ze^2}{R^{k+1}} \Theta_{km}\left(\frac{\pi}{2}\right)\left(1 + \cos\frac{m\pi}{2}\right) & \end{cases}$$

$$Y_{km}(\theta, \varphi) = \Theta_{km}(\theta) e^{im\varphi}$$

$T_{km} = 0$ for k: odd

Octahedron ligan field potential

$$v_{\mathrm{c}}(\boldsymbol{r}) = \frac{6Ze^2}{R} + \frac{2}{5}Der^4\left[C_{40}(\theta,\varphi) + \sqrt{\frac{5}{14}}(C_{44}(\theta,\varphi) + C_{4-4}(\theta,\varphi))\right]$$

$$D = \frac{35Ze}{4R^5}$$

$$\boxed{v_{\mathrm{cb}}(\boldsymbol{r}) = eD\left(x^4 + y^4 + z^4 - \frac{3}{5}r^4\right)}$$

Summary

Electronic states in magnetic ions

- LS coupling approach
- j-j coupling approach

Paramagnetism by magnetic ions in insulators

- Curie law
- Breakdown of LS coupling approach in 3*d* transition metals

Ligand field approach

- Octahedron potential

2022.4.27 Lecture 4

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Review

- Electronic states in magnetic ions

  LS coupling approach

  j-j coupling approach

- Paramagnetism by magnetic ions in insulators

  Curie law

  Breakdown of LS coupling approach in 3*d* transition metals

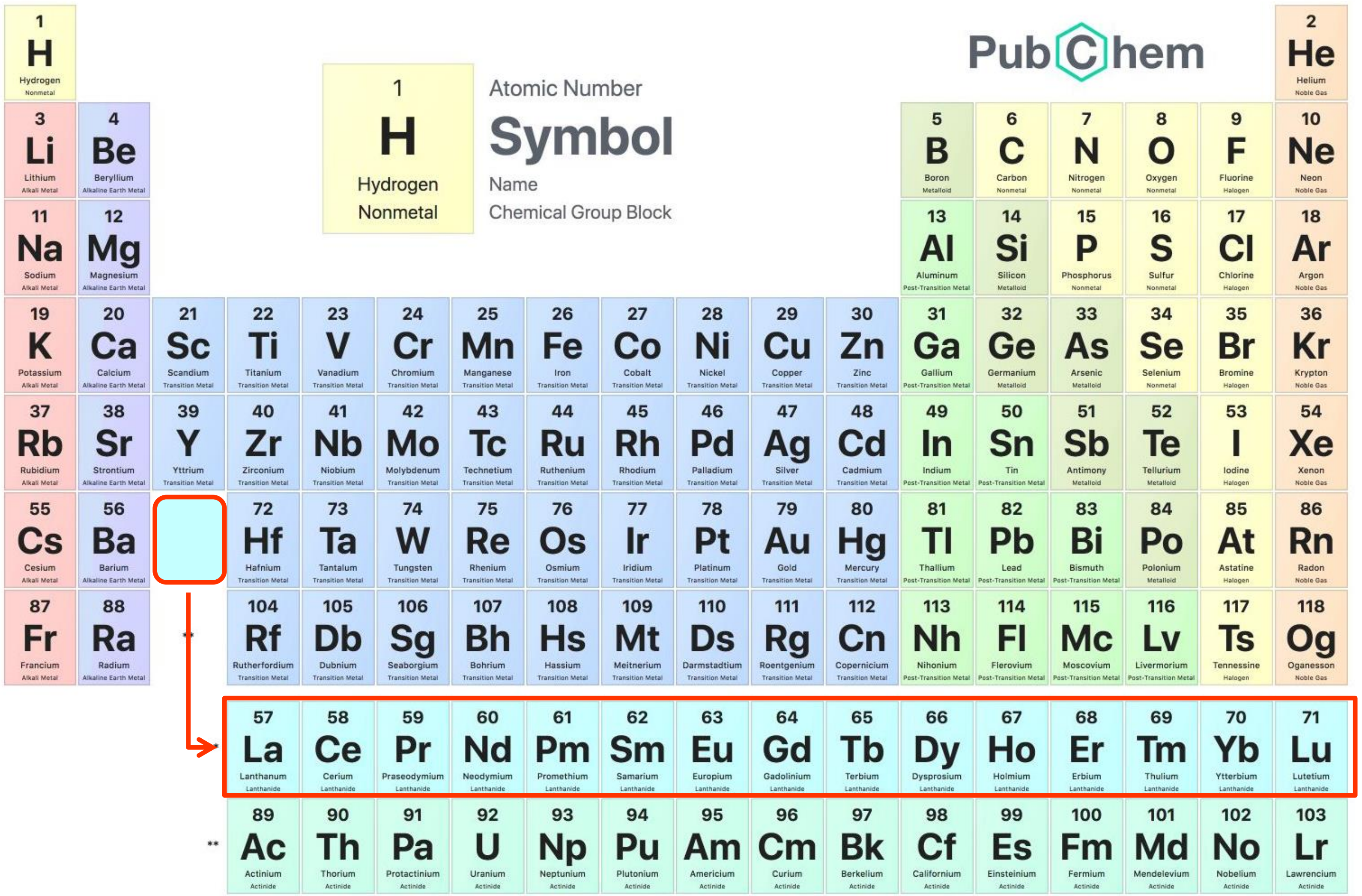
- Ligand field approach

  Octahedron potential

Agenda

- Ligand field approach to 3d orbitals in octahedral potential
- High-spin/ Low-spin state in ligand field potential
- Van Vleck (anomalous) paramagnetism
- Group theoretical approach to level splitting
- Experiments on and applications of paramagnetism

Periodic table of elements



3d transition metals

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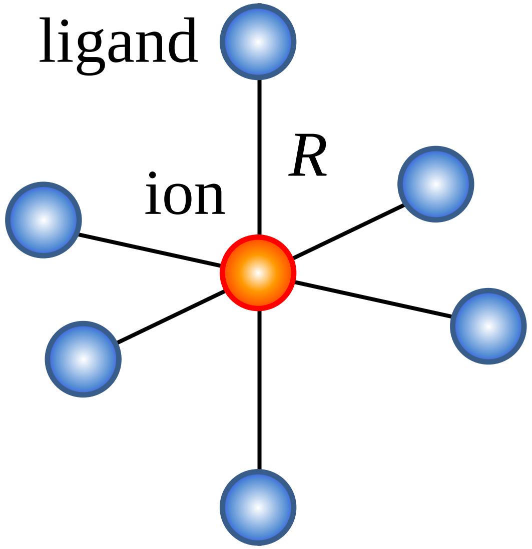
Octahedral ligand field



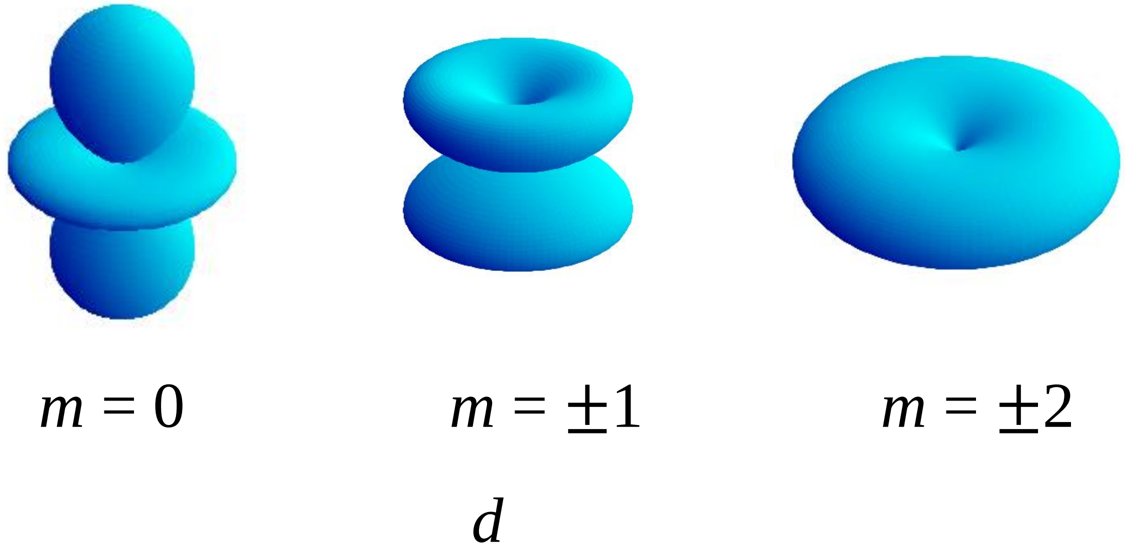
Potential generated by ligands at an octahedron vertices:

$$\frac{r}{R} \ll 1 \qquad v_{\mathrm{cb}}(\boldsymbol{r}) = eD\left(x^4 + y^4 + z^4 - \frac{3}{5}r^4\right) \qquad D = \frac{35Ze}{4R^5}$$

We are considering: Open shell 3*d* electrons

Single (3)*d* electron in $v_{\mathrm{cb}}(\boldsymbol{r})$

Diagonalization in the space of 3*d* wavefunction



$$Y_{20}(\theta,\varphi) = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1),$$

$$Y_{2\pm1}(\theta,\varphi) = \mp\sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta e^{\pm i\varphi},$$

$$Y_{2\pm2}(\theta,\varphi) = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\varphi}$$

Looking for eigenfunction in tetrahedral potential

Linear combination of *d*-orbitals

Radial part → common for 5 orbitals

Angular part → second order in (x, y, z)

$$\left.\begin{array}{ll} (1) & r^2(3\cos^2\theta - 1) = 2(x^2 + y^2) - z^2 \\ (2) & r^2 \cos\theta \sin\theta e^{\pm i\varphi} = z(x \pm iy) \\ (3) & r^2 \sin^2\theta e^{\pm 2i\varphi} = x^2 \pm 2ixy - y^2 \end{array}\right\}$$

Possible terms: $x^2, y^2, z^2, yz, zx, xy$

First order in *x*, *y*, *z* → disappearance of off-diagonal term by integration of odd-function

Candidates: $\frac{yz}{r^2}, \frac{zx}{r^2}, \frac{xy}{r^2}$ Easily obtained by adding/subtracting (2), (3)

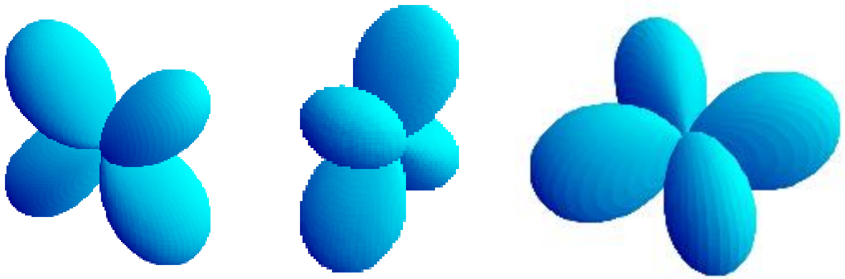
In order for vanishing off-diagonal term of $x^4 + y^4 + z^4$, we should take differences between x^2, y^2, z^2 :

$x^2 - z^2, y^2 - z^2$ orthogonalize $\Longrightarrow$ $3z^2 - r^2, x^2 - y^2$

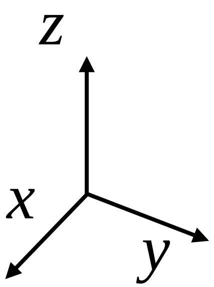
Obtained from (1) (itself), (3) (addition)

Octahedral ligand field (2)

$\phi_\xi\ (yz)$ $\phi_\eta\ (zx)$ $\phi_\zeta\ (xy)$

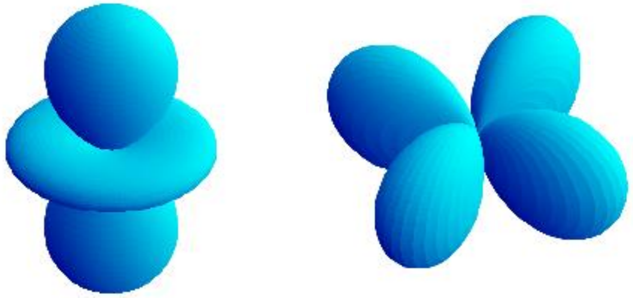


t_{2g}



$$
\begin{cases}
\phi_\xi = \dfrac{i}{\sqrt{2}}(\phi_{321} + \phi_{32-1}) = \sqrt{\dfrac{15}{4\pi}}\dfrac{yz}{r^2}R_{32}(r), \\
\phi_\eta = -\dfrac{1}{\sqrt{2}}(\phi_{321} - \phi_{32-1}) = \sqrt{\dfrac{15}{4\pi}}\dfrac{zx}{r^2}R_{32}(r), \\
\phi_\zeta = -\dfrac{i}{\sqrt{2}}(\phi_{322} - \phi_{32-2}) = \sqrt{\dfrac{15}{4\pi}}\dfrac{xy}{r^2}R_{32}(r)
\end{cases}
$$

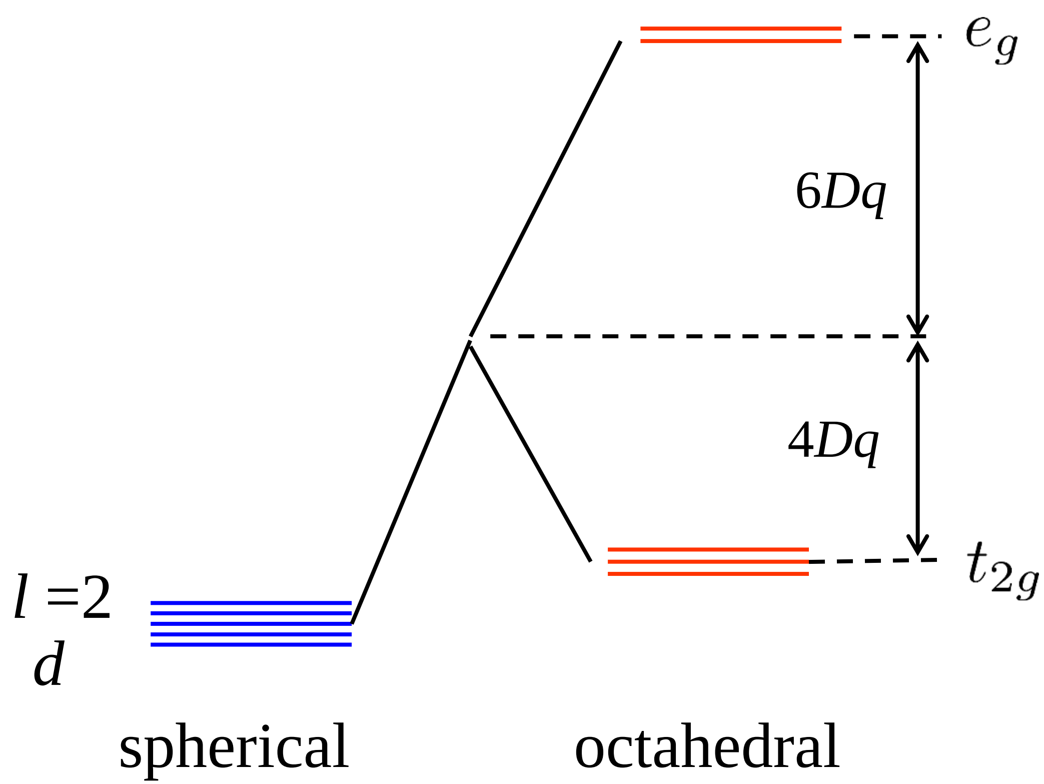
ϕ_u ϕ_v



e_g

$$
\begin{cases}
\phi_u = \phi_{320} = \sqrt{\dfrac{5}{16\pi}}\dfrac{3z^2 - r^2}{r^2}R_{32}(r), \\
\phi_v = -\dfrac{1}{\sqrt{2}}(\phi_{322} + \phi_{32-2}) = \sqrt{\dfrac{5}{16\pi}}\dfrac{x^2 - y^2}{r^2}R_{32}(r)
\end{cases}
$$

Energy level splitting and quenching of orbital magnetic moment



$$q = \frac{2e}{105}\langle r^4\rangle = \frac{2e}{105}\int |R_{32}(r)|^2 r^4 (r^2 dr)$$

Orbital angular momentum:

e.g. $$\phi_\zeta = -\frac{i}{\sqrt{2}}(\phi_{n22} - \phi_{n2-2})$$

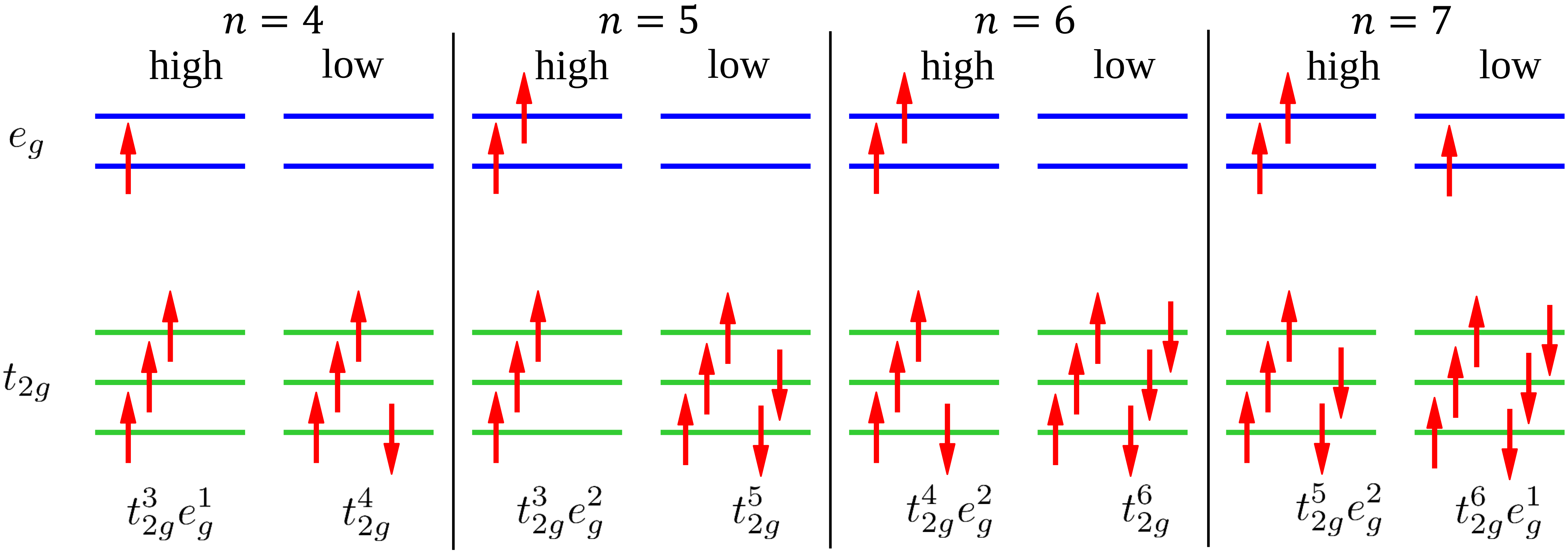
$$\langle \phi_\zeta | l_z | \phi_\zeta \rangle = 2 - 2 = 0$$

Neither t_{2g} nor e_g orbital does not have angular momentum

⇩

Explanation of quenching of orbital angular moment

High-spin and low-spin states



(Effect of crystal field) > (Coulomb repulsion)

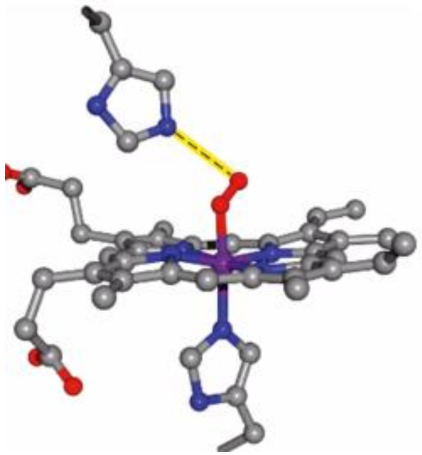
⇩

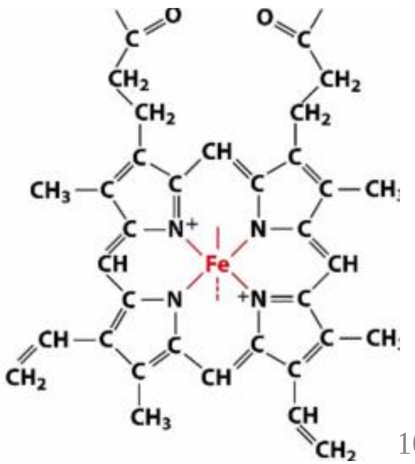
Low spin state

Ex) hemoglobin

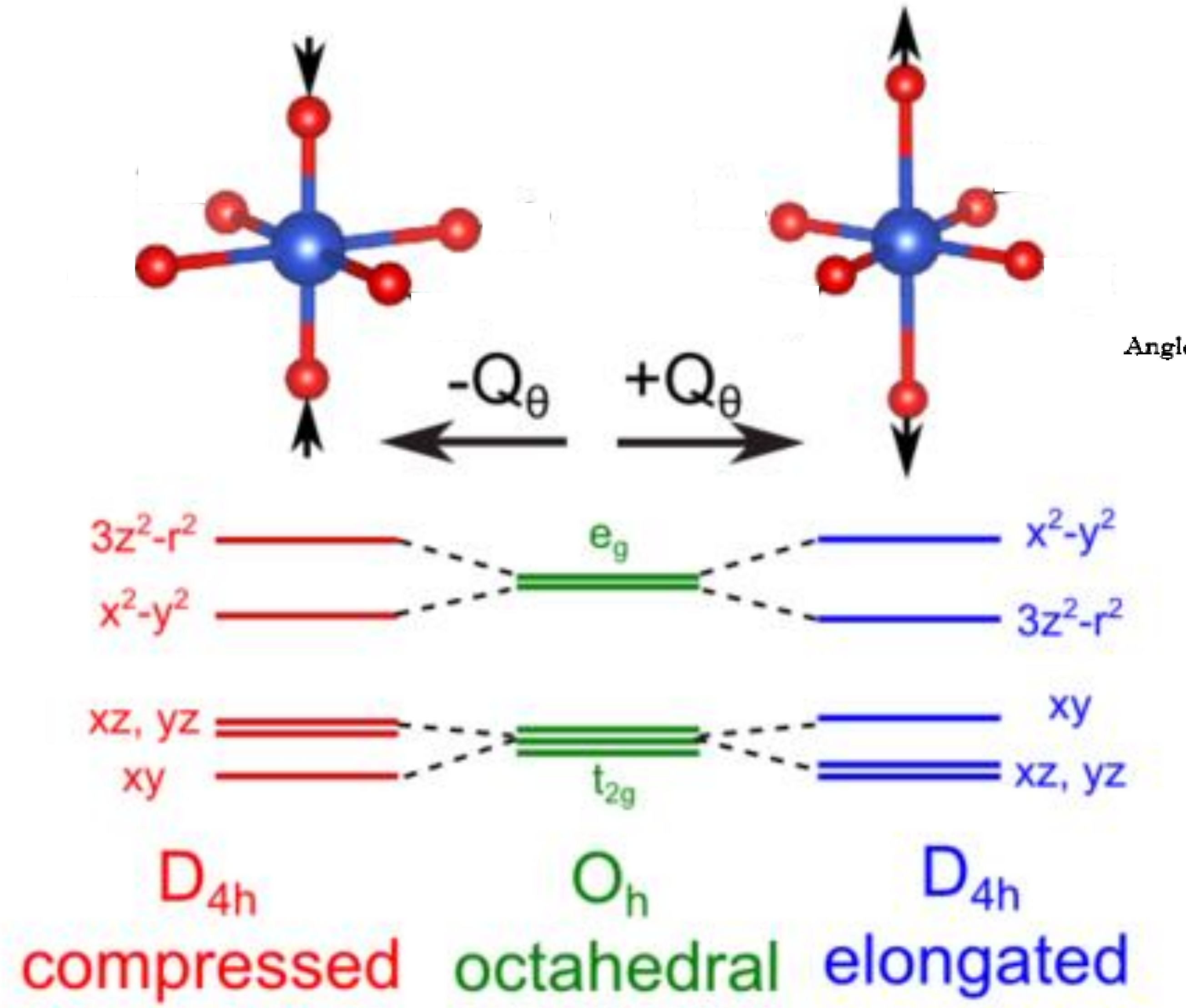
No oxygen: $Fe^{2+}(t_{2g}^4 e_g^2)$ high spin

With oxygen: $Fe^{2+}(t_{2g}^6)$ low spin





Topics in paramagnetism from 3*d*, 4*f* ions



Jahn-Teller distortion

Distortion energy = energy lowering by symmetry lowering

Plane through trigonal axis: Angle with trigonal axis (deg.)	g	Plane normal to trigonal axis: Angle with arbitrary line (deg.)	g
0	2·234	0	2·248
30	2·235	30	2·246
50	2·238	60	2·240
70	2·240	90	2·244
90	2·243		

B.Bleaney, Proc.Phys.Soc.London A63,408(1950).

$CuSiF_6 6H_2O$

Van Vleck (anomalous) paramagnetism

LS coupling approach

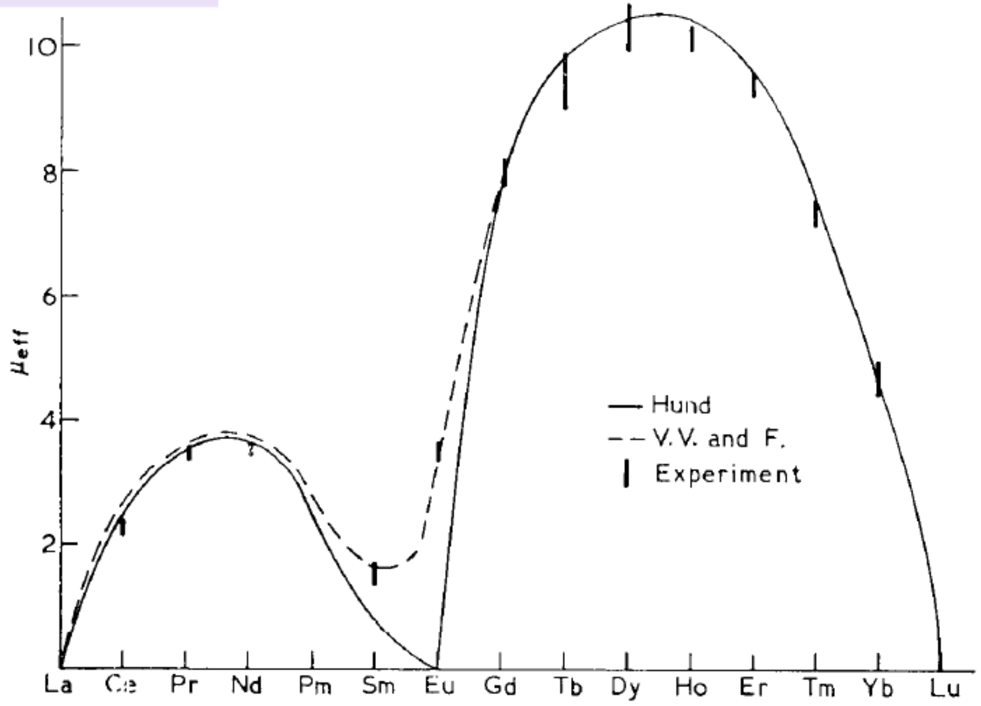
Configuration		ion	p (exp.)	$g_J[J(J+1)]^{1/2}$	$2[S(S+1)]^{1/2}$
$4f^3$	$^4I_{9/2}$	Nd^{3+}	3.8	3.62	3.68
$4f^5$	$^6H_{5/2}$	Sm^{3+}	1.5	0.84	1.53
$4f^6$	$^7F_0$	Eu^{3+}	3.6	0.00	3.40
$4f^7$	$^8S_{7/2}$	Gd^{3+}	7.9	7.94	7.94

$$\mathcal{H}_{\text{SOI}} = \lambda \boldsymbol{L} \cdot \boldsymbol{S}$$
$$= \frac{\lambda}{2}[J(J+1) - S(S+1) - L(L+1)]$$

In the case of Eu^{3+} (J =0)

$$\Delta E_{LS} = E_{LS}(J) - E_{LS}(J-1) = \lambda J$$

Excited state → finite moment



Very short review of point group theory

Group: Set A with operator *

1. $\forall a_1,\ a_2 \in A\ \{a_1 * a_2 \in A\}$ (closed for the operation *)
2. $\forall a_1.\ a_2,\ a_3 \in A\ \{(a_1 * a_2) * a_3 = a_1 * (a_2 * a_3)\}$ (associative law).
3. $\exists E \in A\ \{\forall a_1 \in A\ \{a_1 E = E a_1 = a_1\}\}$ (existence of unit element).
4. $\exists a_1^{-1} \in A\ \{\forall a_1 \in A\ \{a_1 a_1^{-1} = a_1^{-1} a_1 = E\}\}$ (existence of inverse element).

Element a_i $\Rightarrow$ $D(a_i)$ square matrix

$a * b = c$ projection $D(a)D(b) = D(c)$

$\Big\}$ Representation of group A

$$D'(a_i) = S^{-1} D(a_i) S \qquad D'(a_i),\ D(a_i)\ :\ \text{equivalent representation}$$

Symmetry operation of point group

A set of symmetry operations around a point in space is called a point group

E	:	Identical operation
C_n	:	Rotation of $2\pi/n$
C_2'	:	π rotation around two-fold axis perpendicular to the principal axis. Written as C_2' or U_2 and called Umklappung.
I	:	Space inversion $(\boldsymbol{r} \to -\boldsymbol{r})$
σ	:	Mirroring
IC_n	:	Circumference. Space inversion after rotation of $2\pi/n$.
S_n	:	Improper rotation. Mirroring after rotation of $2\pi/n$.

In crystals: requirement of (discrete) translational symmetry 32 crystal point groups

Crystal point groups

system	Schönflies symbol	Hermann-Mauguin symbol: full	Hermann-Mauguin symbol: abbreviated	examples
triclinic	C_1	1	1	
	$C_i, (S_2)$	$\bar{1}$	$\bar{1}$	Al_2SiO_5
monoclinic	$C_{1h}, (S_1)$	m	m	KNO_2
	C_2	2	2	
	C_{2h}	$2/m$	$2/m$	
orthorhombic	C_{2v}	$2mm$	mm	
	$D_2, (V)$	222	222	
	$D_{2h}, (V_h)$	$2/m2/m2/m$	mmm	I, Ga
tetragonal	C_4	4	4	
	S_4	4	4	
	C_{4h}	4/m	4/m	$CaWO_4$
	$D_{2d}, (V_d)$	$\bar{4}2m$	$\bar{4}2m$	
	C_{4v}	$4mm$	$4mm$	
	D_4	422	42	
	D_{4h}	$4/m2/m2/m$	$4/mmm$	TiO_2, In, β-Sn
rhombohedral	C_3	3	3	AsI_3
	$C_3, (S_6)$	3	3	$FeTiO_3$
	C_{3v}	$3m$	$3m$	
	D_3	32	32	Se
	D_{3d}	$32/m$	$3m$	Bi, As, Sb, Al_2O_3
hexagonal	$C_{3h}, (S_3)$	6	6	
	C_6	6	6	
	C_{6h}	$6/m$	$6/m$	
	D_{3h}	$62m$	$62m$	
	C_{6v}	$6mm$	$6mm$	ZnO, NiAs
	D_6	622	62	CeF_3
	D_{6h}	$6/m2/m2/m$	$6/mmm$	Mg, Zn, graphite
cubic	T	23	23	$NaClO_3$
	T_h	$2/m3$	$m3$	FeS_2
	T_d	$43m$	$43m$	ZnS
	O	432	43	β-Mn
	O_h	$4/m32/m$	$m3m$	NaCl, diamond, Cu
icosahedral	C_5	5	5	
	$C_{5i}, (S_{10})$	10	10	
	C_{5v}	$5m$	$5m$	
	C_{5h}, S_5	5	5	
	D_5	52	52	
	D_{5d}	$52/m$	$5/m$	C_{80}
	D_{5h}	$1\bar{0}2/m$	$1\bar{0}2/m$	C_{70}
	I	532	532	
	I_h			C_{60}

Reducible/irreducible representations

R: symmetry operator Symmetry operation on functions $\varphi(\boldsymbol{r}) \to \varphi'(\boldsymbol{r}) = \varphi(R^{-1}\boldsymbol{r})$

$$\mathscr{A}_\varphi = \{\varphi_1, \varphi_2, \cdots\} \xrightarrow{R} \mathscr{A}'_\varphi = \{\varphi'_1, \varphi'_2, \cdots\}$$

If $\mathscr{A}' = \mathscr{A}$ then $\mathscr{A}$ can be a representation basis of *R*

$$D_{ij}(R) = \langle \varphi_i | R | \varphi_j \rangle$$

If block diagonalization is possible:
reducible representation

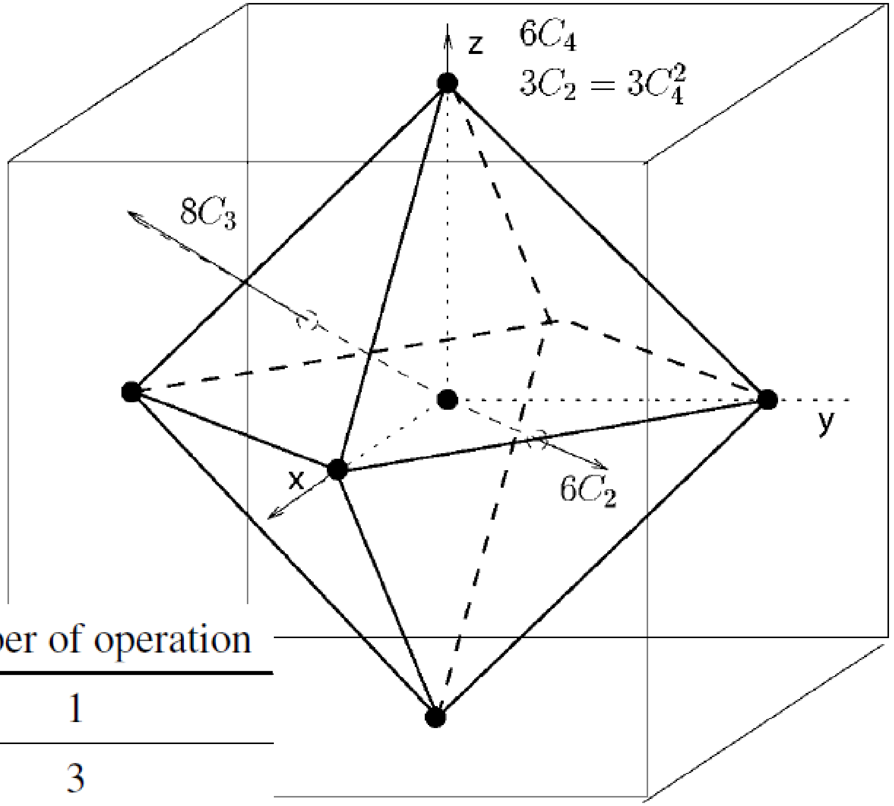
$$SD(R)S^{-1} = \begin{pmatrix} D_1(R) & & 0 \\ & D_2(R) & \\ 0 & & \ddots \end{pmatrix}$$

Direct summation: $D(R) = D_1(R) \oplus D_2(R) \oplus \cdots$

If block diagonalization is impossible:
irreducible representation

$\mathrm{Tr}\,[D(R)]$: character of representation

Symmetry operations in group O



	Symmetry operation	Rotation axis	Number of operation
E	Identical transformation		1
C_4	$\pi/2$ rotation around 4-fold axis	x, y, z	3
$C_2 = C_4^2$	π rotation around 4-fold axis	x, y, z	3
C_4^3	$3\pi/2$ rotation around 4-fold axis	x, y, z	3
C_2	π rotation around 2-fold axis	(0,1,1), (1,0,1), (1,1,0) (0,1,–1), (–1,0,1), (1,–1,0)	6
C_3	$2\pi/3$ rotation around 3-fold axis	(1,1,1), (1,1,–1), (1,–1,1), (–1,1,1)	4
C_3^2	$4\pi/3$ rotation around 3-fold axis	(1,1,1), (1,1,–1), (1,–1,1), (–1,1,1)	4

Simplification to irreducible representation by character table

O	E	$8C_3$	$3C_2 = 3C_4^2$	$6C_2'$	$6C_4$
$\Gamma_{l=0}$	1	1	1	1	1
$\Gamma_{l=1}$	3	0	-1	-1	1
$\Gamma_{l=2}$	5	-1	1	1	-1
$\Gamma_{l=3}$	7	1	-1	-1	-1
$\Gamma_{l=4}$	9	0	1	1	1
$\Gamma_{l=5}$	11	-1	-1	-1	1

Simplification of representation $\Gamma_{l=2} = E \oplus T_2$

Symmetry operation and level degeneracy

Symmetry operator *R* $\varphi' = R\varphi$

Transformation of operator: $\mathscr{O}$ $\mathscr{O} \xrightarrow{R} \mathscr{O}'$ $\mathscr{O}' R\varphi = R\mathscr{O}\varphi = R\mathscr{O}R^{-1}R\varphi$ $\mathscr{O} \xrightarrow{R} R\mathscr{O}R^{-1}$

Assume the system is invariant by operator *R*

$$R\mathscr{H}R^{-1} = \mathscr{H}, \quad \therefore [R, \mathscr{H}] = 0$$

$$\mathscr{H}\phi = E\phi$$

$$\mathscr{H}R\phi = R\mathscr{H}R^{-1}R\phi = RE\phi = ER\phi$$

$R\phi$: eigenfunction of eigenvalue E

Symmetry connected eigenfunctions

$\{\phi_i\}$: degenerated function set with eigenvalue E of $\mathscr{H}$

$$R\phi_\nu = \sum_{\mu=1}^{d} D_{\mu\nu}(R)\phi_\mu$$ must be irreducible

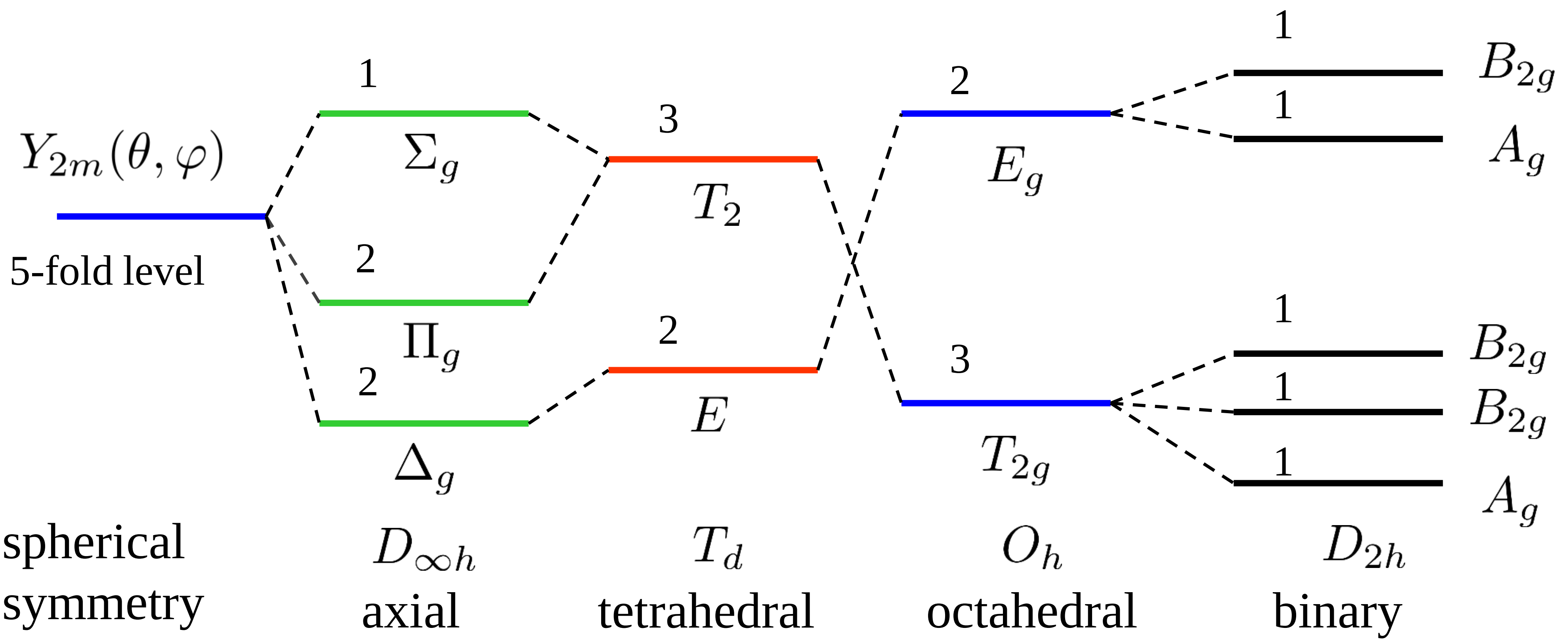
otherwise $D(R) = D_1(R) \oplus D_2(R) = \begin{pmatrix} D_1(R) & 0 \\ 0 & D_2(R) \end{pmatrix}$

not symmetry-connected

accidental degeneracy

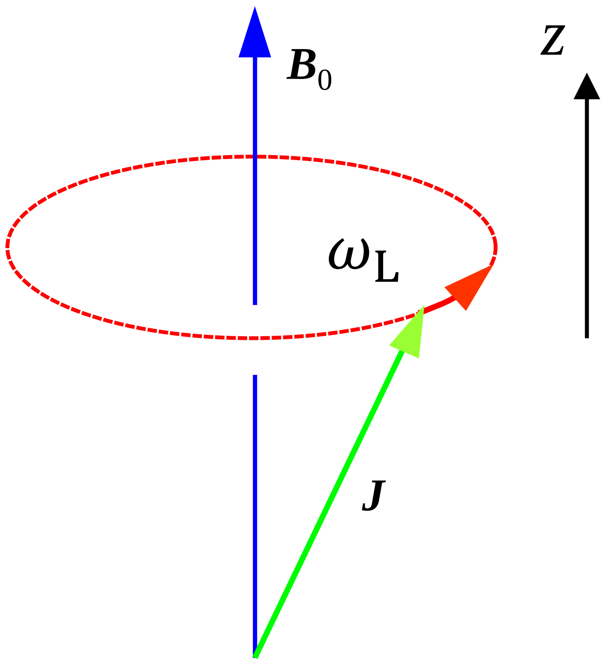
d-level splitting in various crystal fields

Simplification of representation $\Gamma_{l=2} = E \oplus T_2$



Experiments of magnetic moments on atoms/ions and applications

Magnetic resonance

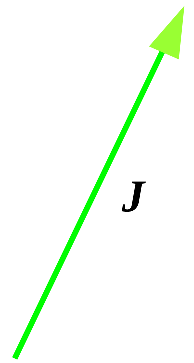


$$\mathcal{H}_1 = g_J \mu_B \boldsymbol{J} \cdot \boldsymbol{B}_0$$

$$J_y J_z - J_z J_y = i J_x, \quad J_z J_x - J_x J_z = i J_y, \quad J_x J_y - J_y J_x = i J_z$$

$$\frac{d\boldsymbol{J}}{dt} = \frac{g_J \mu_B}{\hbar} \boldsymbol{B}_0 \times \boldsymbol{J}$$

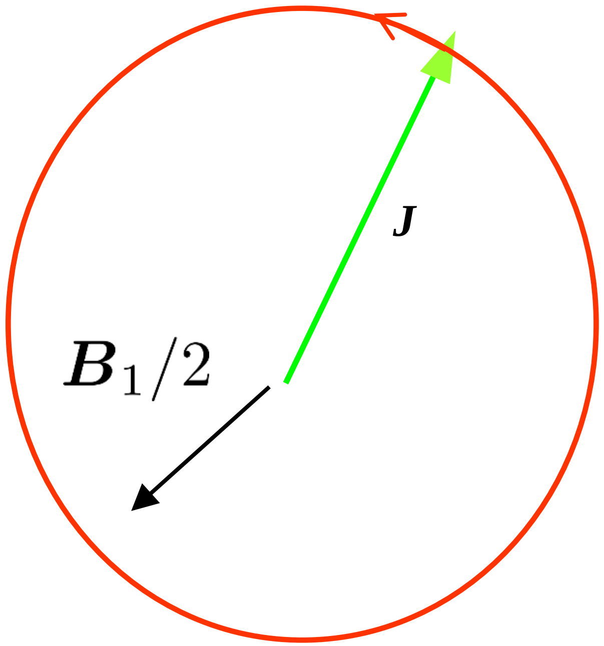
$$\omega_L = g_J \frac{eB_0}{2m}$$ Larmor precession

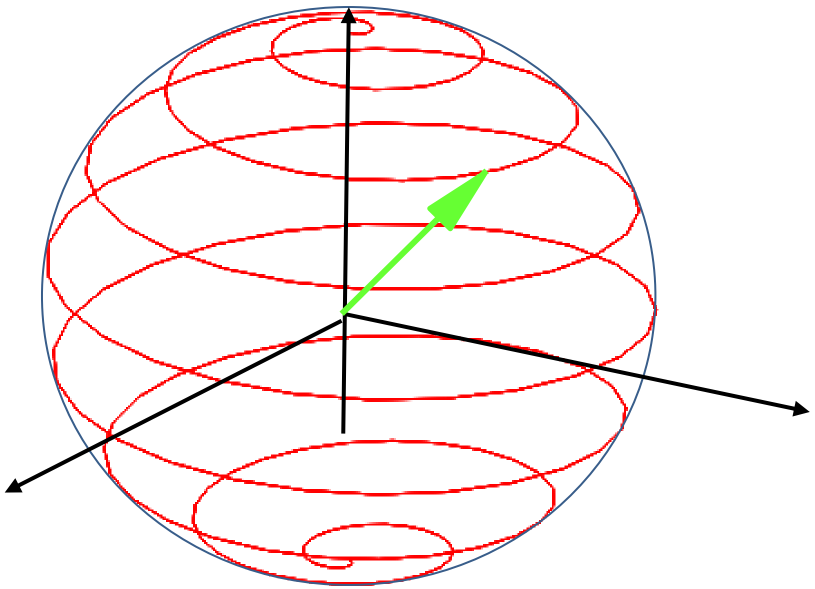


If we observe from rotational coordinate with frequency ω_L

Precession stops: the effect of magnetic field is renormalized into the rotation

Magnetic resonance (2)





High frequency magnetic field in *xy*-plane

$$\boldsymbol{B}(t) = \boldsymbol{B}_1 \cos(\omega t)$$
$$= \frac{\boldsymbol{B}_1}{2}[\exp(i\omega t) + \exp(-i\omega t)]$$

Two rotational magnetic fields

when $\omega \approx \omega_{\mathrm{L}}$

On the rotational coordinate: $\omega \approx 0, 2\omega_{\mathrm{L}}$

Ignore $2\omega_{\mathrm{L}}$ component: rotational wave approximation

Precession around $\boldsymbol{B_1}$ $\omega_1 = g_j \dfrac{eB_1}{2m}$

Total motion: spiral

Summary

- Ligand field approach to 3d orbitals in octahedral potential
- High-spin/ Low-spin state in ligand field potential
- Van Vleck (anomalous) paramagnetism
- Group theoretical approach to level splitting
- Experiments on and applications of paramagnetism

2022.5.11 Lecture 5

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Review of last four lectures

Chapter 1 Basic Notions of Magnetism

Classical pictures of magnetic moments in materials:

- Magnetic charges
- Circular currents

Breakdown of classical magnetism: cancellation of paramagnetic and diamagnetic terms (Bohr-van Leeuwen theorem)

Quest for the sources of magnetic dipoles in materials.

Spins and spin-orbit interactions

Chapter 2 Magnetism of Localized Electrons

Spherical potential, closed shell magnetization

Electronic states of magnetic ions

- LS (j-j) coupling, Hund's rule
- Ligand field

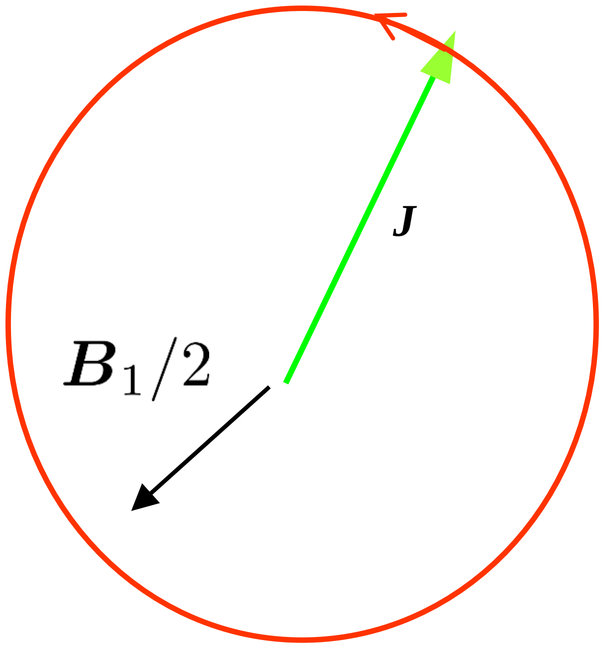
Representative experimental method: magnetic resonance

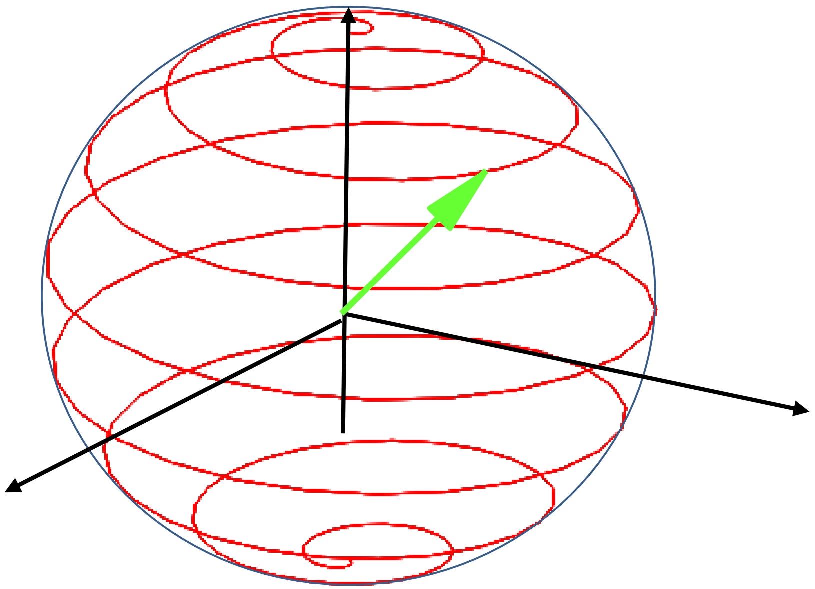
Outline

- Magnetic resonance (continued)
- Spin Hamiltonian
- Example of analyzing experimental data on electron paramagnetic resonance
- Application of paramagnetism: magnetic refrigeration

Chapter 3 Magnetism of conduction electrons

- Pauli paramagnetism
- Landau diamagnetism





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when $\omega \approx \omega_\mathrm{L}$

On the rotational coordinate: $\omega \approx 0, 2\omega_\mathrm{L}$

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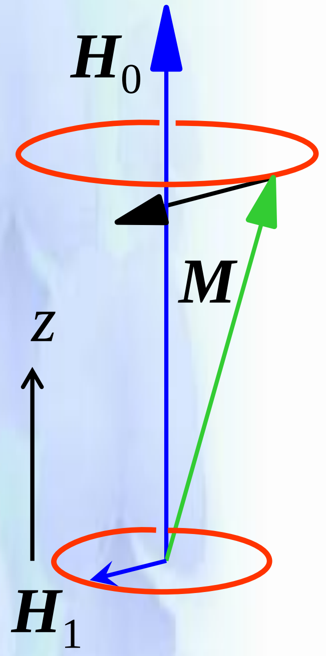
Precession around $\boldsymbol{B}_1$ $\omega_1 = g_j \dfrac{eB_1}{2m}$

Total motion: spiral

Magnetic resonance



Macroscopic magnetization $\boldsymbol{M}$

Classical equation of motion

Phenomenological introduction of relaxation time

$$\begin{cases} \dfrac{dM_z}{dt} = \gamma[\boldsymbol{M}\times\boldsymbol{H}]_z + \dfrac{M_0 - M_z}{T_1}, \\ \dfrac{dM_{x,y}}{dt} = \gamma[\boldsymbol{M}\times\boldsymbol{H}]_{x,y} - \dfrac{M_{x,y}}{T_2}. \end{cases}$$

T_1: energy relaxation time, T_2: phase relaxation time

$\boldsymbol{H}_0$: static field (z)

$\boldsymbol{H}_1$: rotating field with $-\omega$

$$\boldsymbol{H} = (\frac{H_1}{2}\cos\omega t, -\frac{H_1}{2}\sin\omega t, H_0)$$

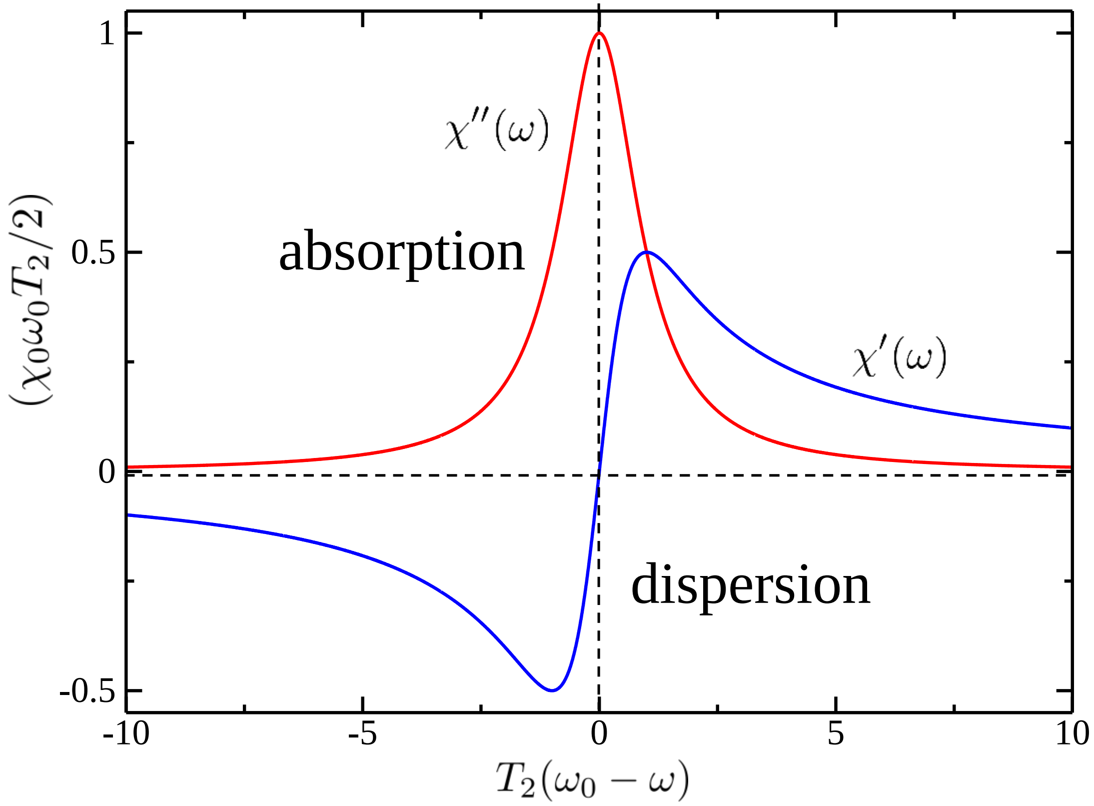
Then the equation of motion is given as

$$\begin{cases} \dfrac{dM_x}{dt} = \gamma[M_y H_0 + M_z \dfrac{H_1}{2}\sin\omega t] - \dfrac{M_x}{T_2}, \\ \dfrac{dM_y}{dt} = \gamma[M_z \dfrac{H_1}{2}\cos\omega t - M_x H_0] - \dfrac{M_y}{T_2}, \\ \dfrac{dM_z}{dt} = \gamma[-M_x H_1 \sin\omega t - M_y \dfrac{H_1}{2}\cos\omega t] + \dfrac{M_0 - M_z}{T_1} \end{cases}$$

Magnetic resonance (2)

We introduce the coordinate system (x', y', z') rotating around z-axis with freq. ω.

$$\begin{cases} M_{x'} = M_x \cos\omega t - M_y \sin\omega t, \\ M_{y'} = M_x \sin\omega t + M_y \cos\omega t \end{cases}$$



conditions

$$\begin{cases} \dfrac{dM_{x'}}{dt} = \dfrac{dM_{y'}}{dt} = 0 \quad \text{(stationary state)}, \\ M_z \simeq M_0 = \chi_0 H_0 \quad \text{(oblique angle is small)} \end{cases}$$

Solution

$$\begin{cases} M_{x'} = \chi_0\omega_0 T_2 \dfrac{(\omega_0-\omega)T_2 H_1/2}{1+(\omega_0-\omega)^2T_2^2+\gamma^2(H_1/2)^2T_1T_2} \\ M_{y'} = \chi_0\omega_0 T_2 \dfrac{H_1/2}{1+(\omega_0-\omega)^2T_2^2+\gamma^2(H_1/2)^2T_1T_2} \end{cases}$$

Original coordinate

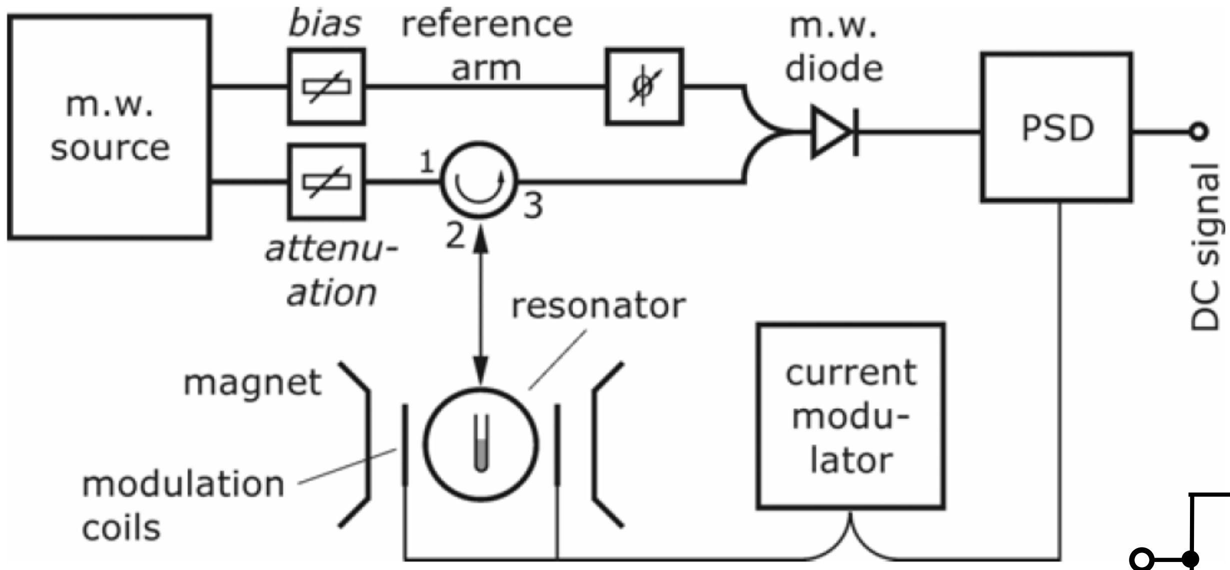
$$M_x = \chi'(\omega)H_1\cos\omega t + \chi''(\omega)H_1\sin\omega t,$$
$$M_y = -\chi'(\omega)H_1\sin\omega t + \chi''(\omega)H_1\cos\omega t$$

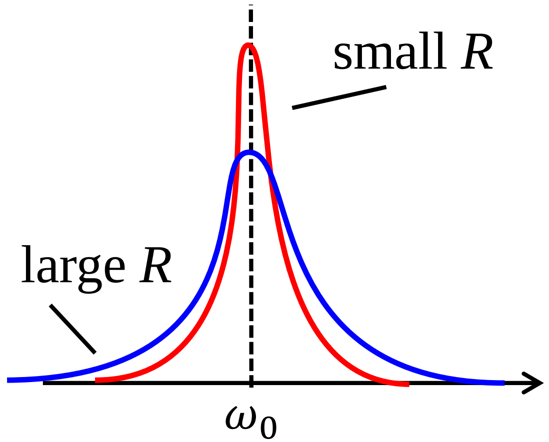
large relaxation

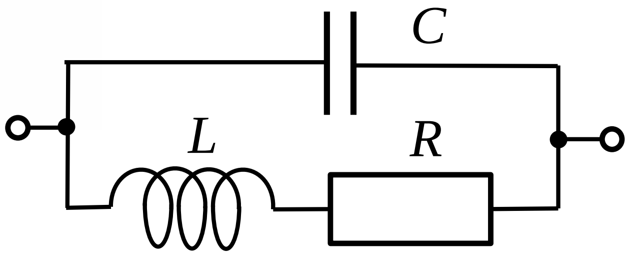
$\gamma^2 H_1^2 T_1 T_2 \ll 1$

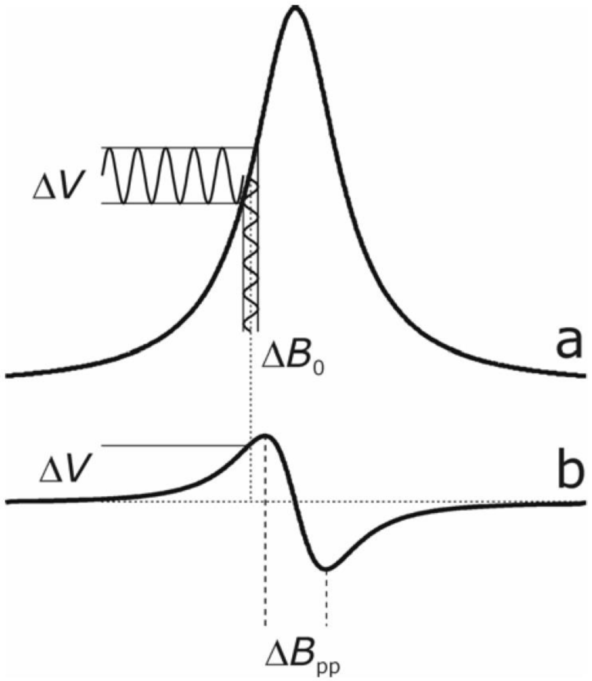
$$\boxed{\begin{aligned} \chi'(\omega) &= \frac{\chi_0\omega_0}{2}T_2\frac{(\omega_0-\omega)T_2}{1+(\omega_0-\omega)^2T_2^2}, \\ \chi''(\omega) &= \frac{\chi_0\omega_0}{2}T_2\frac{1}{1+(\omega_0-\omega)^2T_2^2} \end{aligned}}$$

Electron paramagnetic resonance (EPR) experimental setup









Double resonator sample + cavity

Continuous wave (CW) measurement: detection of resonance dissipation

Pulse, Fourier transform measurement: detection of magnetic field due to the precession of magnetic moment

Spin Hamiltonian

For the comparison of the theory with EPR experiments we need to go a little further in approximation.

Effective spin Hamiltonian: (in case $\mathcal{H}_{\mathrm{CF}}$ is diagonalized)

Only contains spin operators, i.e. the orbital part is already integrated out.

{o}

Orbital basis: $\{\varphi_0, \varphi_1, \cdots, \}$ diagonalizes $\mathcal{H}_{\mathrm{orb}} = \mathcal{H}_0 + \mathcal{H}_{\mathrm{CF}}$

In ket form: $|\varphi_n\rangle = |n\rangle_{\mathrm{o}}$

Energy eigenstates: ${}_{\mathrm{o}}\langle n|\mathcal{H}_{\mathrm{orb}}|n'\rangle_{\mathrm{o}} = E_n\delta_{nn'}$

{s} Spin basis for total spin *S*: $\{\phi_{-2S}, \phi_{-2S+1}, \cdots, \phi_{2S}\}$

In ket form: $|\phi_m\rangle = |m\rangle_{\mathrm{s}}$

Perturbation Hamiltonian: $\mathcal{H}' = \lambda \boldsymbol{L}\cdot\boldsymbol{S} + \mu_{\mathrm{B}}(\boldsymbol{L} + g_{\mathrm{e}}\boldsymbol{S})\cdot\boldsymbol{H}$

spin-orbit Zeeman

g_e : g-factor of electron

Expand the wavefunction with {o} and {s}as:

$$\Psi = \sum_{nm} a_{nm}\varphi_n\phi_m = \sum_{nm} a_{nm}|n\rangle_{\mathrm{o}}|m\rangle_{\mathrm{s}}$$

Spin Hamiltonian (2)

Eigenenergy equation: $\mathcal{H}\Psi = (\mathcal{H}_{\rm orb} + \mathcal{H}')\Psi = E\Psi.$

Second order perturbation in energy: $\tilde{\mathcal{H}} = {}_{\rm o}\langle 0|\mathcal{H}'|0\rangle_{\rm o} + \sum_{n\neq 0} \frac{{}_{\rm o}\langle 0|\mathcal{H}'|n\rangle_{\rm o}\,{}_{\rm o}\langle n|\mathcal{H}'|0\rangle_{\rm o}}{E_0 - E_n}$

Orbital angular moment is quenched: ${}_{\rm o}\langle 0|\boldsymbol{L}|0\rangle_{\rm o} = 0 \longrightarrow {}_{\rm o}\langle 0|\mathcal{H}'|0\rangle_{\rm o} = g_{\rm e}\mu_{\rm B}\boldsymbol{S}\cdot\boldsymbol{H}$

The second order term
→ reduced to second order in $\boldsymbol{L}$: ${}_{\rm o}\langle 0|\mathcal{H}'|n\rangle_{\rm o} = {}_{\rm o}\langle 0|\boldsymbol{L}|n\rangle_{\rm o}\cdot \underbrace{(\lambda\boldsymbol{S} + \mu_{\rm B}\boldsymbol{H})}_{\text{effective magnetic field for } \boldsymbol{L}}$

The effective spin Hamiltonian: $\tilde{\mathcal{H}} = g_{\rm e}\mu_{\rm B}\boldsymbol{S}\cdot\boldsymbol{H} - (\lambda\boldsymbol{S} + \mu_{\rm B}\boldsymbol{H})\Lambda(\lambda\boldsymbol{S} + \mu_{\rm B}\boldsymbol{H})$

where Λ is a tensor given by

$$\Lambda_{ij} = \sum_{n\neq 0} \frac{{}_{\rm o}\langle 0|L_i|n\rangle_{\rm o}\,{}_{\rm o}\langle n|L_j|0\rangle_{\rm o}}{E_n - E_0} \quad (i,j = x,y,z)$$

Expansion: $\tilde{\mathcal{H}} = \mu_{\rm B}\boldsymbol{S}g_{\rm e}(\boldsymbol{1} - \lambda\Lambda)\boldsymbol{H} - \lambda^2\boldsymbol{S}\Lambda\boldsymbol{S} - \mu_{\rm B}^2\boldsymbol{H}\Lambda\boldsymbol{H}$

Spin Hamiltonian (3)

$$\tilde{\mathcal{H}} = \mu_{\mathrm{B}} \boldsymbol{S} g_{\mathrm{e}}(\mathbf{1} - \lambda\Lambda)\boldsymbol{H} - \lambda^2 \boldsymbol{S}\Lambda\boldsymbol{S} - \mu_{\mathrm{B}}^2 \boldsymbol{H}\Lambda\boldsymbol{H}$$

The third term is small, does not contribute to level splitting → Drop

The first term: extension of Zeeman energy with effective g-tensor: $\tilde{\boldsymbol{g}} = g_{\mathrm{e}}(\mathbf{1} - \lambda\Lambda)$

The second term is written as $-\lambda^2 \boldsymbol{S}\Lambda\boldsymbol{S} = D\left[S_z^2 - \frac{S(S+1)}{3}\right] + E(S_x^2 - S_y^2)$

principal axes: *x*, *y*, *z*

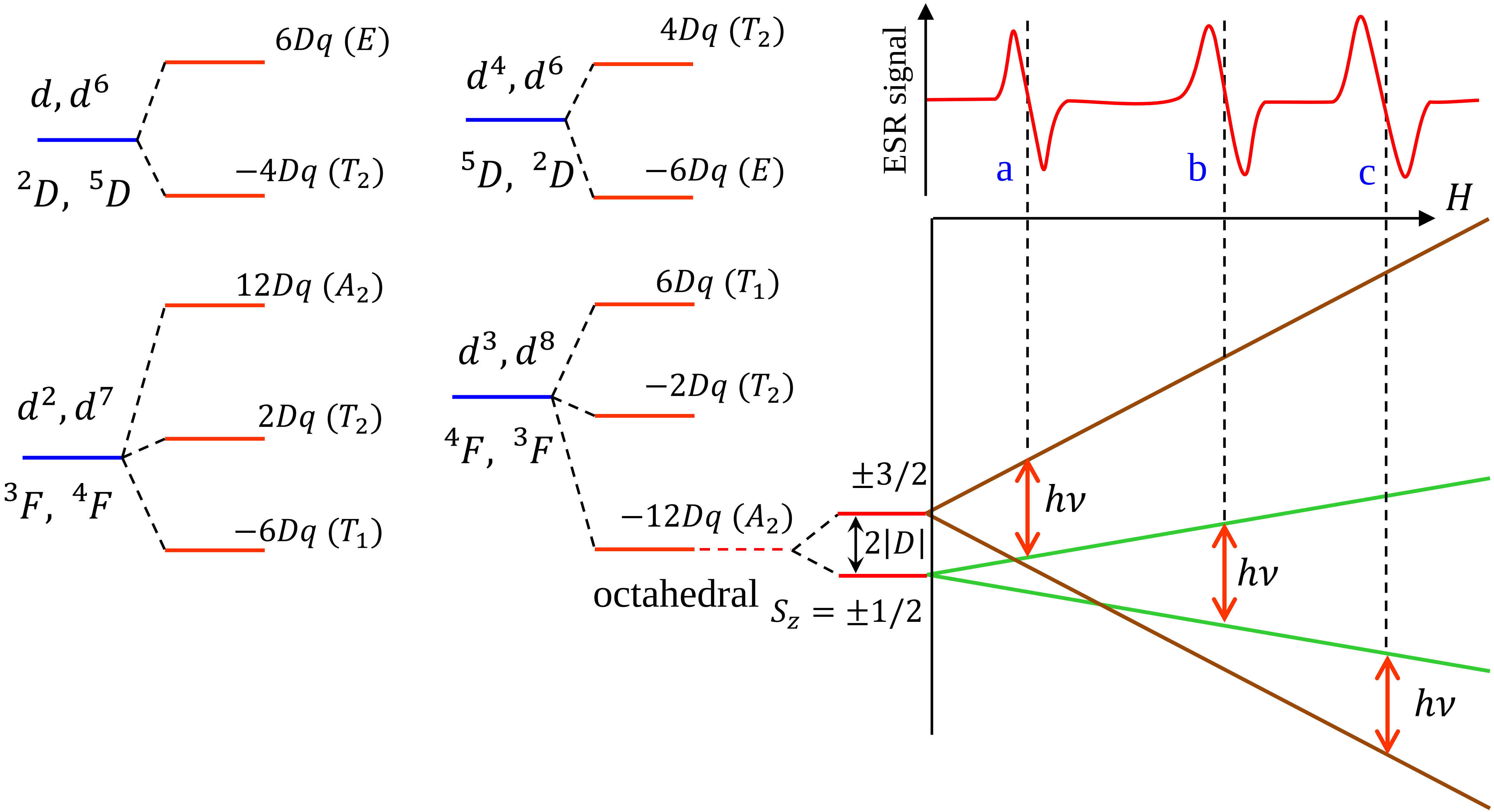
D: axial fine structure parameter

E: rhombic fine structure parameter

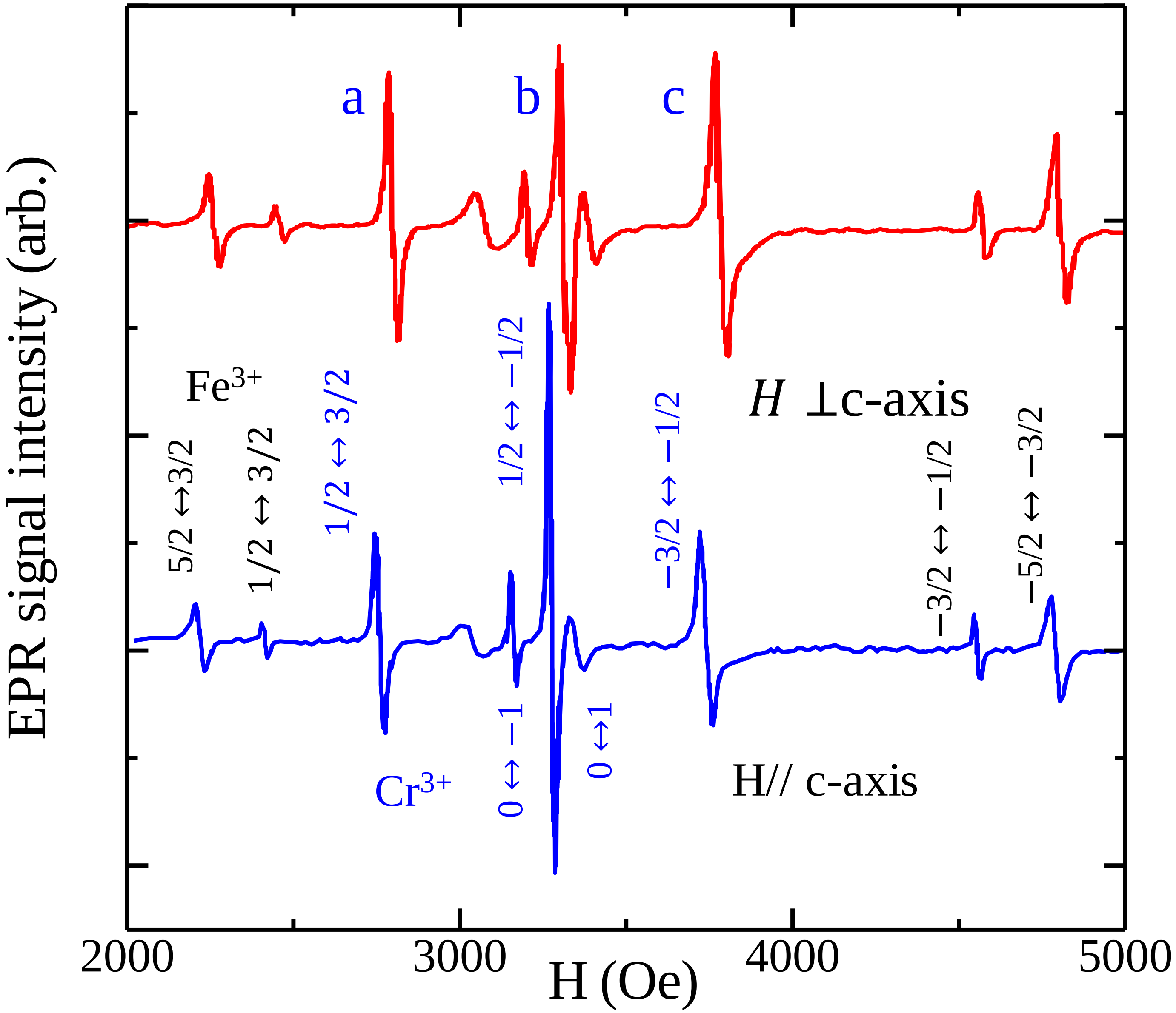
The form frequently used for the analysis of experiments

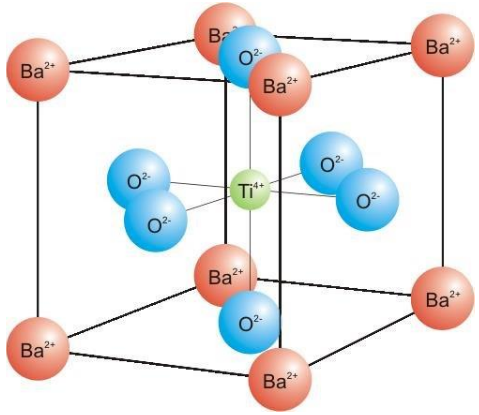
$$\boxed{\tilde{\mathcal{H}} = \mu_{\mathrm{B}} \boldsymbol{S}\tilde{\boldsymbol{g}}\boldsymbol{H} + D\left[S_z^2 - \frac{S(S+1)}{3}\right] + E(S_x^2 - S_y^2)}$$

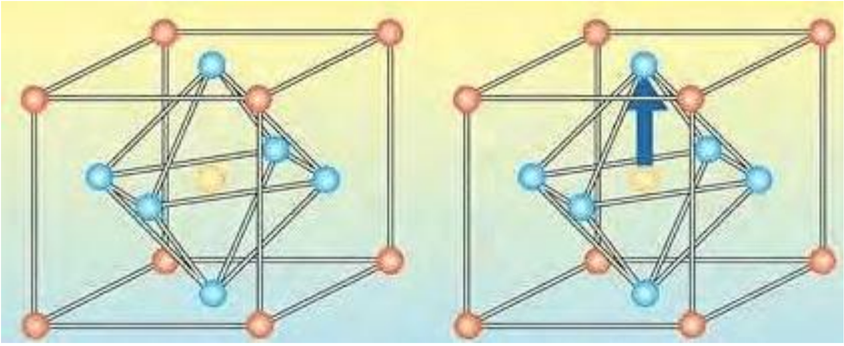
Weak crystal field approximation



EPR signal from Cr^{3+} and Fe^{3+} ions in $BaTiO_3$







hexagonal

$E = 0$

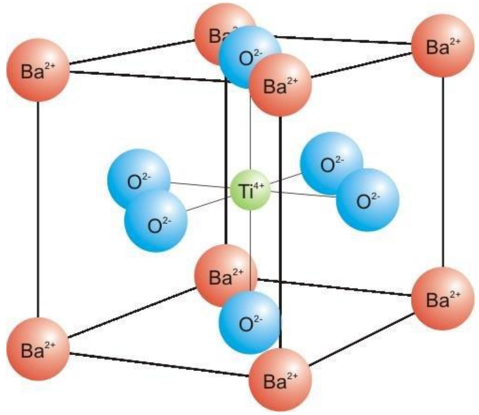
tetragonal

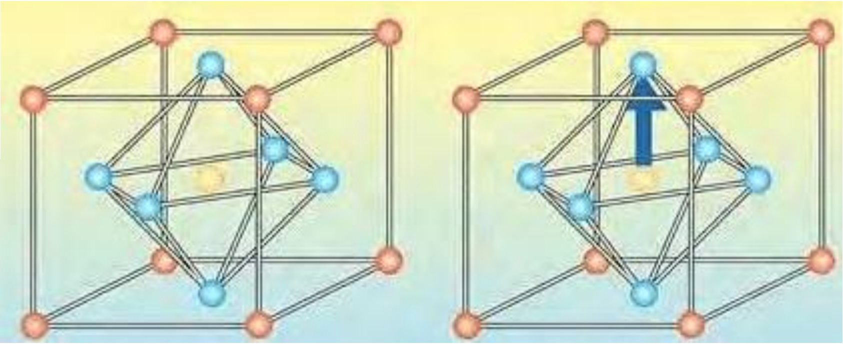
$E \neq 0$

Bairavarasu et al. SPIE Proc. 6698-05

EPR signal from Cr^{3+} and Fe^{3+} ions in $BaTiO_3$

Ion	Crystal	g		$\lvert D\rvert$ (cm^{-1})	$\lvert E\rvert$ (cm^{-1})
Fe^{3+}	$BaTiO_3$	2.000		0.022	0.0079
another report		2.003		0.0987	
Cr^{3+}	$BaTiO_3$	1.975		0.046	0.0055
	h-$BaTiO_3$	H1 g_z=	1.9797	0.105	
		H1 $g_{x,y}$=	1.9857		
		H2 g_z=	1.9736	0.3220	
		H2 $g_{x,y}$=	1.9756		





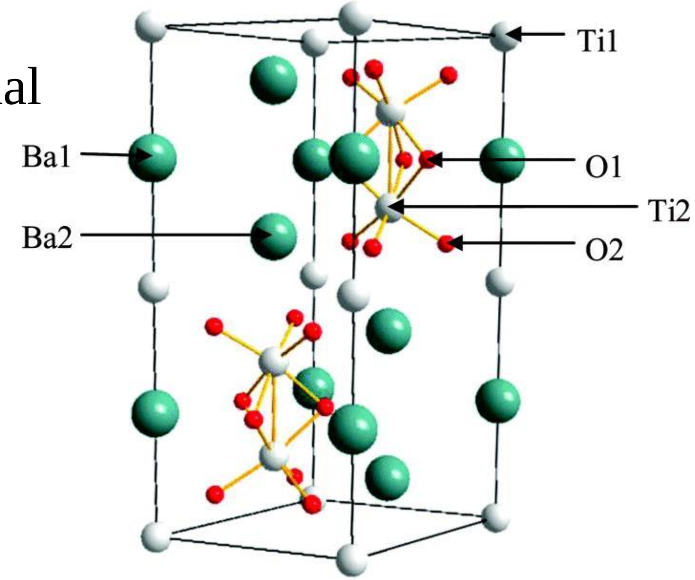
cubic

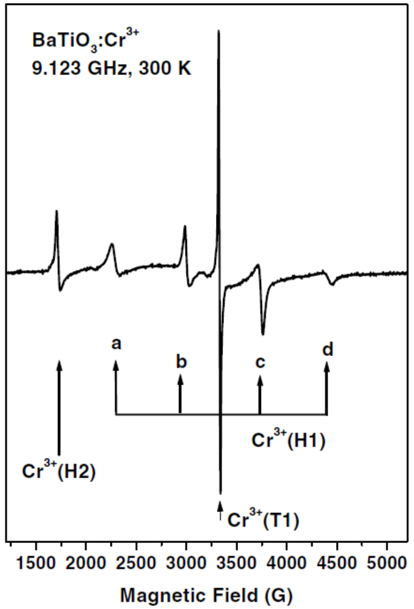
$E = 0$

tetragonal

$E \neq 0$

hexagonal

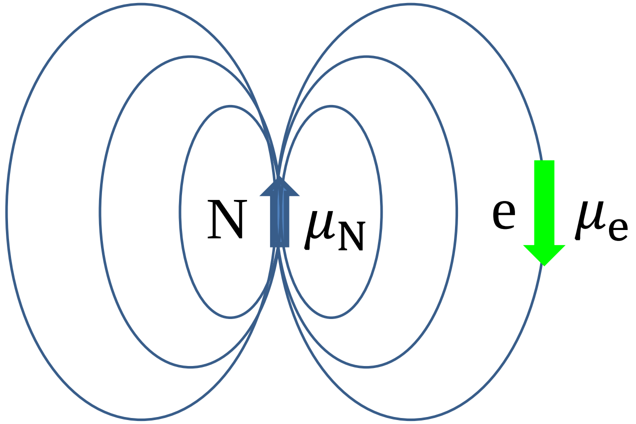




Boettcher et al. JPCM **17**, 2763 (2005)

Bairavarasu et al. SPIE Proc. 6698-05

electron-nuclear spin exchange interaction:

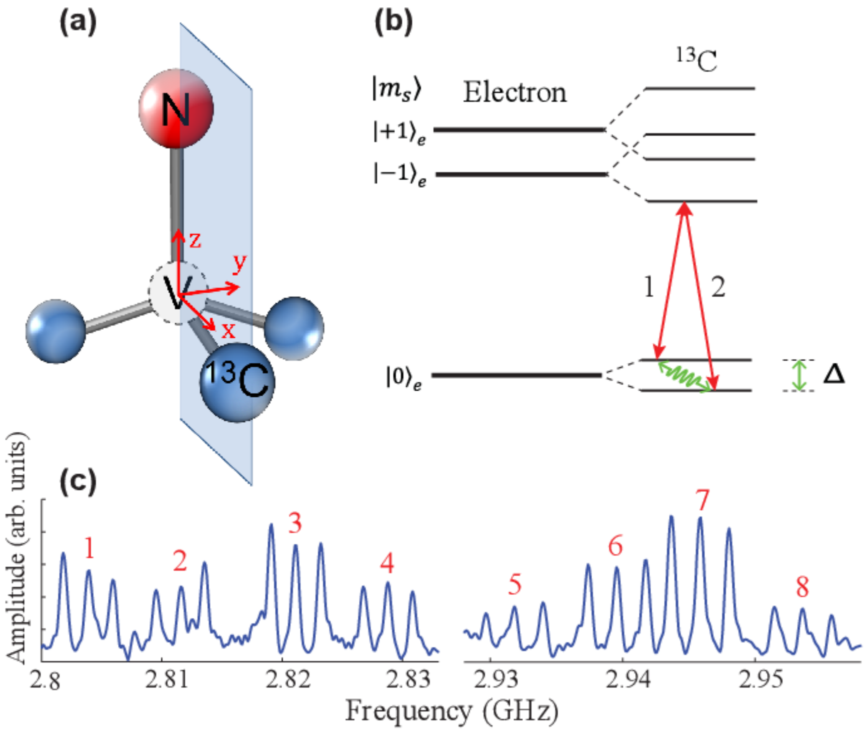


$$\mathcal{H}_{\rm HF} = A\boldsymbol{I}\cdot\boldsymbol{J}$$

the same form as spin-orbit interaction

$$\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}$$

$$\mathcal{H}_{\rm HF}\,|F, M_F\rangle = A\frac{\boldsymbol{F}^2 - \boldsymbol{I}^2 - \boldsymbol{J}^2}{2}|F, M_F\rangle$$
$$= A\frac{F(F+1) - I(I+1) - J(J+1)}{2}|F, M_F\rangle$$



NV center

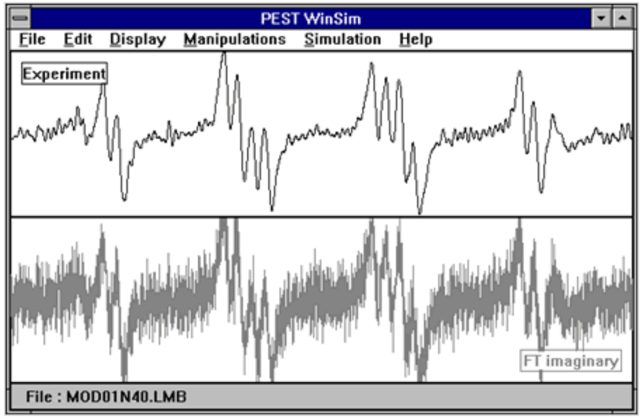
Rama et al., PRB 94, 060101 (`16).

ESR detector/analyzer

EPR public software

EPR-WinSim

https://www.niehs.nih.gov/research/resources/software/tox-pharm/tools/

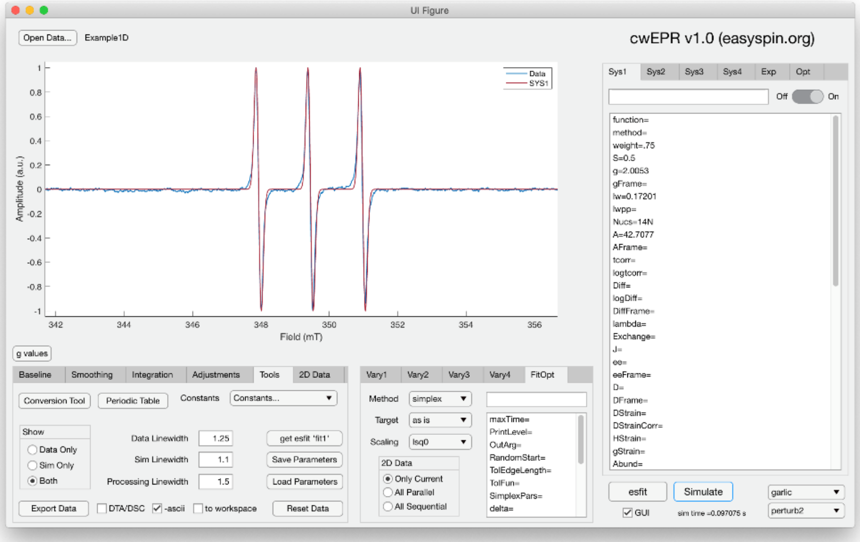


Easyspin

https://www.easyspin.org/

Works on MATLAB

GUI front: cwEPR etc.



Announcement of Easyspin for Octave

https://octave.discourse.group/t/easyspin-for-octave/1177

Commercial machines

Magnetic refrigeration

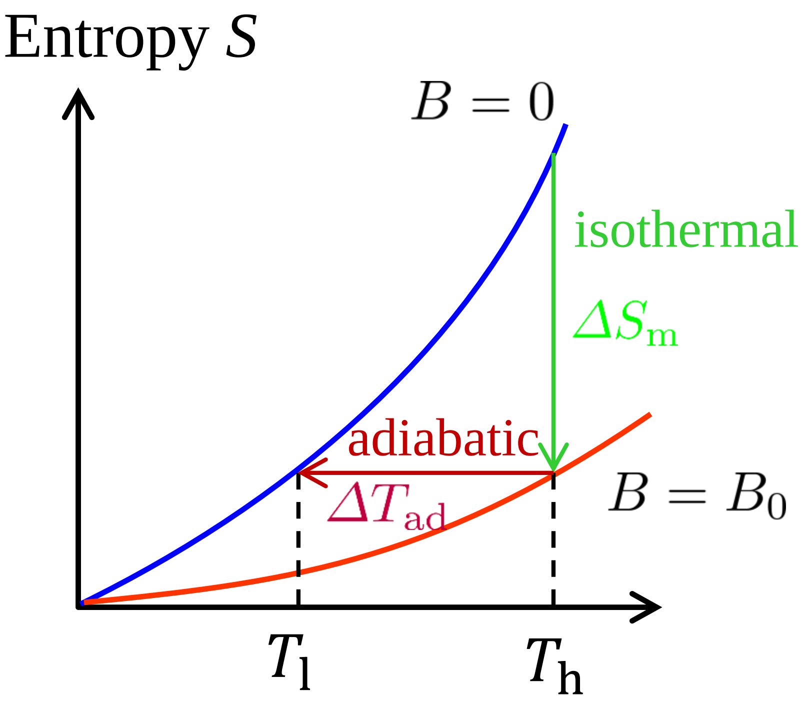
Many attempts for commercial use

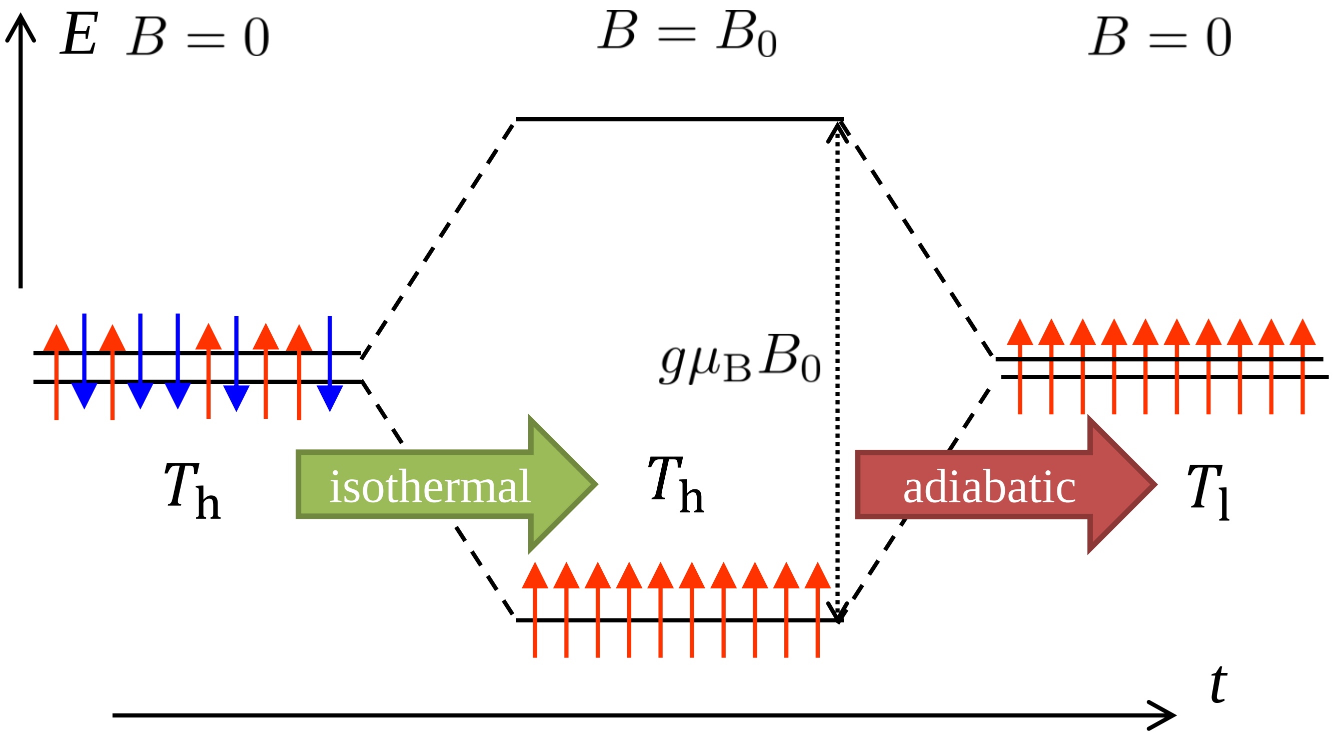
Air Conditioning with Magnetic Refrigeration

- Building Efficiency
- Efficiency

PRINT

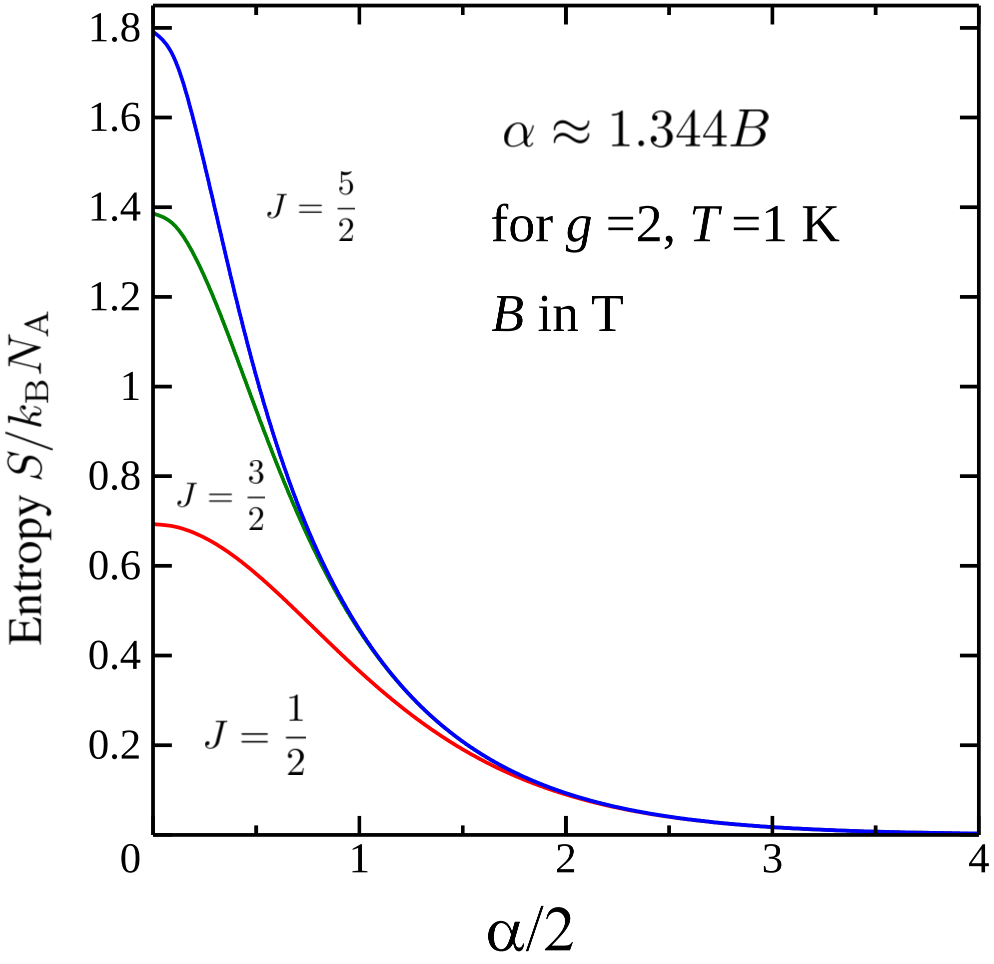
arpa·e PROJECT





Magnetic refrigeration (2)

Entropy of a free spin system



$$\Delta S(B, T_i) = S(0, T_i) - S(B, T_i) = \int_{T_f}^{T_i} \frac{C_m}{T} dT,$$

$$C_m = T\left(\frac{\partial S}{\partial T}\right)_{B=0}$$

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

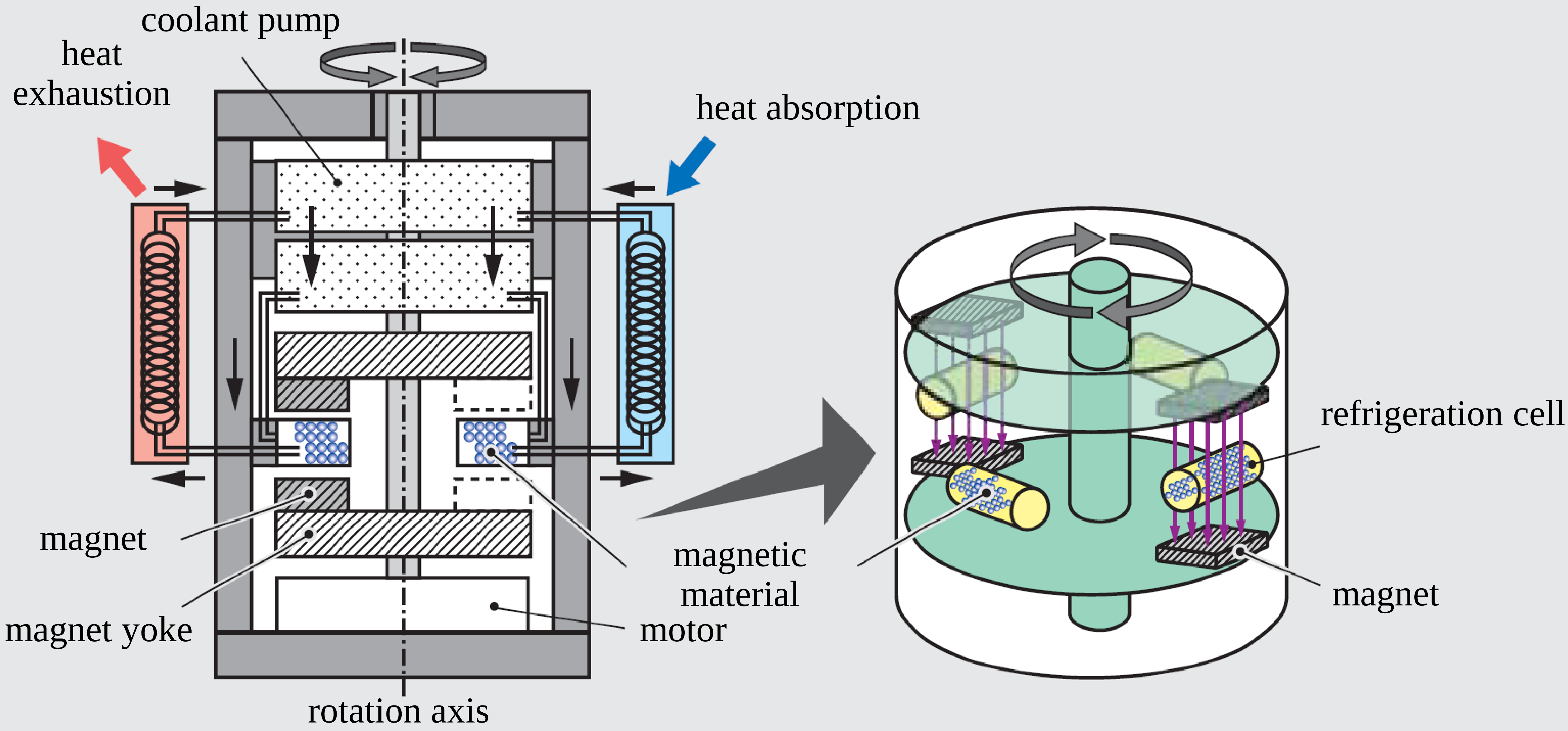
$$\alpha \equiv \frac{g\mu_B B}{k_B T}$$

$$\frac{S}{N_A k_B} = \frac{\alpha}{2}\coth\frac{\alpha}{2} - \frac{2J+1}{2}\alpha\coth\left[\frac{2J+1}{2}\alpha\right] + \ln\left[\frac{\sinh[(2J+1)\alpha/2]}{\sinh\alpha/2}\right].$$

Cooling material

Maxwell relation: $\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$

Active magnetic refrigeration



Chapter 3 Magnetism of Conduction Electrons

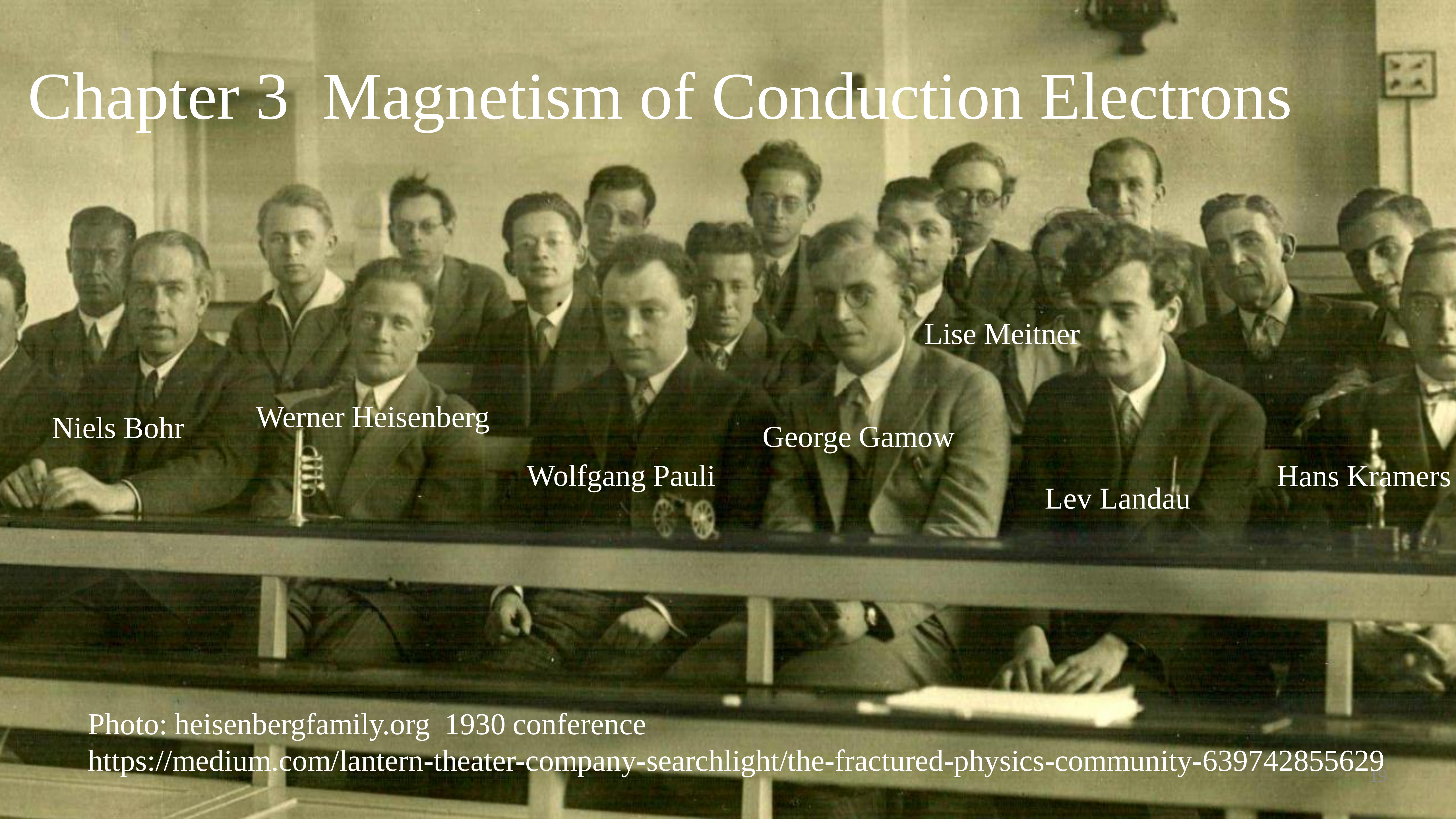


Photo: heisenbergfamily.org 1930 conference
https://medium.com/lantern-theater-company-searchlight/the-fractured-physics-community-639742855629

Chapter 3 Magnetism of Conduction Electrons

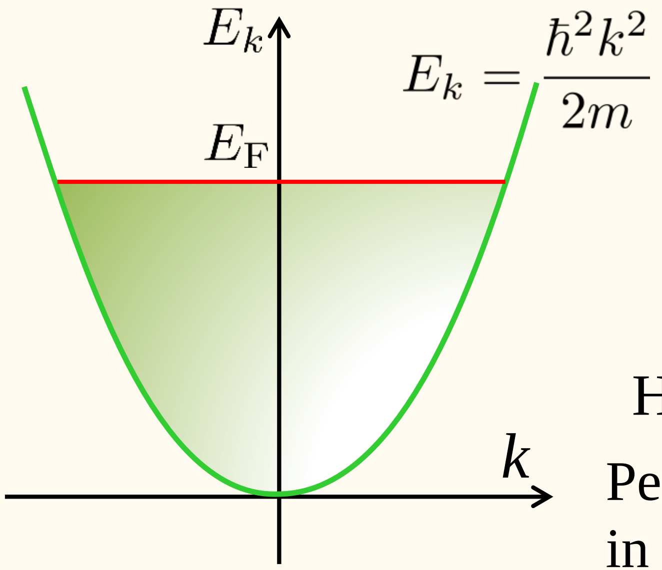
3.1 Pauli paramagnetism

3.2 Landau diamagnetism

3.3 An example of orbital diamagnetism

https://sci-toys.com/scitoys/scitoys/magnets/pyrolytic

Spin paramagnetism in free electrons



Hamiltonian: kinetic energy + spin

$$\mathscr{H} = \sum_{\boldsymbol{k}\sigma} E_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \frac{1}{2} g\mu_{\mathrm{B}} B \sum_{\boldsymbol{k}\sigma} \sigma c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma}$$

spin variable: $\sigma \ : \ (\uparrow, \downarrow) \to (1, -1)$

How to count k in metals?

Periodic boundary condition in L-cube

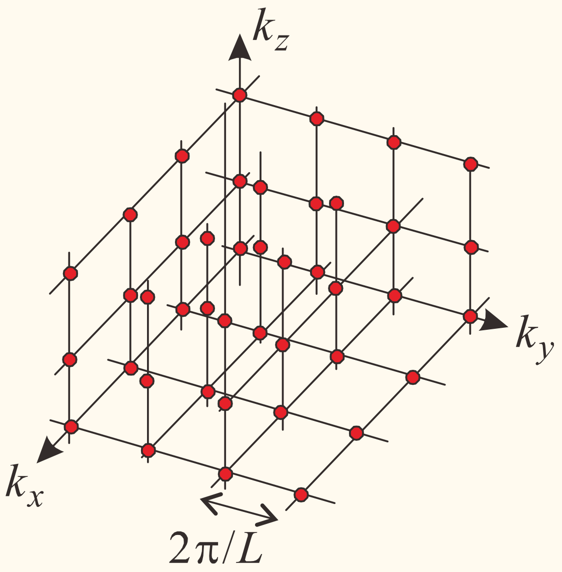
$$\boldsymbol{k} = \frac{2\pi}{L}(n_x, n_y, n_z) \quad (n_x, n_y, n_z : \ \text{integers})$$

$$E_k = \frac{\hbar^2 k^2}{2m}$$

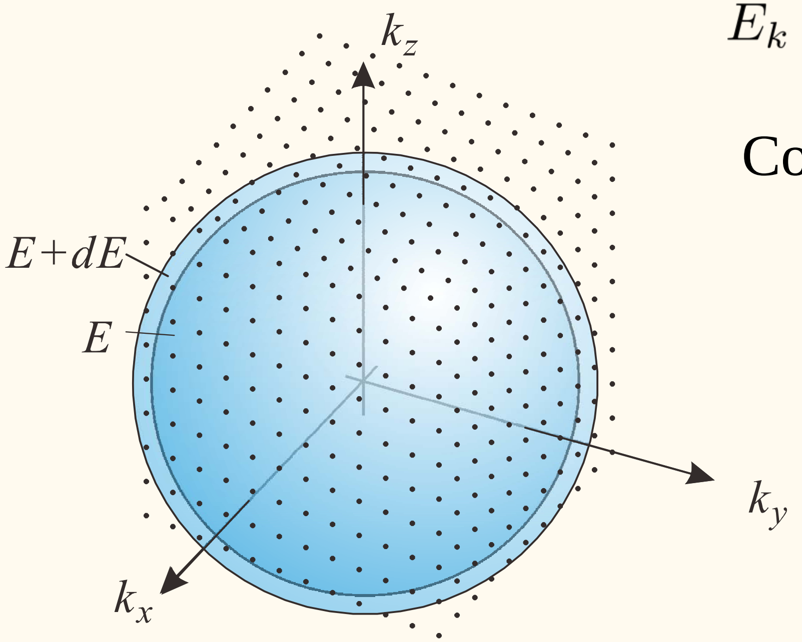
Constant E sphere radius: $k_E = \frac{\sqrt{2mE}}{\hbar}$

$$\rho(E) = \frac{1}{L^3}\left(\frac{L}{2\pi}\right)^3 4\pi k_E^2 \frac{dk_E}{dE}$$

$$= \frac{1}{\pi^2 \hbar^3}\sqrt{\frac{mE}{2}}$$



(a)



(b)

Pauli paramagnetism

Expectation value of magnetic moment: $-\frac{g\mu_\mathrm{B}}{2}\sum_{\boldsymbol{k}\sigma}\sigma\left\langle c^\dagger_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}\sigma}\right\rangle = \frac{g\mu_\mathrm{B}}{2}\sum_{\boldsymbol{k}}\left[f\left(E_{\boldsymbol{k}}-\frac{g\mu_\mathrm{B}B}{2}\right)-f\left(E_{\boldsymbol{k}}+\frac{g\mu_\mathrm{B}B}{2}\right)\right]$

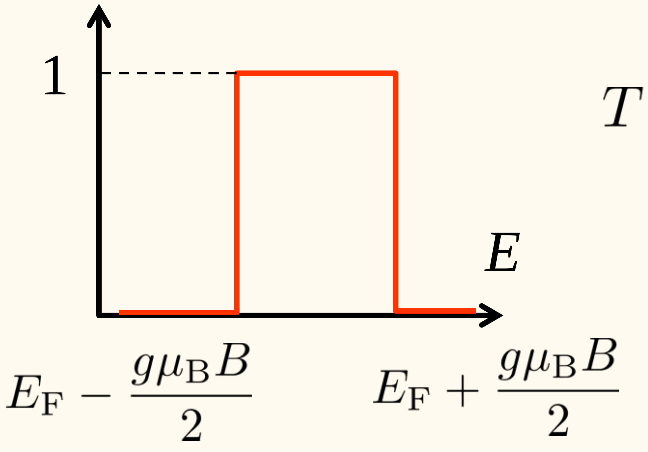
Fermi distribution function: $f(E)=\frac{1}{\exp[(E-\mu)/k_\mathrm{B}T]+1}$

Chemical potential μ is determined from $N_\mathrm{e}=\int_0^\infty dE\rho(E)\left[f\left(E_{\boldsymbol{k}}-\frac{g\mu_\mathrm{B}B}{2}\right)+f\left(E_{\boldsymbol{k}}+\frac{g\mu_\mathrm{B}B}{2}\right)\right]$

$\mu\to E_\mathrm{F}$

Magnetization: $M=\frac{g\mu_\mathrm{B}}{2}\int_0^\infty dE\rho(E)\left[f\left(E_{\boldsymbol{k}}-\frac{g\mu_\mathrm{B}B}{2}\right)-f\left(E_{\boldsymbol{k}}+\frac{g\mu_\mathrm{B}B}{2}\right)\right]$

$$\frac{\left[f\left(E_{\boldsymbol{k}}-\frac{g\mu_\mathrm{B}B}{2}\right)-f\left(E_{\boldsymbol{k}}+\frac{g\mu_\mathrm{B}B}{2}\right)\right]}{2\left(\frac{g\mu_\mathrm{B}B}{2}\right)}$$



$T\to 0$

$\frac{\partial M}{\partial B}\to$

Pauli paramagnetic susceptibility

$$\chi_\mathrm{Pauli}=\left(\frac{g\mu_\mathrm{B}}{2}\right)^2[2\rho(E_\mathrm{F})]$$

Landau quantization

Hamiltonian free electron + magnetic field

$$\mathscr{H} = \frac{1}{2m}\sum_i (\boldsymbol{p}_i + e\boldsymbol{A})^2$$

Landau gauge: $\boldsymbol{A} = (0, Bx, 0)$

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

Schrödinger equation:

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} + \left(\frac{\partial}{\partial y} - i\frac{eB}{\hbar}x\right)^2\right]\psi = E\psi$$

Homogeneous for *y* and *z*

→ Functional form assumption: $\psi = \exp[i(k_y y + k_z z)]u(x)$

Differential equation for *x*

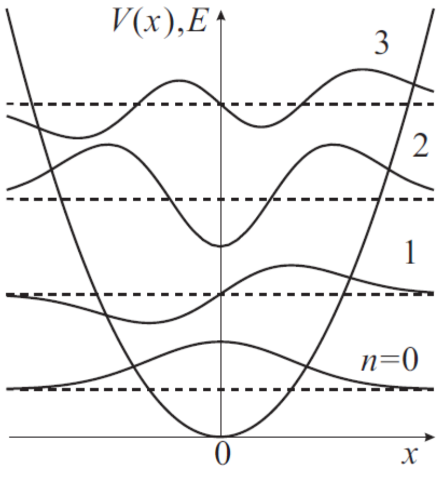
$$-\frac{\hbar^2}{2m}\left[\frac{d^2u}{dx^2} + \left(k_y - \frac{eB}{\hbar}x\right)^2 u\right] = \left(E - \frac{\hbar^2 k_z^2}{2m}\right)u$$

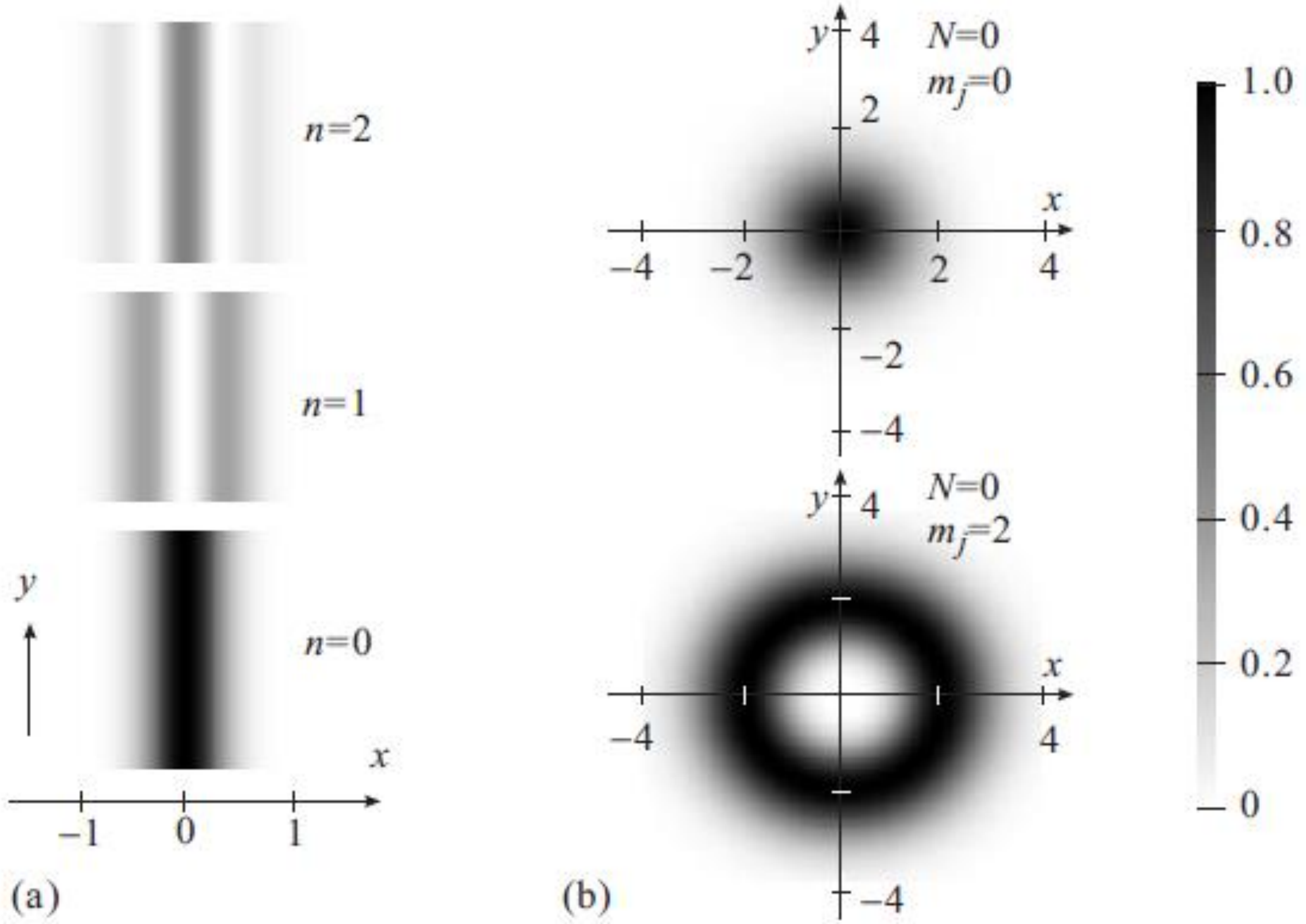
Harmonic oscillator at $x_{\mathrm{c}} = \dfrac{\hbar k_y}{eB}$ $\qquad \dfrac{m\omega_{\mathrm{c}}^2}{2} = \dfrac{(eB)^2}{2m} \qquad \therefore\ \omega_{\mathrm{c}} = \dfrac{eB}{m}$: Cyclotron frequency

Landau quantization

$$E(n, k_z) = \frac{\hbar^2 k_z^2}{2m} + \boxed{\left(n + \frac{1}{2}\right)\hbar\omega_{\mathrm{c}}} = \frac{\hbar^2 k_z^2}{2m} + (2n+1)\mu_{\mathrm{B}}B \quad (n = 0, 1, 2, \cdots)$$

Landau quantization: forms of wavefunctions





Diagonalize X

Diagonalize $X^2 + Y^2$ $\leftarrow$ Symmetric gauge

$$\boldsymbol{A} = \boldsymbol{B} \times \boldsymbol{r}/2$$

Orbital diamagnetism

How to count density of states?

Periodic boundary condition in a cube with side length L

z-direction $\quad k_z = \frac{2\pi}{L} n_z \ (n_z = 0, \pm 1, \cdots) \qquad E_z = \frac{\hbar^2 k_z^2}{2m}$ $\quad$ Number of k_z below E_z $\quad \frac{2L\sqrt{2mE_z}}{h}$

y-direction $\quad k_y = \frac{2\pi}{L} n_y \ (n_y = 0, \pm 1, \cdots)$

x-direction $\quad -\frac{L}{2} \le x_c \le \frac{L}{2} \qquad -\frac{L}{2} \le \frac{\hbar}{eB} k_y = \frac{\hbar}{eB} \frac{2\pi}{L} n_y \le \frac{L}{2} \qquad \therefore \ |n_y| \le \frac{eBL^2}{4\pi\hbar}$

Landau level degeneracy (in xy-plane) is $\frac{eBL^2}{h}$

the number of states below the total energy: $\quad \Omega(E) = \frac{L^3}{h^2}\sqrt{8meB} \sum_{n=0}^{n_{\max}} \sqrt{E - (2n+1)\mu_B B} \qquad n_{\max} = \mathrm{int}\left(\frac{E - \mu_B B}{2}\right)$

Free energy: $\quad F = N\mu - 2k_B T \int \frac{d\Omega}{dE} \ln\{1 + \exp[-(E-\mu)/k_B T]\} dE$

Orbital diamagnetism (2)

Partial integration

$$\int \frac{d\Omega}{dE}\ln\{1+\exp[-(E-\mu)/k_\mathrm{B}T]\}dE = -\int \Omega(E)\left(-\frac{1}{k_\mathrm{B}T}\right)\frac{\exp[-(E-\mu)/k_\mathrm{B}T]}{1+\exp[-(E-\mu)/k_\mathrm{B}T]}dE$$

$$= \frac{1}{k_\mathrm{B}T}\int\left[\int \Omega(E)dE\right]\frac{d}{dE}\frac{1}{1+\exp[(E-\mu)/k_\mathrm{B}T]}dE$$

$$= \frac{1}{k_\mathrm{B}T}\frac{2\sqrt{8m}}{3}\frac{eBL^3}{h^2}\int\sum_{n=0}^{n_\mathrm{max}}[E-(2n+1)\mu_\mathrm{B}B]^{3/2}\frac{d}{dE}\frac{1}{1+\exp[(E-\mu)/k_\mathrm{B}T]}dE$$

$$F = N_\mathrm{e}\mu - A\int \phi(E)\frac{d}{dE}\frac{1}{1+\exp[(E-\mu)/k_\mathrm{B}T]}dE$$

$$\begin{cases} A = \dfrac{16L^3}{3\pi^2\hbar^3}m^{3/2}(\mu_\mathrm{B}B)^{5/2}, \\ \phi(E) = \displaystyle\sum_{n=0}^{n_\mathrm{max}}\left[\frac{E}{2\mu_\mathrm{B}B}-\left(n+\frac{1}{2}\right)\right]^{3/2} \end{cases}$$

$$T\to 0 \qquad F = N_\mathrm{e}E_\mathrm{F} - A\phi(E_\mathrm{F})$$

$$\mu_\mathrm{B} = \frac{e\hbar}{2m}$$

Orbital diamagnetism (3)

To calculate $$\phi(E) = \sum_{n=0}^{n_{\max}} \left[\frac{E}{2\mu_{\mathrm{B}}B} - \left(n + \frac{1}{2}\right)\right]^{3/2}$$

We use an asymptotic expansion $x \gg 1$ $$\sum_{n=0}^{n_{\max}} \left[x - \left(n + \frac{1}{2}\right)\right]^{3/2} \approx \frac{2}{5}x^{5/2} - \frac{1}{16}x^{1/2} + \cdots$$

which can be obtained by applying Euler-Maclaurin formula to $F(y) = (x-y)^{3/2}$

$$\sum_{n=0}^{n_0} F(n+1/2) \approx \int_0^{n_0+1} dy F(y) - \frac{1}{24}[F'(n_0+1) - F'(0)] \approx \frac{2}{5}x^{5/2} - \frac{1}{16}x^{1/2}$$

The free energy: $$F = \text{const.} - \frac{L^3}{3}\rho(E_{\mathrm{F}})(\mu_{\mathrm{B}}B)^2 + \cdots$$

Landau orbital diamagnetism: $$\chi_{\text{Landau}} = -\frac{2}{3}\rho(E_{\mathrm{F}})\mu_{\mathrm{B}}^2$$

Total susceptibility of free electrons: $$\chi = \chi_{\text{Pauli}} + \chi_{\text{Landau}} = \frac{4}{3}\rho(E_{\mathrm{F}})\mu_{\mathrm{B}}^2$$

Summary

- Magnetic resonance (continued)
- Spin Hamiltonian
- Example of analyzing experimental data on electron paramagnetic resonance
- Application of paramagnetism: magnetic refrigeration

Chapter 3 Magnetism of conduction electrons

- Pauli paramagnetism
- Landau diamagnetism

2022.5.18 Lecture 6

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Review

- Magnetic resonance (continued)
- Spin Hamiltonian
- Example of analyzing experimental data on electron paramagnetic resonance
- Application of paramagnetism: magnetic refrigeration

Chapter 3 Magnetism of conduction electrons

- Pauli paramagnetism
- Landau quantization ($\rightarrow$ diamagnetism)

Outline

1. Landau diamagnetism
2. de Haas-van Alphen effect
3. Orbital diamagnetism of graphene, graphite

Chapter 4 Interaction between spins

1. Exchange interaction from Heitler-London approximation

Landau quantization

Hamiltonian free electron + magnetic field $\mathscr{H} = \dfrac{1}{2m}\sum_i (\boldsymbol{p}_i + e\boldsymbol{A})^2$

Landau gauge: $\boldsymbol{A} = (0, Bx, 0)$ $\boldsymbol{B} = \mathrm{rot}\,\boldsymbol{A} = (0, 0, B)$

Schrödinger equation: $-\dfrac{\hbar^2}{2m}\left[\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial z^2} + \left(\dfrac{\partial}{\partial y} - i\dfrac{eB}{\hbar}x\right)^2\right]\psi = E\psi$

Homogeneous for *y* and *z*

→ Functional form assumption: $\psi = \exp[i(k_y y + k_z z)]u(x)$

Differential equation for *x* $-\dfrac{\hbar^2}{2m}\left[\dfrac{d^2 u}{dx^2} + \left(k_y - \dfrac{eB}{\hbar}x\right)^2 u\right] = \left(E - \dfrac{\hbar^2 k_z^2}{2m}\right)u$

Harmonic oscillator at $x_\mathrm{c} = \dfrac{\hbar k_y}{eB}$ $\dfrac{m\omega_\mathrm{c}^2}{2} = \dfrac{(eB)^2}{2m}$ $\therefore\ \omega_\mathrm{c} = \dfrac{eB}{m}$: Cyclotron frequency

Landau quantization $E(n, k_z) = \dfrac{\hbar^2 k_z^2}{2m} + \boxed{\left(n + \dfrac{1}{2}\right)\hbar\omega_\mathrm{c}} = \dfrac{\hbar^2 k_z^2}{2m} + (2n+1)\mu_\mathrm{B} B \quad (n = 0, 1, 2, \cdots)$

Orbital diamagnetism

How to count density of states?

Periodic boundary condition in a cube with side length L

z-direction $$k_z = \frac{2\pi}{L} n_z \ (n_z = 0, \pm 1, \cdots) \qquad E_z = \frac{\hbar^2 k_z^2}{2m}$$ Number of k_z below E_z $$\frac{2L\sqrt{2mE_z}}{h}$$

y-direction $$k_y = \frac{2\pi}{L} n_y \ (n_y = 0, \pm 1, \cdots)$$

x-direction $$-\frac{L}{2} \leq x_c \leq \frac{L}{2} \qquad -\frac{L}{2} \leq \frac{\hbar}{eB} k_y = \frac{\hbar}{eB} \frac{2\pi}{L} n_y \leq \frac{L}{2} \qquad \therefore \ |n_y| \leq \frac{eBL^2}{4\pi\hbar}$$

Landau level degeneracy (in *xy*-plane) is $\frac{eBL^2}{h}$

the number of states below the total energy: $$\Omega(E) = \frac{L^3}{h^2} \sqrt{8m} eB \sum_{n=0}^{n_{\max}} \sqrt{E - (2n+1)\mu_B B} \qquad n_{\max} = \mathrm{int}\left(\frac{E - \mu_B B}{2} \right)$$

Free energy: $$F = N\mu - 2k_B T \int \frac{d\Omega}{dE} \ln\{1 + \exp[-(E-\mu)/k_B T]\} dE$$

Orbital diamagnetism (2)

Partial integration

$$\int \frac{d\Omega}{dE} \ln\{1+\exp[-(E-\mu)/k_\mathrm{B}T]\} dE = -\int \Omega(E) \left(-\frac{1}{k_\mathrm{B}T}\right) \frac{\exp[-(E-\mu)/k_\mathrm{B}T]}{1+\exp[-(E-\mu)/k_\mathrm{B}T]} dE$$

$$= \frac{1}{k_\mathrm{B}T} \int \left[\int \Omega(E) dE\right] \frac{d}{dE} \frac{1}{1+\exp[(E-\mu)/k_\mathrm{B}T]} dE$$

$$= \frac{1}{k_\mathrm{B}T} \frac{2\sqrt{8m}}{3} \frac{eBL^3}{h^2} \int \sum_{n=0}^{n_\mathrm{max}} [E-(2n+1)\mu_\mathrm{B}B]^{3/2} \frac{d}{dE} \frac{1}{1+\exp[(E-\mu)/k_\mathrm{B}T]} dE$$

$$F = N_\mathrm{e}\mu - A \int \phi(E) \frac{d}{dE} \frac{1}{1+\exp[(E-\mu)/k_\mathrm{B}T]} dE$$

$$\begin{cases} A = \dfrac{16L^3}{3\pi^2\hbar^3} m^{3/2} (\mu_\mathrm{B}B)^{5/2}, \\ \phi(E) = \displaystyle\sum_{n=0}^{n_\mathrm{max}} \left[\frac{E}{2\mu_\mathrm{B}B} - \left(n+\frac{1}{2}\right)\right]^{3/2} \end{cases}$$

$$B \to 0 \qquad F = N_\mathrm{e}E_\mathrm{F} - A\phi(E_\mathrm{F})$$

$$\mu_\mathrm{B} = \frac{e\hbar}{2m}$$

Orbital diamagnetism (3)

To calculate $$\phi(E) = \sum_{n=0}^{n_{\max}} \left[\frac{E}{2\mu_{\mathrm{B}} B} - \left(n + \frac{1}{2} \right) \right]^{3/2}$$

We use an asymptotic expansion $x \gg 1$ $$\sum_{n=0}^{n_{\max}} \left[x - \left(n + \frac{1}{2} \right) \right]^{3/2} \approx \frac{2}{5} x^{5/2} - \frac{1}{16} x^{1/2} + \cdots$$

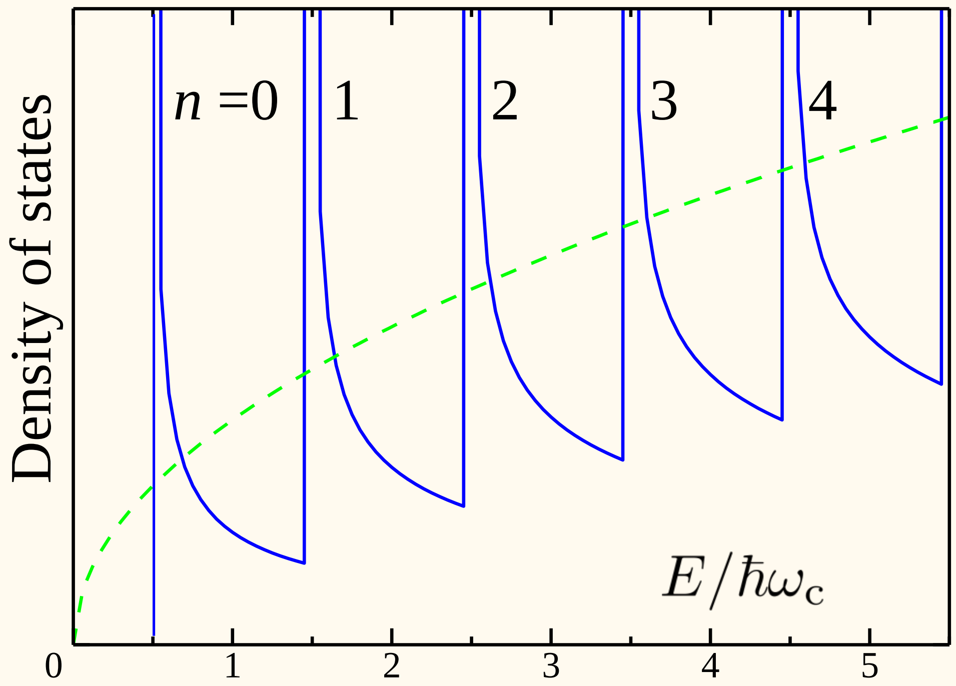
which can be obtained by applying Euler-Maclaurin formula to $F(y) = (x-y)^{3/2}$

$$\sum_{n=0}^{n_0} F(n+1/2) \approx \int_0^{n_0+1} dy F(y) - \frac{1}{24}[F'(n_0+1) - F'(0)] \approx \frac{2}{5} x^{5/2} - \frac{1}{16} x^{1/2}$$

The free energy: $$F = \text{const.} - \frac{L^3}{3} \rho(E_{\mathrm{F}}) (\mu_{\mathrm{B}} B)^2 + \cdots$$

Landau orbital diamagnetism: $$\chi_{\text{Landau}} = -\frac{2}{3} \rho(E_{\mathrm{F}}) \mu_{\mathrm{B}}^2$$

Total susceptibility of free electrons: $$\chi = \chi_{\text{Pauli}} + \chi_{\text{Landau}} = \frac{4}{3} \rho(E_{\mathrm{F}}) \mu_{\mathrm{B}}^2$$



Free energy expression

$$\frac{F}{n_e} = \mu - \frac{\hbar\omega_c}{E_F^{3/2}} \int_0^\infty dE \sum_{n=0} \left[E - \left(n + \frac{1}{2}\right)\hbar\omega_c \right]^{3/2} \left(-\frac{\partial f}{\partial E} \right)$$

$$n_e = N_e / L^3$$

Rapid change in the free energy at $(n+1/2)\hbar\omega_c \approx E_F$

Motion in z-direction: Density of states in one-dimensional system

$$E_k = \frac{\hbar^2 k^2}{2m}, \quad \rho_{1d}(E) = \frac{1}{L}\frac{L}{2\pi}\left(\frac{\hbar^2 k}{m}\right)^{-1} = \frac{1}{2\pi\hbar}\sqrt{\frac{m}{2E}}$$

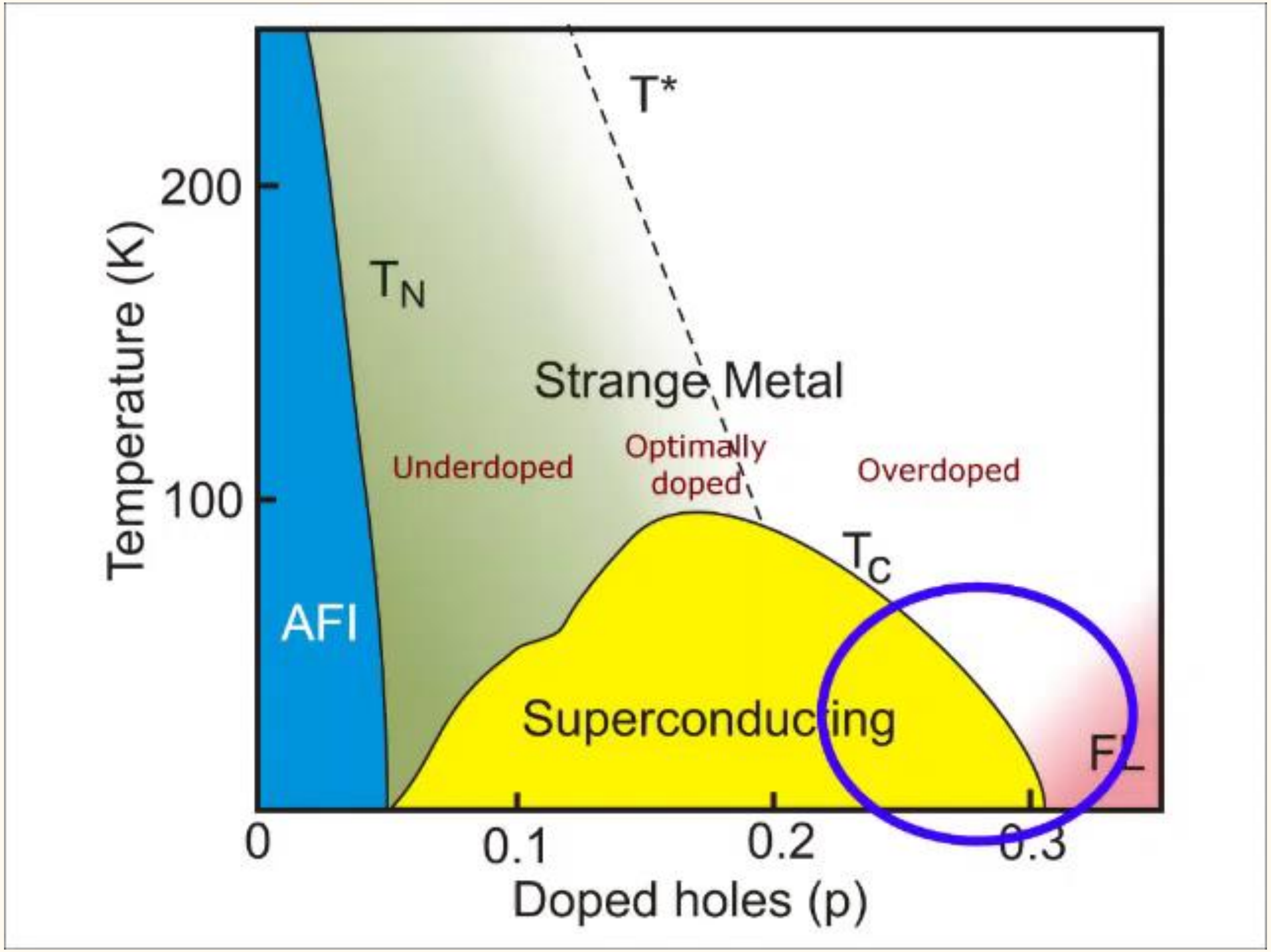
Then the density of states is given by $\rho(E) = \frac{1}{2\pi\hbar}\sqrt{\frac{m}{2}} \sum_{n=0} \frac{1}{\sqrt{(E-(n+1/2)\hbar\omega_c}}$

Magnetization formula for a spherical Fermi surface

$$M = \frac{e}{4\pi^3}\sum_p \frac{(-1)^p}{p}\int_{-k_F}^{k_F} dk_z \cdot E_F' \sin\left[\frac{p\pi}{\hbar\omega_c}\left(E_F - \frac{\hbar^2 k_z^2}{2m}\right)\right]$$

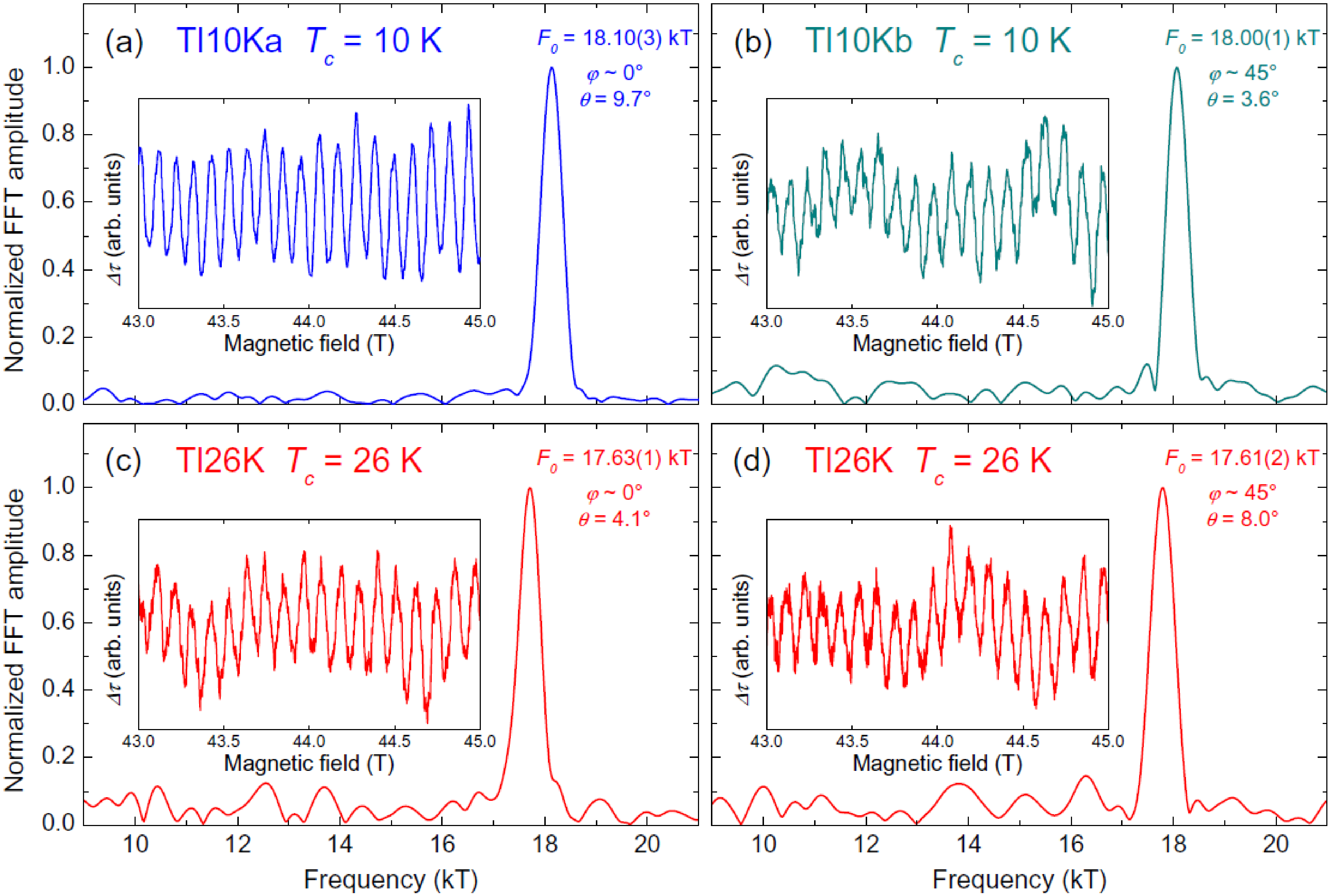
$E_F' = E_F - \frac{\hbar^2 k_z^2}{2m}$ varies slowly compared with the rapidly oscillating sine term other than at around $k_z = 0$

de Haas-van Alphen effect in $Tl_2Ba_2CuO_{6+\delta}$



Rourke et al., New J. Phys. 12, 105009 (2010).

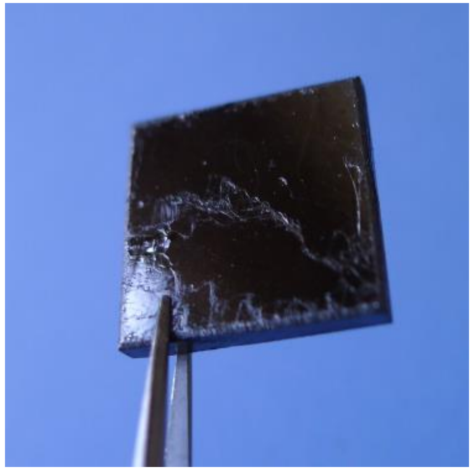
Experimental data on $Tl_2Ba_2CuO_{6+\delta}$



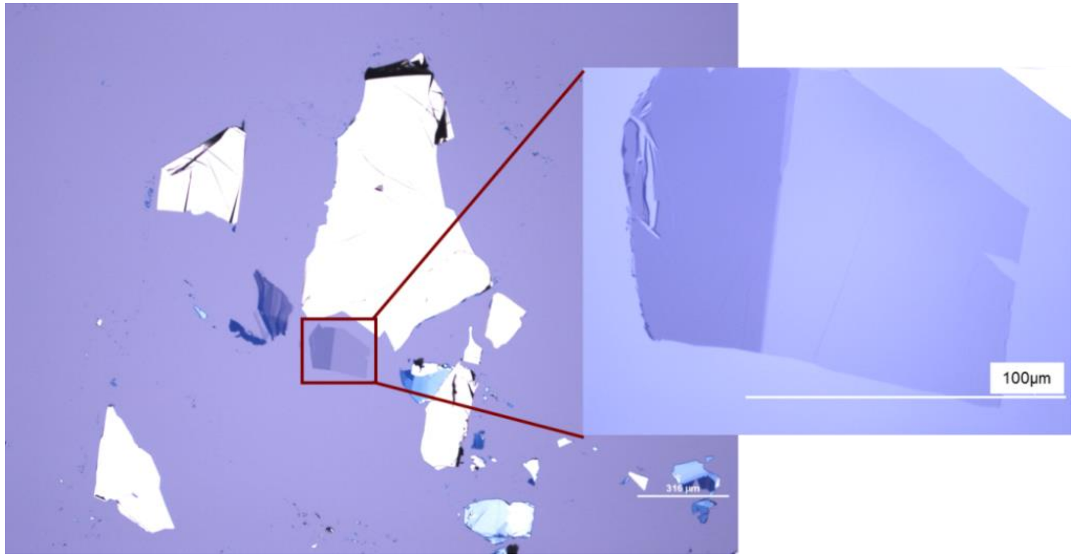
Torque measurement to detect the oscillations in magnetization

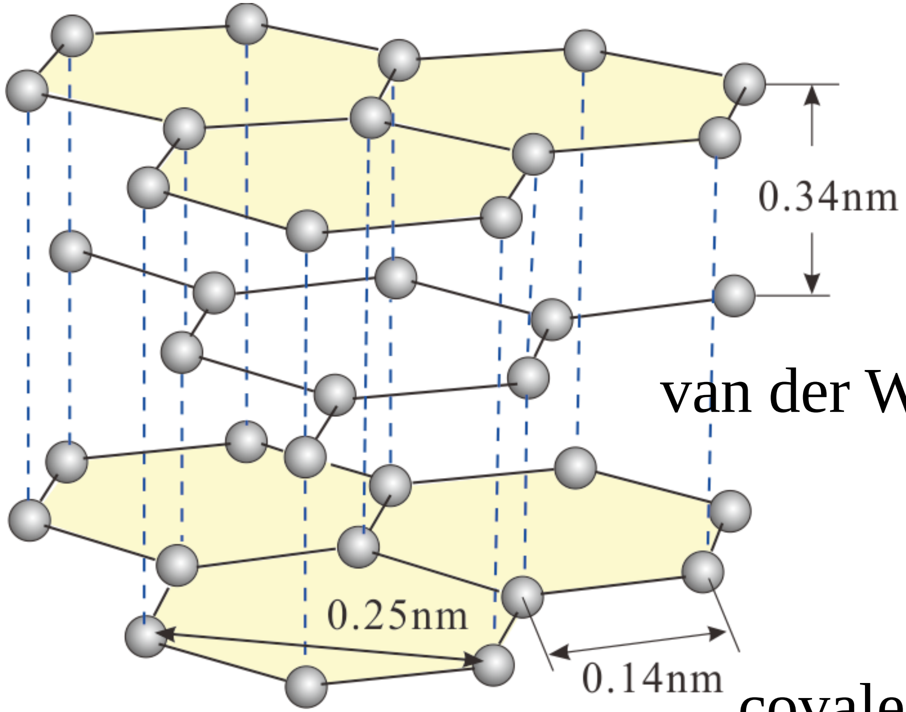
Graphite and Graphene

Graphite



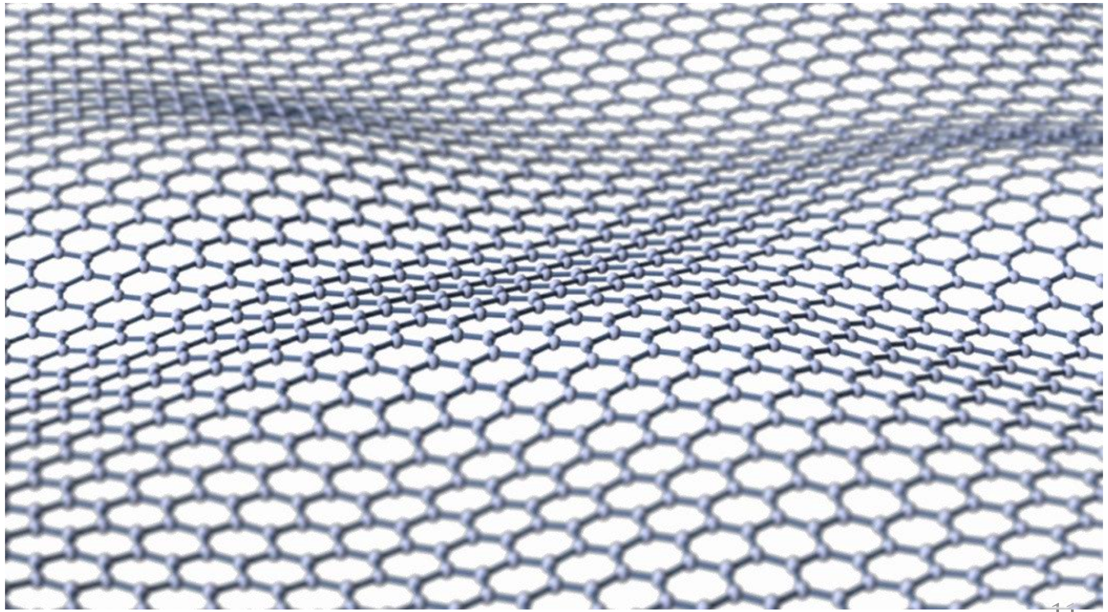
Graphene





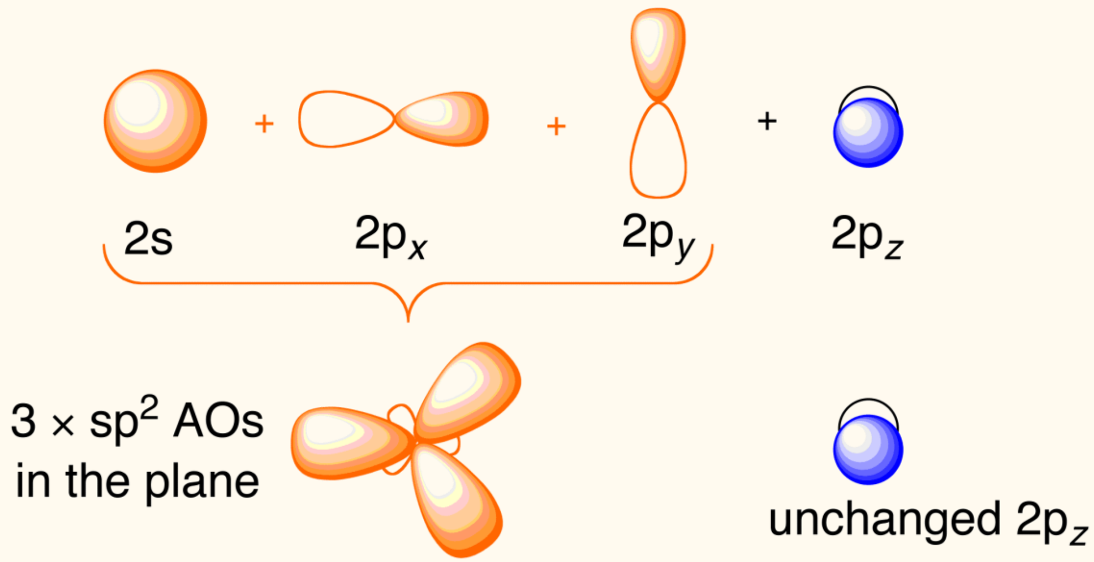
van der Waals

covalent

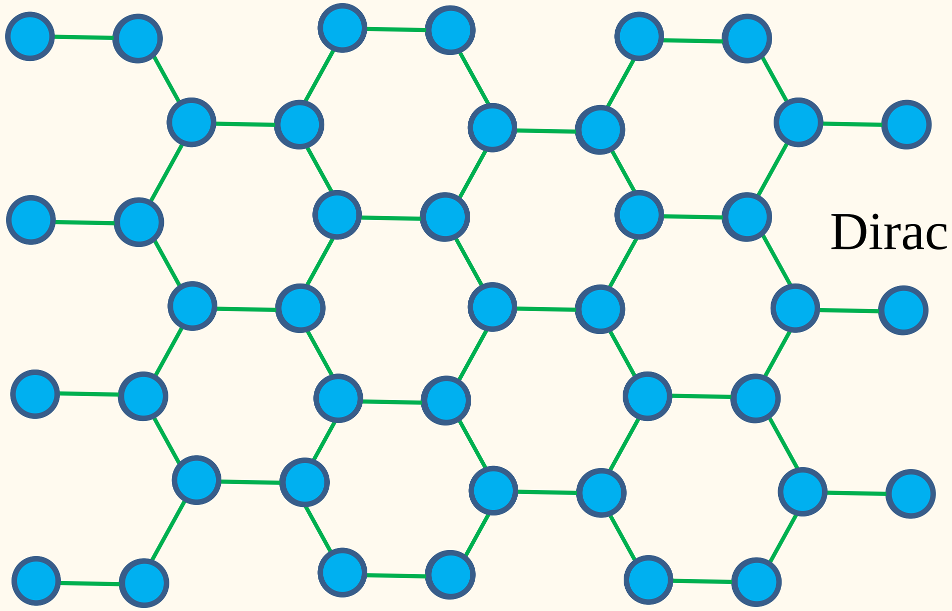


Graphene lattice structure and a simple thought on the band structure

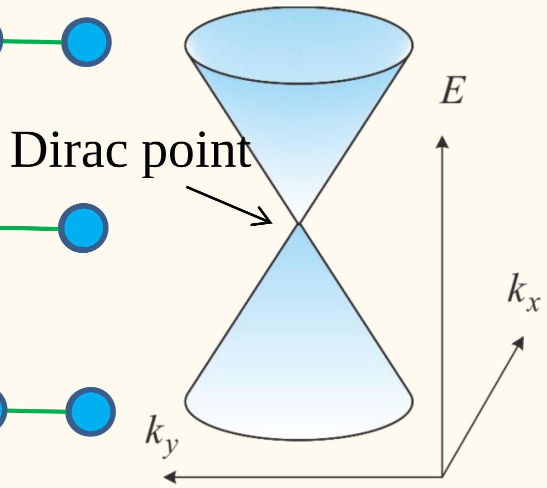
Atomic orbitals



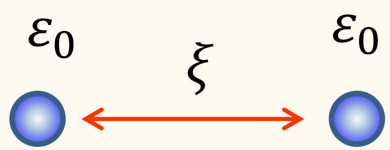
Honeycomb lattice



Dirac corn



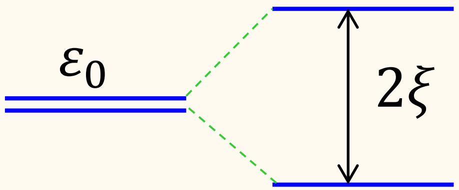
Simple thought on band gap opening



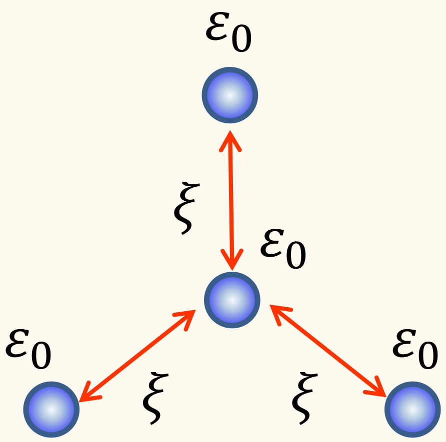
1d nearest neighbor

$$\epsilon = \epsilon_0 \pm \xi$$

$$\mathcal{H} = \begin{pmatrix} \epsilon_0 & \xi \\ \xi & \epsilon_0 \end{pmatrix}$$

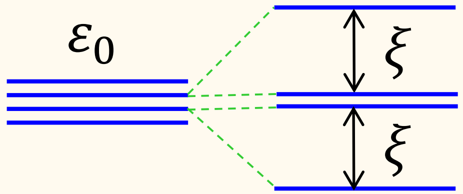


Triangular neighborhood



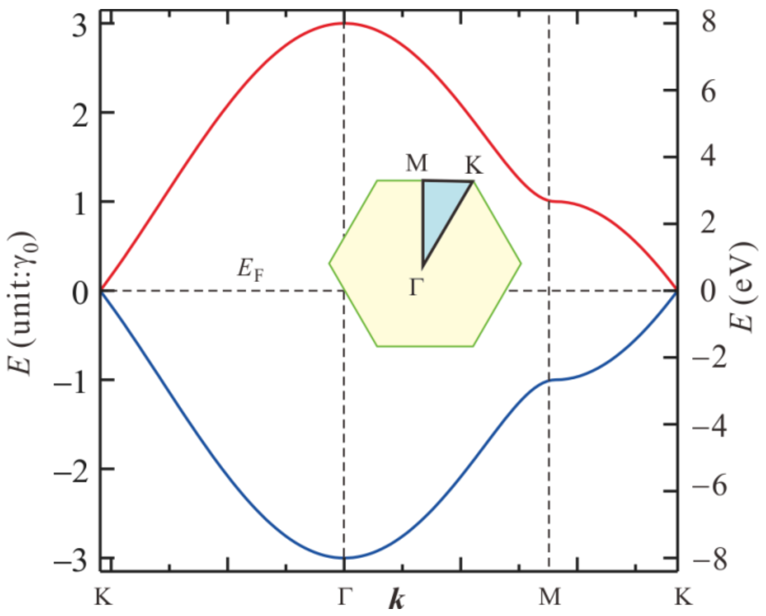
$$\mathcal{H} = \begin{pmatrix} \epsilon_0 & \xi & \xi & \xi \\ \xi & \epsilon_0 & 0 & 0 \\ \xi & 0 & \epsilon_0 & 0 \\ \xi & 0 & 0 & \epsilon_0 \end{pmatrix}$$

$$\epsilon = \epsilon_0(\times 2), \quad \epsilon_0 \pm \xi$$



Degeneracy remains

Graphene band structure: Dirac points in *k* -space



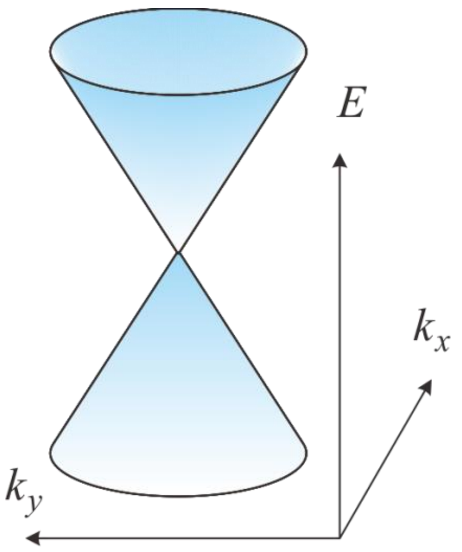
$$E = h_{\mathrm{AA}} \pm \xi \sqrt{1 + 4\cos\frac{\sqrt{3}k_x a}{2}\cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}}$$

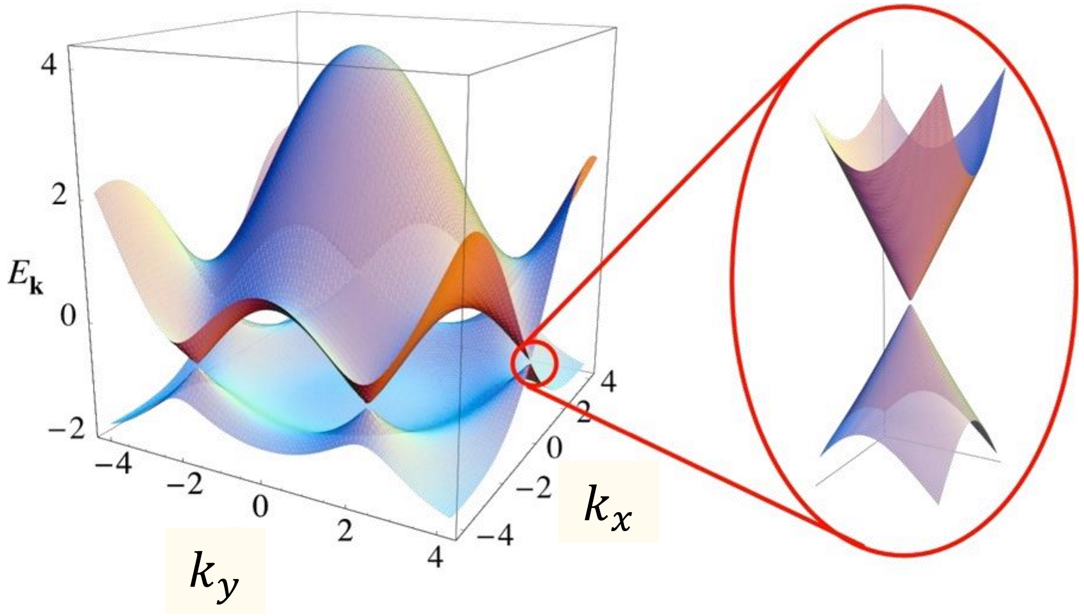
$$k_x = 0$$

$$E = h_{\mathrm{AA}} \pm \xi \left| 1 + 2\cos\frac{k_y a}{2} \right|$$

$$E\left(k_x, \frac{4\pi}{3a}\right) \approx h_{\mathrm{AA}} + \frac{\sqrt{3}\xi a}{2}|k_x|$$

A Dirac point





Graphene magnetic susceptibility

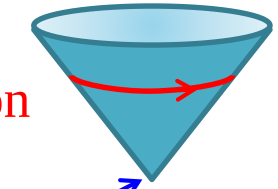
$$\chi(E_{\mathrm{F}}) = -\frac{g_v g_s e^2}{6\pi}\left(\frac{e}{c}\right)^2 \delta(E_{\mathrm{F}})$$

Why this happens?

Remember classical diamagnetism

$$\frac{dL}{dt} = r \times (-eE) = e\frac{r^2}{2}\frac{dB}{dt}$$

No acceleration



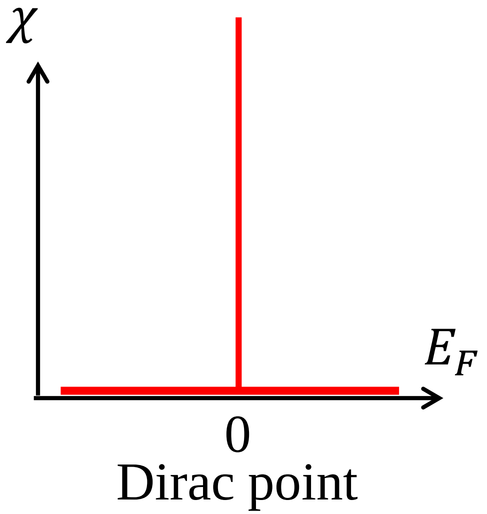
Infinite acceleration

Measurement of graphene diamagnetic susceptibility

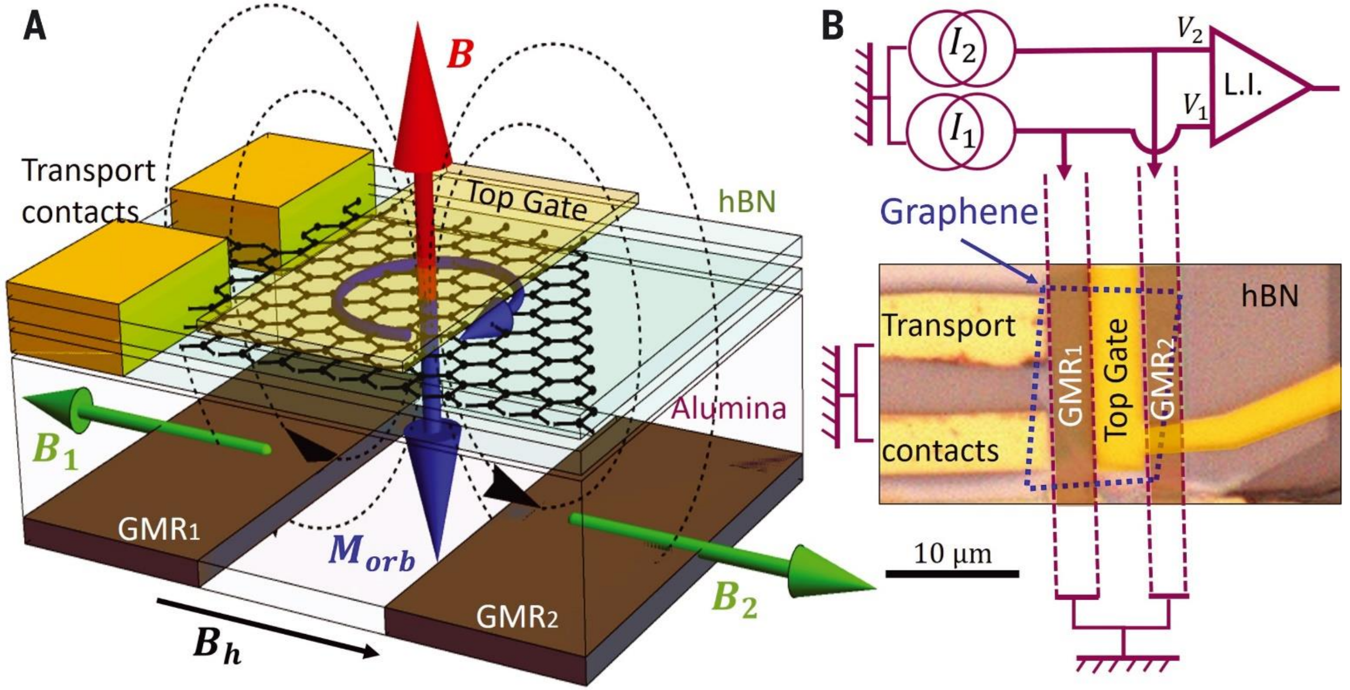
Graphene magnetic susceptibility

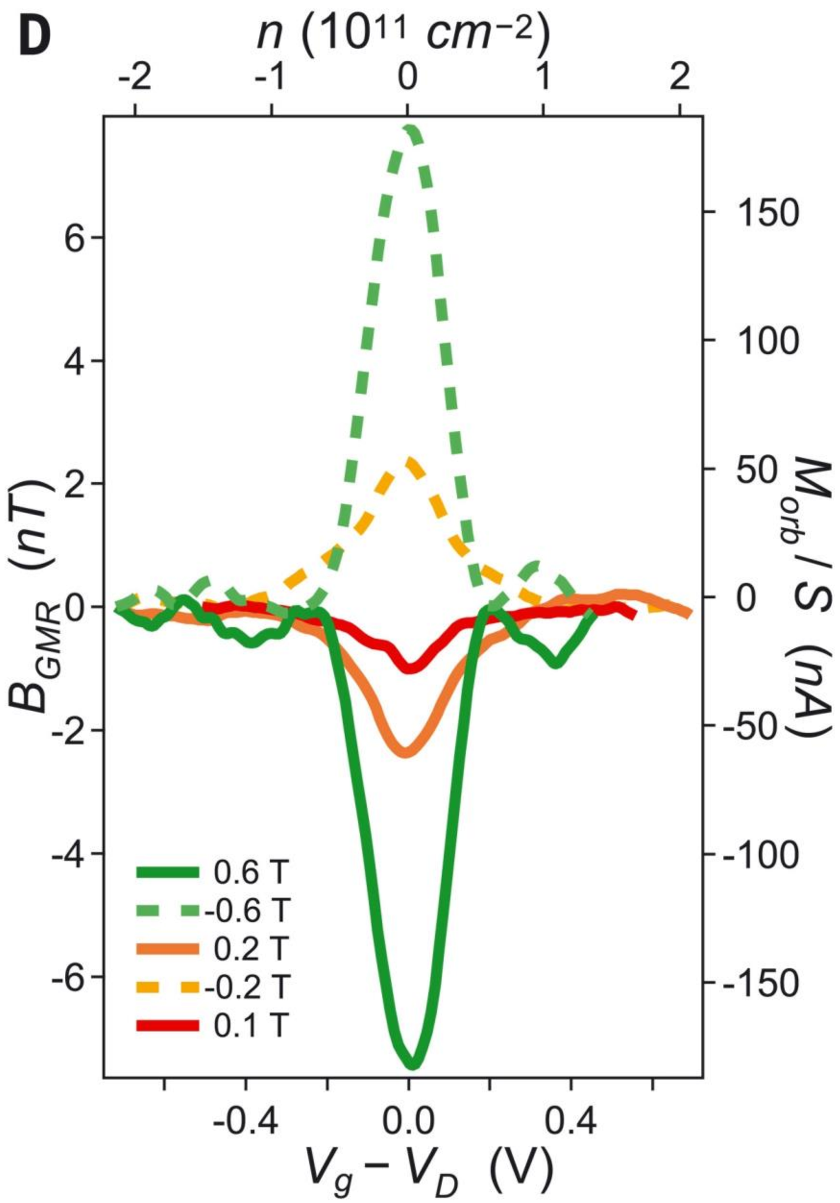
$$\chi(E_{\mathrm{F}}) = -\frac{g_v g_s e^2}{6\pi}\left(\frac{e}{c}\right)^2 \delta(E_{\mathrm{F}})$$

McClure, Phys. Rev. **104**, 666 (1956).

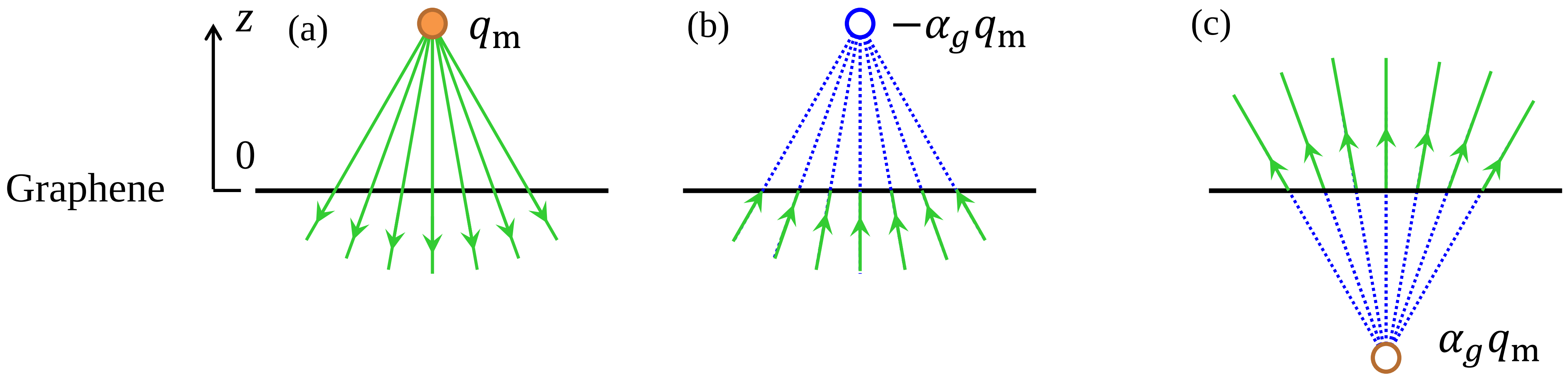


Bustamante et al., Science **374**, 6573 (`21).





Magnetic field screening, repulsion in graphene



Magnetic charge magnetic force line

Virtual charge to express induction field in the region $z < 0$.

Mirror charge to express induction field in the region $z > 0$.

$$B(\boldsymbol{r}) = B(q)\cos qx$$

Magnetic field induced current and magnetization

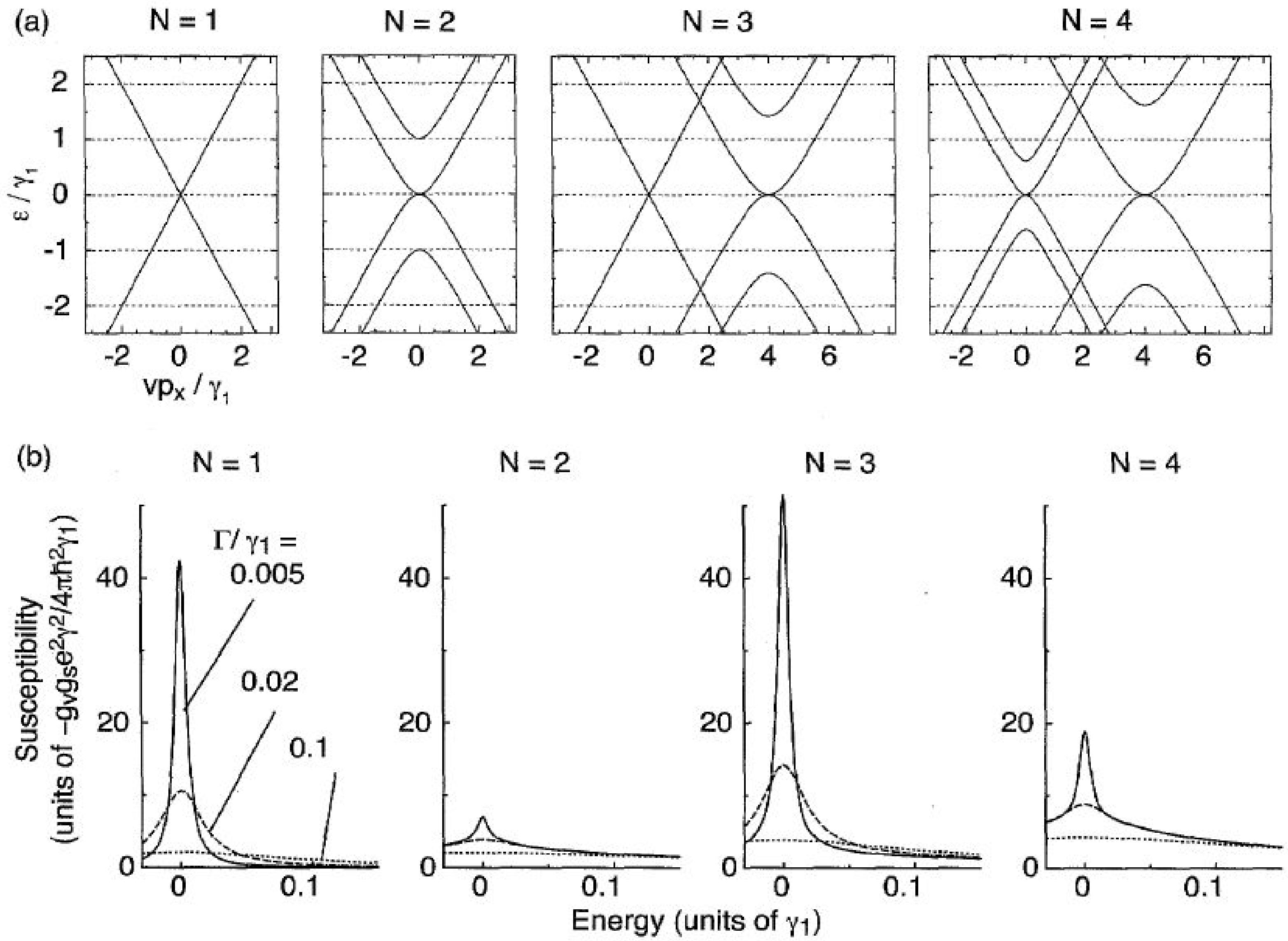
$$j_y = -c\frac{\partial m}{\partial x} \rightarrow m(\boldsymbol{r}) = m(q)\cos qx \quad m(q) = -\frac{j_y(q)}{cq}$$

$$j_y(\boldsymbol{r}) = -\frac{g_v g_s e^2 v}{16\hbar c} B(q)\sin qx$$

$$B_{\text{ind}}(\boldsymbol{r}) = -\alpha_g B(\boldsymbol{r}), \quad \alpha_g = \frac{2\pi g_v g_s e^2 v}{16\hbar c^2} \approx 4\times 10^{-5}$$

$\sigma_{\text{m}} \sim 1\ \text{T}$ 0.16 g/cm^2

Multi-layer graphene

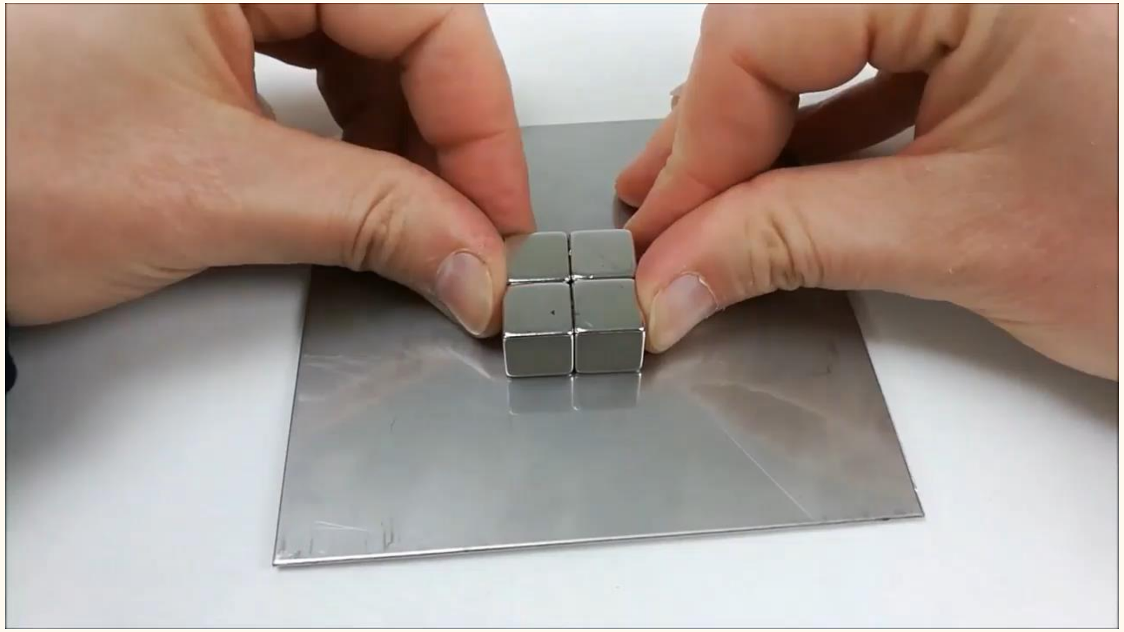


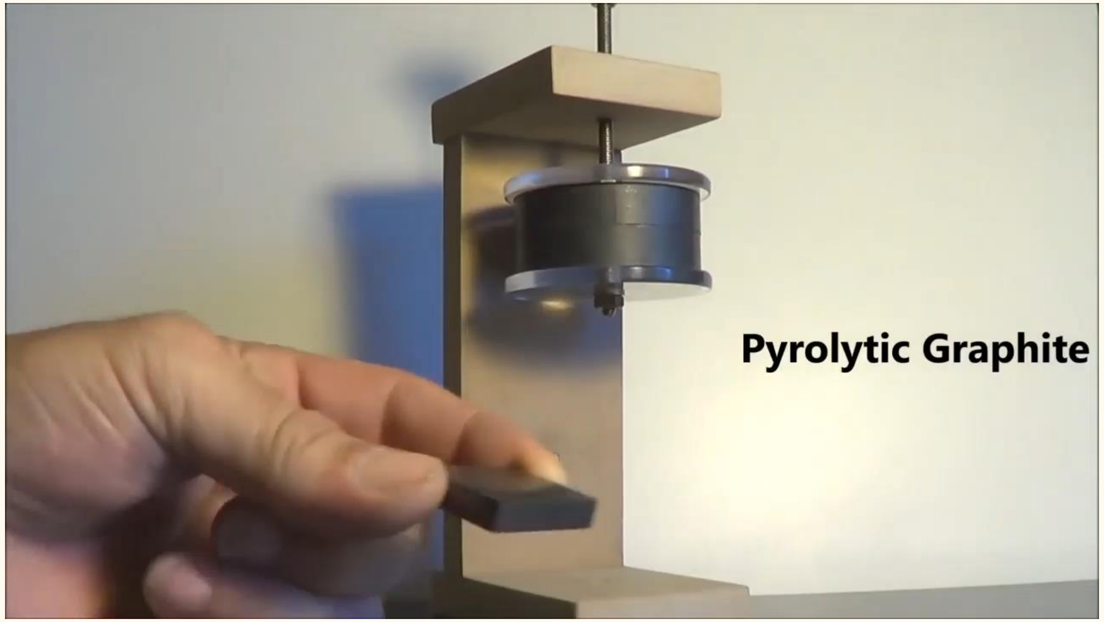
N=2M+1 layers

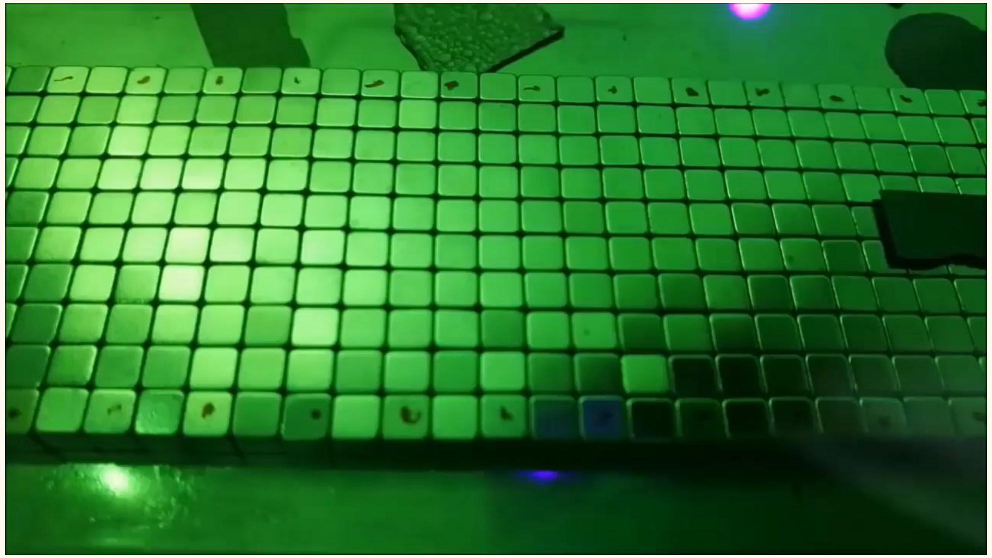
1: Dirac point

M: zero gap+ gapped

Magnetic levitation of graphite







Chapter 4

Interaction between Spins

Chiririn Goma　　小泉製作所

Exchange interaction

Classical dipole interaction: $$U(\boldsymbol{\mu}_1, \boldsymbol{\mu}_2, \boldsymbol{r}_{12}) = \frac{\mu_0}{4\pi}\left[\frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{r_{12}^3} - 3\frac{(\boldsymbol{r}_1 \cdot \boldsymbol{r}_{12})(\boldsymbol{r}_2 \cdot \boldsymbol{r}_{12})}{r_{12}^5}\right]$$

This cannot explain ferromagnetism $\mu_1 = \mu_2 = 5\mu_{\mathrm{B}}, r_{12} = 0.2\ \mathrm{nm} \to U \sim 2\ \mathrm{K}$

Quantum mechanical origin of spin-spin interaction: Symmetry of wavefunction

Fermion wavefunction is anti-symmetric: (Orbital part: anti-symmetric) → (Spin part: Symmetric)

If the anti-symmetric orbital part is energetically favorable, this should work as ferromagnetic coupling.

Heitler-London approximation: A two-atom system without hopping

Atomic orbitals: φ_a, φ_b Spin states: χ_a, χ_b

Spin up (α): $\chi(1/2) = 1, \quad \chi(-1/2) = 0$

Spin down (β): $\chi(1/2) = 0, \quad \chi(-1/2) = 1$

Wavefunction Slater determinant

$$\Psi = \frac{1}{\sqrt{N}}\begin{vmatrix} \varphi_a(\boldsymbol{r}_1)\chi_a(s_1) & \varphi_b(\boldsymbol{r}_1)\chi_b(s_1) \\ \varphi_a(\boldsymbol{r}_2)\chi_a(s_2) & \varphi_b(\boldsymbol{r}_2)\chi_b(s_2) \end{vmatrix}$$

Heitler-London approximation

Pauli exclusion: $\Psi(\boldsymbol{r}_1, s_1; \boldsymbol{r}_1, s_1) = 0, \quad \Psi(\boldsymbol{r}_1, s_1; \boldsymbol{r}_2, s_2) = -\Psi(\boldsymbol{r}_2, s_2; \boldsymbol{r}_1, s_1)$

Basis: $\{\Psi_{\alpha\alpha}, \Psi_{\alpha\beta}, \Psi_{\beta\alpha}, \Psi_{\beta\beta}\}$

Example of interaction Hamiltonian calculation:

$$\langle\alpha\alpha|\mathscr{H}_{\rm int}|\alpha\alpha\rangle = \sum_{s_1,s_2}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \Psi^*_{\alpha\alpha}\mathscr{H}_{\rm int}\Psi_{\alpha\alpha}$$

$$= \underbrace{\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \varphi_a^*(\boldsymbol{r}_1)\varphi_b^*(\boldsymbol{r}_2)\mathscr{H}_{\rm int}\varphi_a(\boldsymbol{r}_1)\varphi_b(\boldsymbol{r}_2)}_{K_{ab}} \underbrace{- \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \varphi_a^*(\boldsymbol{r}_1)\varphi_b^*(\boldsymbol{r}_2)\mathscr{H}_{\rm int}\varphi_b(\boldsymbol{r}_1)\varphi_a(\boldsymbol{r}_2)}_{J_{ab}}$$

Exchange integral

Matrix elements:

	$\alpha\alpha$	$\alpha\beta$	$\beta\alpha$	$\beta\beta$
$\alpha\alpha$	$K_{ab} - J_{ab}$	0	0	0
$\alpha\beta$	0	K_{ab}	$-J_{ab}$	0
$\beta\alpha$	0	$-J_{ab}$	K_{ab}	0
$\beta\beta$	0	0	0	$K_{ab} - J_{ab}$

Spin Hamiltonian

Eigenstates:

$$\left.\begin{array}{c}\Psi_{\alpha\alpha}\\ \frac{1}{\sqrt{2}}(\Psi_{\alpha\beta}+\Psi_{\beta\alpha})\\ \Psi_{\beta\beta}\end{array}\right\}(s_1+s_2=1),\qquad \frac{1}{\sqrt{2}}(\Psi_{\alpha\beta}-\Psi_{\beta\alpha})\ (s_1+s_2=0)$$

Spin triplet

Spin singlet

Spin operators: $\boldsymbol{s}_a$, $\boldsymbol{s}_b$

$$2\boldsymbol{s}_a\cdot\boldsymbol{s}_b=(\boldsymbol{s}_a+\boldsymbol{s}_b)^2-\boldsymbol{s}_a^2-\boldsymbol{s}_b^2=\boldsymbol{S}^2-\boldsymbol{s}_a^2-\boldsymbol{s}_b^2$$

$$\langle\uparrow\uparrow|\boldsymbol{S}^2|\uparrow\uparrow\rangle=S(S+1)=2,\qquad \boldsymbol{S}^2\,|\uparrow\downarrow\rangle=0,$$

$$\boldsymbol{s}_a^2=\boldsymbol{s}_b^2=\frac{1}{2}\left(\frac{1}{2}+1\right)=\frac{3}{4}$$

$$(\uparrow\uparrow)\to 2\boldsymbol{s}_a\cdot\boldsymbol{s}_b=2-2\times\frac{3}{4}=\frac{1}{2}\implies\frac{1}{2}(1+4\boldsymbol{s}_a\cdot\boldsymbol{s}_b)=+1,$$

$$(\uparrow\downarrow)\to 2\boldsymbol{s}_a\cdot\boldsymbol{s}_b=2-2\times\frac{3}{4}=-\frac{3}{2}\implies\frac{1}{2}(1+4\boldsymbol{s}_a\cdot\boldsymbol{s}_b)=-1$$

Heisenberg Hamiltonian

Effective Hamiltonian: $\mathscr{H}_{\text{int}} = K_{ab} - \frac{1}{2} J_{ab}(1 + 4\boldsymbol{s}_a \cdot \boldsymbol{s}_b)$ Direct exchange interaction

Heisenberg Hamiltonian: $\mathscr{H} = -2 \sum_{\langle i,j \rangle} J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j$ Exchange interaction

Exchange integral: $J_{ab} = \frac{e^2}{4\pi\epsilon_0} \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \varphi_a^*(\boldsymbol{r}_1) \varphi_b^*(\boldsymbol{r}_2) \frac{1}{r_{12}} \varphi_b(\boldsymbol{r}_1) \varphi_a(\boldsymbol{r}_2)$

Positive → Ferromagnetic interaction

Weak hopping correction. Superposition of $\Psi' = \frac{1}{\sqrt{N'}} \begin{vmatrix} \varphi_a(\boldsymbol{r}_1)\chi_a(s_1) & \varphi_a(\boldsymbol{r}_1)\chi'_a(s_1) \\ \varphi_a(\boldsymbol{r}_2)\chi_a(s_2) & \varphi_a(\boldsymbol{r}_2)\chi'_a(s_2) \end{vmatrix}$

Electron hopping: $\varphi_b \chi_b \to \varphi_a \chi'_a$ $\quad \langle \Psi | \mathscr{H} | \Psi' \rangle \neq 0$

$\boldsymbol{s}_a,\ \boldsymbol{s}_b:\ \text{anti-parallel}$ ⟶ Energy gain $W_{ab} = -\frac{1}{\Delta E} | \langle \Psi' | \mathscr{H} | \Psi \rangle |^2$

$\frac{1}{2}(1 - 4\boldsymbol{s}_a \cdot \boldsymbol{s}_b) W_{ab}$ $\quad \mathscr{H}'_{\text{int}} = \frac{1}{2}(-J_{ab} + W_{ab}) - 2(J_{ab} + W_{ab}) \boldsymbol{s}_a \cdot \boldsymbol{s}_b$

Summary

1. Landau diamagnetism
2. de Haas-van Alphen effect
3. Orbital diamagnetism of graphene, graphite

Chapter 4 Interaction between spins

1. Exchange interaction from Heitler-London approximation

2022.5.25 Lecture 7

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Review

1. Landau diamagnetism
2. de Haas-van Alphen effect
3. Orbital diamagnetism of graphene, graphite

Chapter 4 Interaction between spins

1. Exchange interaction from Heitler-London approximation

Outline

Spin Hamiltonian and quantum entanglement

Hubbard Hamiltonian

Superexchange interaction

RKKY interaction

Double exchange interaction

Theory of Magnetic insulators

Molecular field approximation

Spin Hamiltonian and quantum entanglement

Spin Hamiltonian for EPR analysis:

Obtained by integrating out the orbital part in the second order perturbation.

$$\tilde{\mathcal{H}} = \mu_{\mathrm{B}} \boldsymbol{S}\tilde{\boldsymbol{g}}\boldsymbol{H} + D\left[S_z^2 - \frac{S(S+1)}{3}\right] + E(S_x^2 - S_y^2)$$

Direct exchange interaction:

$$\mathscr{H}_{\mathrm{int}} = K_{ab} - \frac{1}{2}J_{ab}(1 + 4\boldsymbol{s}_a \cdot \boldsymbol{s}_b)$$

This gives the same matrix elements for the basis of relevant levels.

Quantum entanglement

Two systems, freedoms

bases $\begin{cases} \{|1\rangle, |2\rangle\} \\ \{|p\rangle, |q\rangle\} \end{cases}$

states

$$|\psi\rangle = a_1|1\rangle + a_2|2\rangle$$

$$|\phi\rangle = a_p|p\rangle + a_q|q\rangle$$

Not entangled:

The state is written as a direct product.

$$|\Psi_{\mathrm{n}}\rangle = |\psi\rangle \otimes |\phi\rangle = a_1a_p\underline{|1\rangle|p\rangle} + a_1a_q|1\rangle|q\rangle + a_2a_p|2\rangle|p\rangle + a_2a_q\underline{|2\rangle|q\rangle}$$

Maximally entangled state:

$$|\xi\rangle = \frac{1}{\sqrt{2}}(|1\rangle|p\rangle + |2\rangle|q\rangle)$$

Two states are unseparable.

Quantum entanglement and effective Hamiltonian

Maximally entangled state: $|\xi\rangle = \frac{1}{\sqrt{2}}(|1\rangle\,|p\rangle + |2\rangle\,|q\rangle)$

Another maximally entangled state: $|\zeta\rangle = \frac{1}{\sqrt{2}}(|1\rangle\,|q\rangle + |2\rangle\,|p\rangle)$

Let us consider the case the basis is limited to $\{|\xi\rangle\,,|\zeta\rangle\}$

Consider a Hamiltonian working on $\{|1\rangle, |2\rangle\}$ $\mathscr{H}_{\mathrm{n}} = \begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix}$

$$\langle\xi|\mathscr{H}_{\mathrm{n}}|\xi\rangle = h_{11} + h_{22}, \quad \langle\xi|\mathscr{H}_{\mathrm{n}}|\zeta\rangle = h_{12} + h_{21},$$
$$\langle\zeta|\mathscr{H}_{\mathrm{n}}|\zeta\rangle = h_{11} + h_{22}$$

Consider a Hamiltonian working on $\{|p\rangle, |q\rangle\}$ $\mathscr{H}_{\mathrm{a}} = \begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix}$

Though $\mathscr{H}_{\mathrm{n}}$ and $\mathscr{H}_{\mathrm{a}}$ are completely different, as long as we limit the basis to $\{|\xi\rangle\,,|\zeta\rangle\}$ we cannot distinguish $\mathscr{H}_{\mathrm{n}}$ and $\mathscr{H}_{\mathrm{a}}$.

Quantum measurement and entanglement

$$N_{\rm min} = \frac{3k_{\rm B}TV}{2\pi g^2\mu_{\rm B}^2 S(S+1)Q_0}\left(\frac{\Delta H_0}{H_0}\right)\sqrt{\frac{k_{\rm B}T_{\rm d}FB}{P_0}}$$

In inductive measurement the EPR needs $N_{min}{\sim}10^{10}$

How you make this to one?

What is measurement?

System to be measured: $\{|\uparrow\rangle\,,|\downarrow\rangle\}$

Degree of freedom which human can distinguish: $\{|A\rangle\,,|B\rangle\}$

Measurement is to create a maximally entangled state between them.

$$\Psi = \frac{1}{\sqrt{2}}[|\uparrow\rangle|A\rangle + |\downarrow\rangle|B\rangle]$$

Schrödinger’s cat problem is a problem of measurement.

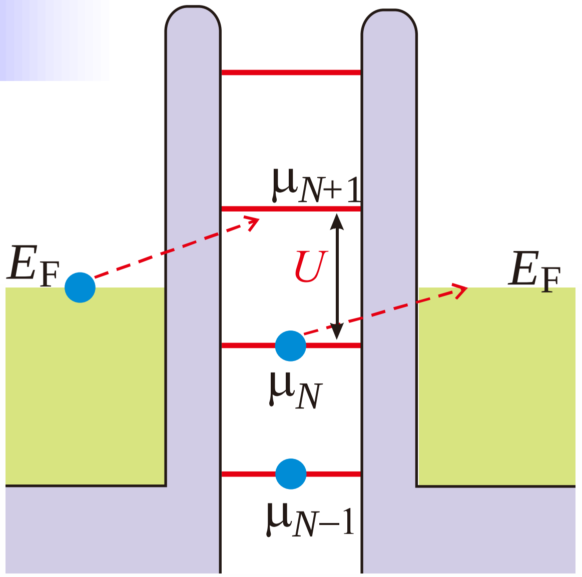
$$|\text{Alive cat}\rangle|\gamma-\rangle + |\text{Dead cat}\rangle|\gamma+\rangle$$

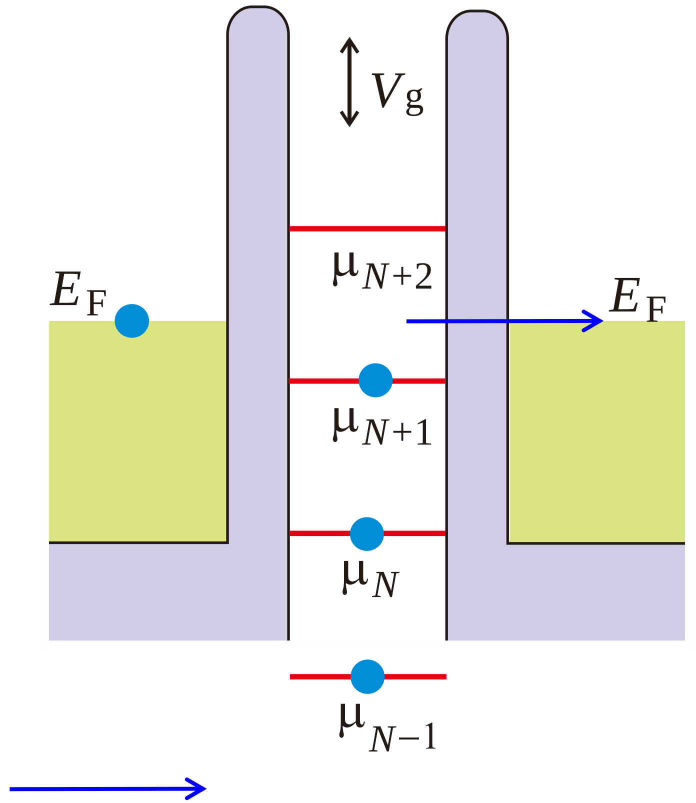
Coulomb blockade in quantum dots

Constant interaction: U

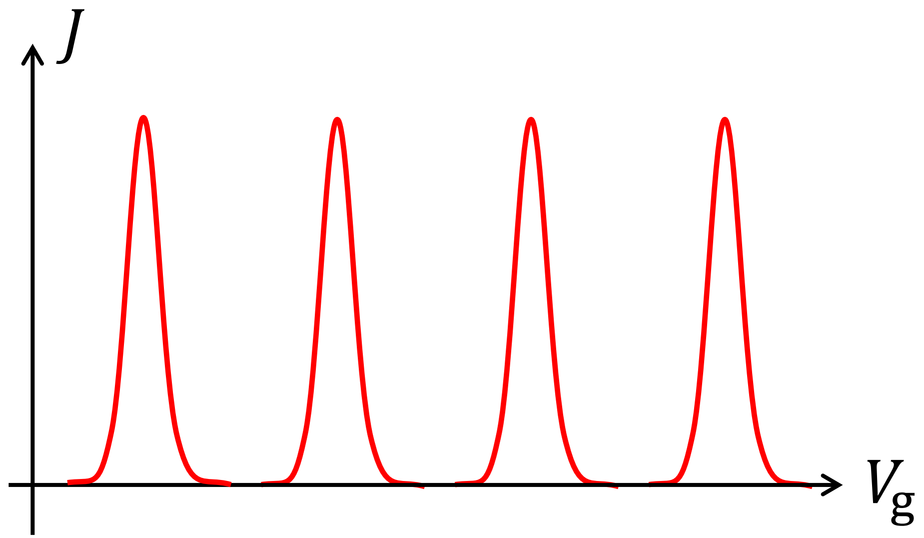
Electron number: N
Interaction energy
$$E_{cN} = {}_N C_2 U = \frac{N(N-1)U}{2} = \frac{U(N-1/2)^2}{2} - \frac{U}{8}$$

Chemical potential
$$\Delta E_+(N) = (N-1)U$$

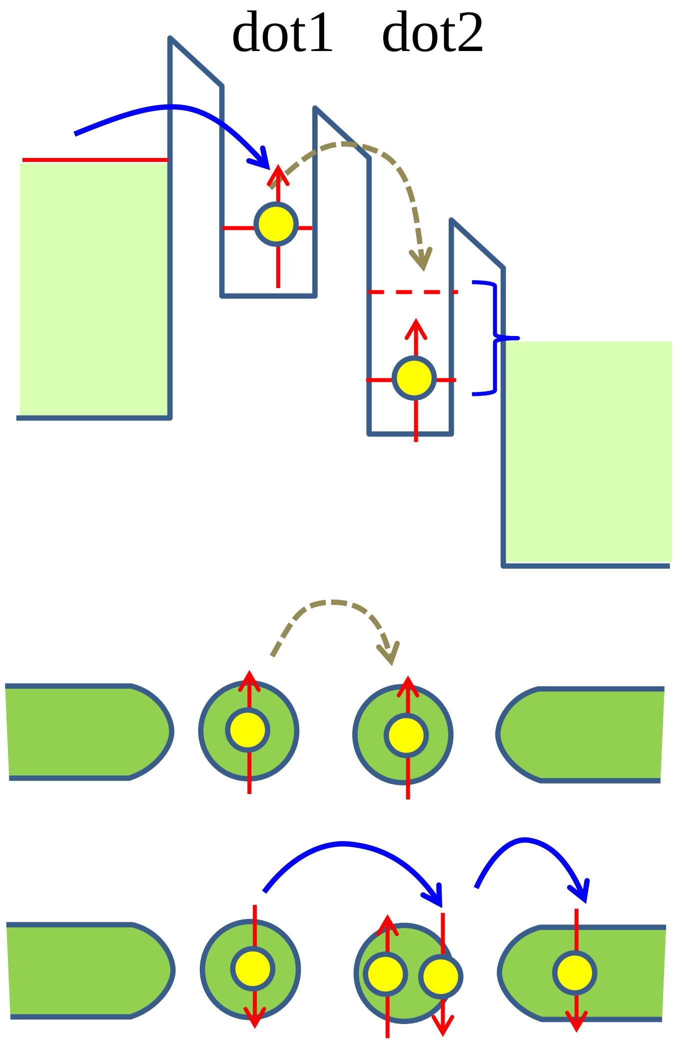




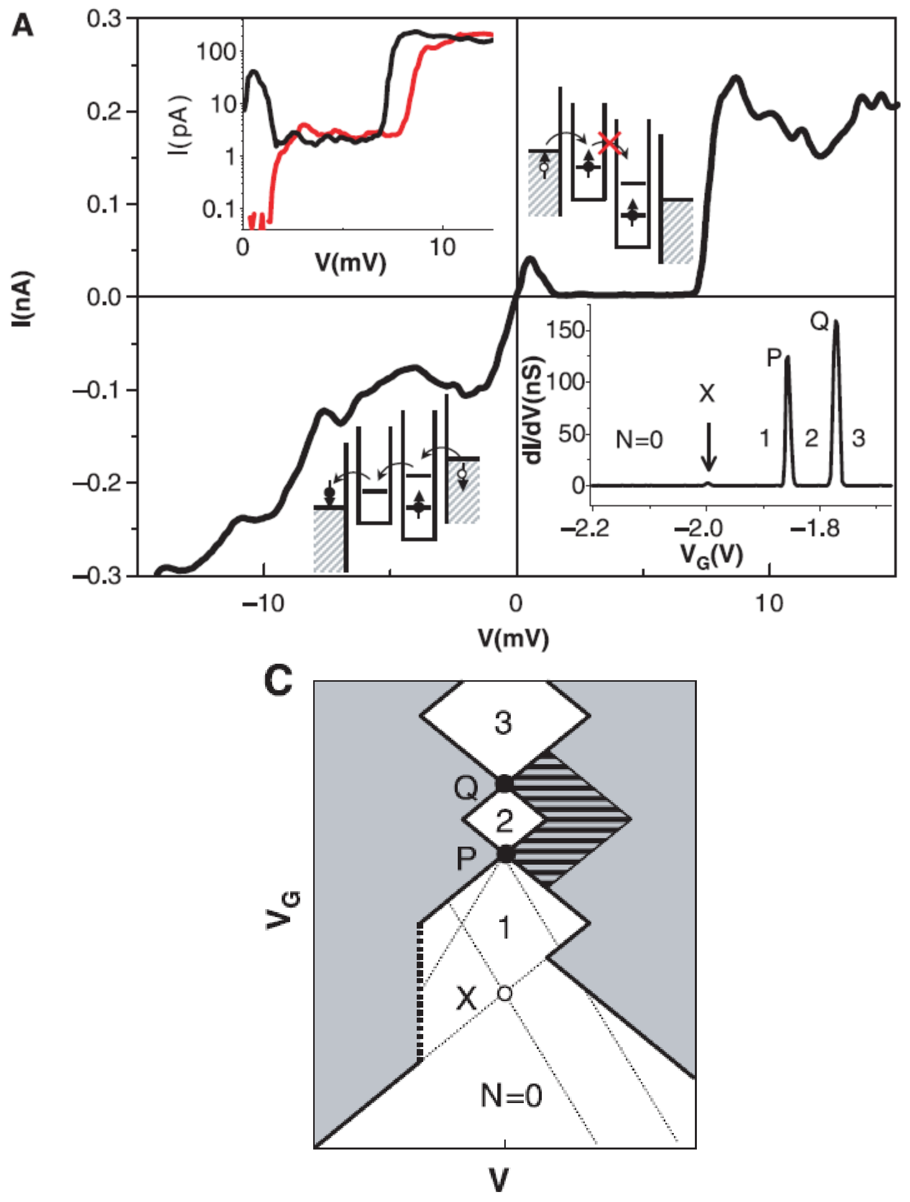
Coulomb oscillation



Pauli blockade

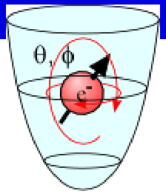


When both dot1 and dot2 are occupied by up (down) spin, the conduction is blocked.

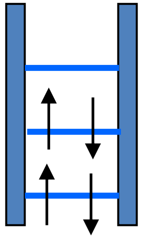


K. Ono et al., Science **297**, 1313 (2002)

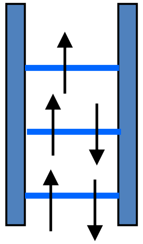
Spin quantum bit



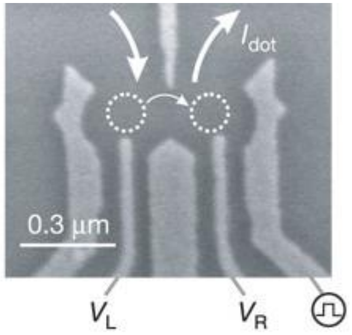
F. H. Koppens et al. Nature 442, 766 (2006)

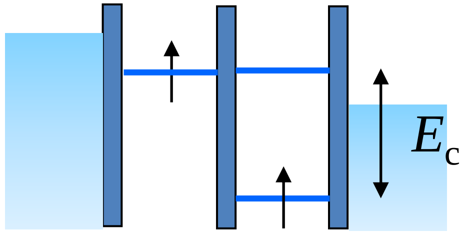


Even electron QD
No spin

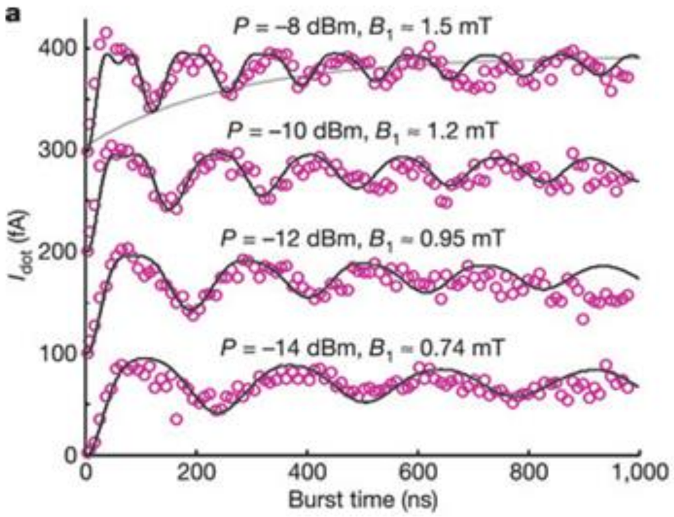


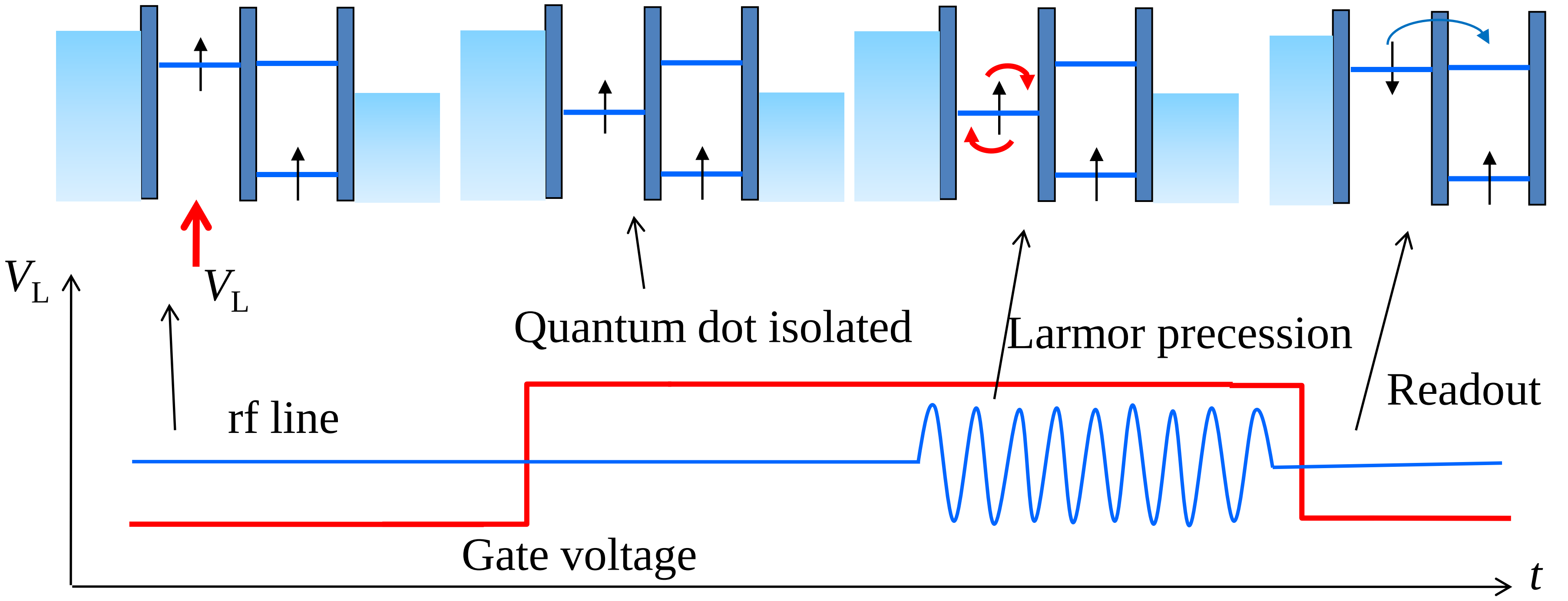
Odd electron QD
Spin 1/2





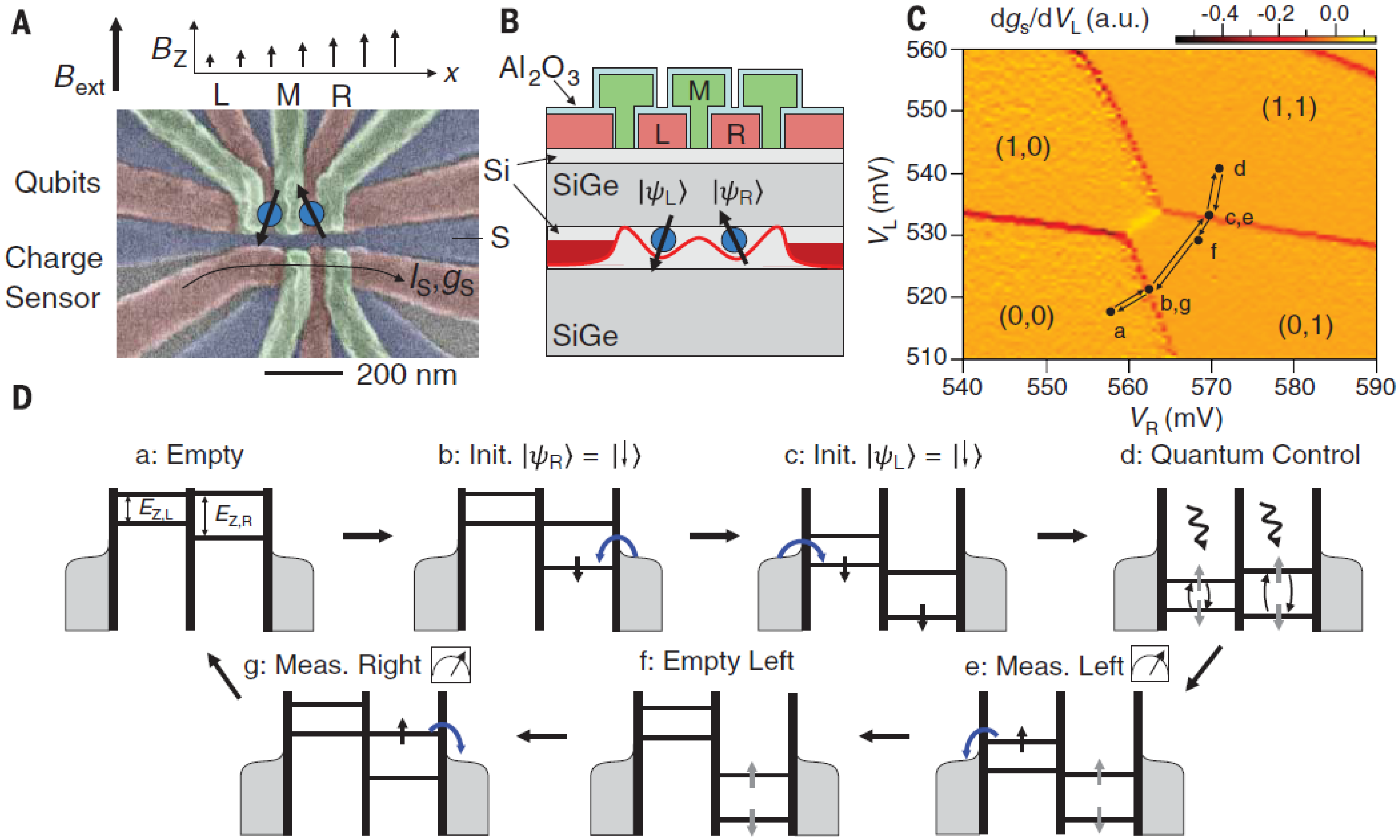
Pauli blockade



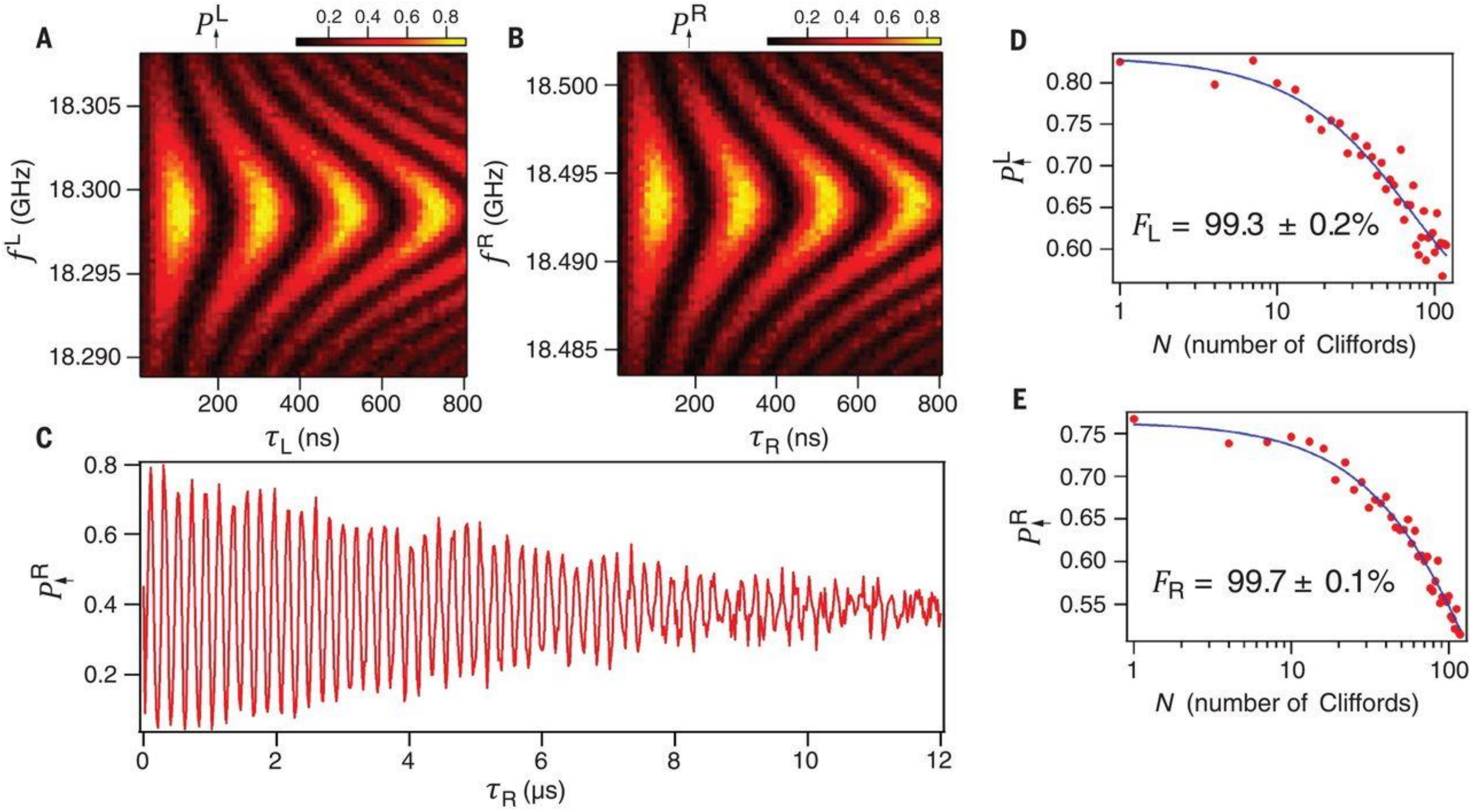


CNOT gate for electron spins

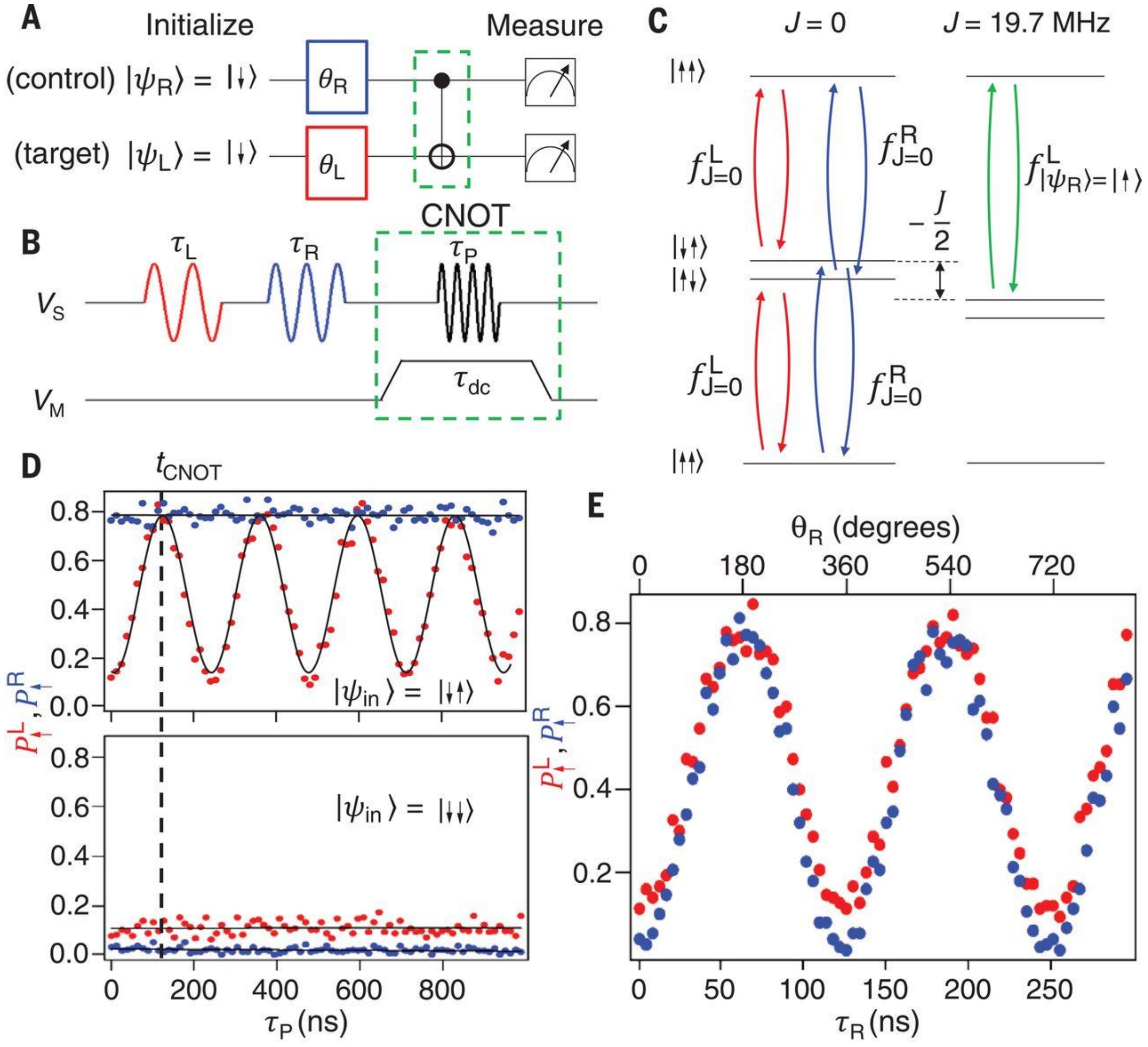
Zajac et al. Science **359**, 439 (2018).



Detection of Larmor precession



Spin-charge entanglement and detection of spin-spin interaction



Hubbard model

Anti-ferromagnetic exchange interaction by electron transfer

Two site model: (i, j)

Hopping operator: $t(a_{i\sigma}^{\dagger} a_{j\sigma} + \mathrm{h.c.})$

$$|n;m\rangle = |\sigma;-\sigma\rangle \xrightarrow{t} |0;\sigma,-\sigma\rangle \xrightarrow{t} |\sigma;-\sigma\rangle$$

Intermediate state
Enhancement U

Second perturbation energy gain

$$\frac{t^2}{U}$$

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

In Hamiltonian form: $$\mathscr{H} = t \sum_{\sigma=\uparrow\downarrow} (a_{1\sigma}^{\dagger} a_{2\sigma} + a_{2\sigma}^{\dagger} a_{1\sigma}) + U(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow})$$

Two-site Hubbard Hamiltonian

Effective Hamiltonian for 2-site Hubbard Hamiltonian

Possible 6-states: $|\uparrow\downarrow;0\rangle\,,\ |0;\uparrow\downarrow\rangle\,,\ |\uparrow;\uparrow\rangle\,,\ \frac{1}{\sqrt{2}}(|\uparrow;\downarrow\rangle+|\downarrow;\uparrow\rangle),\ |\downarrow;\downarrow\rangle\,,\ \frac{1}{\sqrt{2}}(|\uparrow;\downarrow\rangle-|\downarrow;\uparrow\rangle)$

Good quantum number operators

$$\boldsymbol{s}_i=\sum_{\sigma\sigma'}a^\dagger_{i\sigma}\left(\frac{\boldsymbol{\sigma}}{2}\right)_{\sigma\sigma'}a_{i\sigma'},\quad \boldsymbol{S}=\sum_{i=1,2}\boldsymbol{s}_i,\quad N=\sum_{i,\sigma}n_{i\sigma}$$

$$a^{-2}=1+(4t/U)^2$$

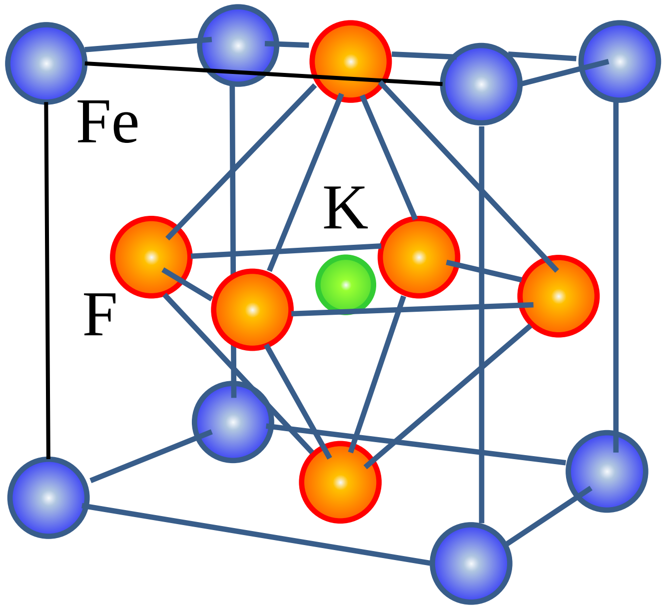
No.	S	S_z	E	Eigenstate
1	0	0	U	$\frac{1}{\sqrt{2}}(\lvert\uparrow\downarrow;0\rangle-\lvert 0;\uparrow\downarrow\rangle)$
2			$\left(1+\frac{1}{a}\right)\frac{U}{2}$	$\frac{\sqrt{1+a}}{2}(\lvert\uparrow\downarrow;0\rangle+\lvert 0;\uparrow\downarrow\rangle)+\sqrt{\frac{1-a}{2}}\lvert 0,0\rangle$
3			$\left(1-\frac{1}{a}\right)\frac{U}{2}$	$\sqrt{\frac{1+a}{2}}\lvert 0,0\rangle-\frac{\sqrt{1-a}}{2}(\lvert\uparrow\downarrow;0\rangle+\lvert 0;\uparrow\downarrow\rangle)$
4	1	+1	0	$\lvert 1,+1\rangle$
5		0		$\lvert 1,0\rangle$
6		−1		$\lvert 1,-1\rangle$

$$\mathscr{H}_{\text{eff}}=-J\left(\boldsymbol{s}_1\cdot\boldsymbol{s}_2-\frac{1}{4}\right),$$

$$J=-\frac{4t^2}{U}$$

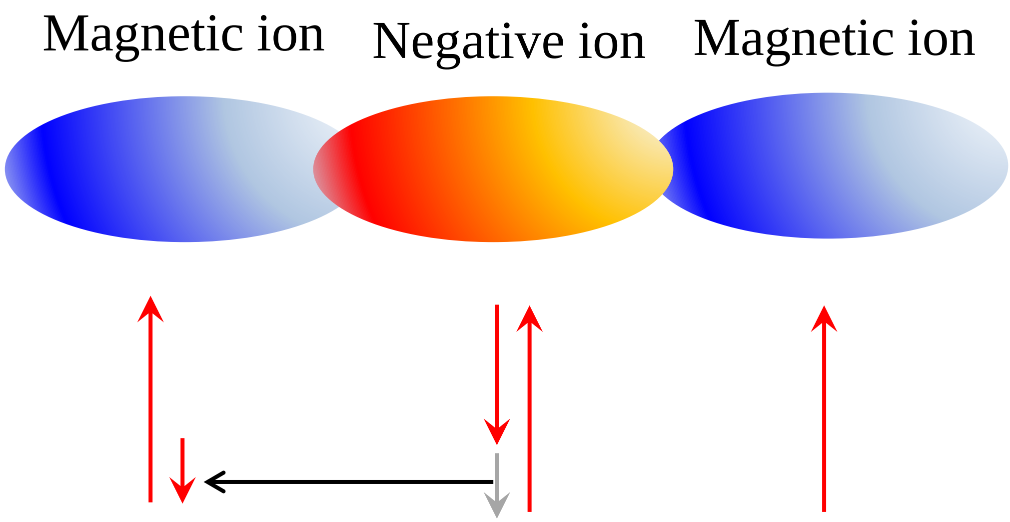
Anti-ferromagnetic

Superexchange interaction



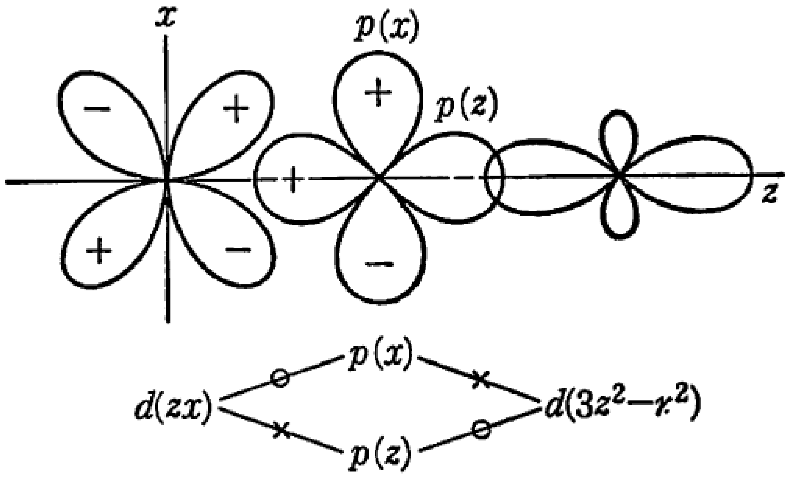
Compounds of magnetic ions and closed shell negative ions often have anti-ferromagnetism or ferromagnetism.

What is the mechanism (spin-spin interaction?) of magnetism?

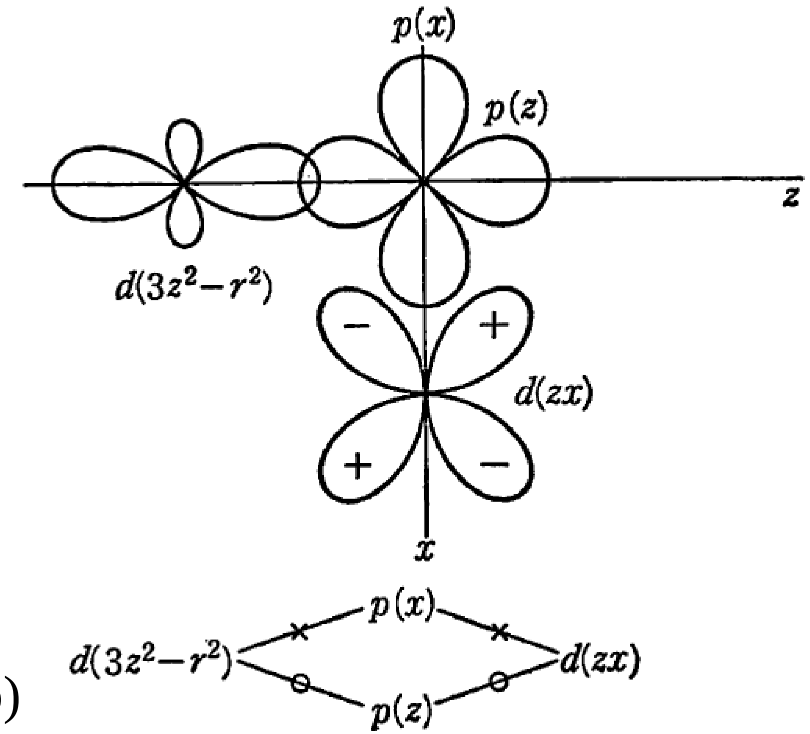


Superexchange mechanism
Small amount of electrons on a negative ions moves to a neighboring magnetic ion. Then spin appears on the negative ion which have exchange interaction with another neighboring magnetic ion.

Goodenough-Kanamori rules



(a)



(b)

Angles, orbitals, electrons numbers determine ferromagnetic, anti-ferromagnetic and the strength

s-d exchange interaction

Scattering of electrons ***s*** by a local magnetic ion ***S*** at the origin.

$$|\boldsymbol{k},\sigma\rangle \to |\boldsymbol{k}',\sigma'\rangle \qquad \mathscr{H}_{\rm scatt} = -2J\delta(\boldsymbol{r})\boldsymbol{S}\cdot\boldsymbol{s}$$

This works as if a delta-function magnetic field: $2J\boldsymbol{S}\delta(\boldsymbol{r})/(g_{\rm e}\mu_{\rm B})$

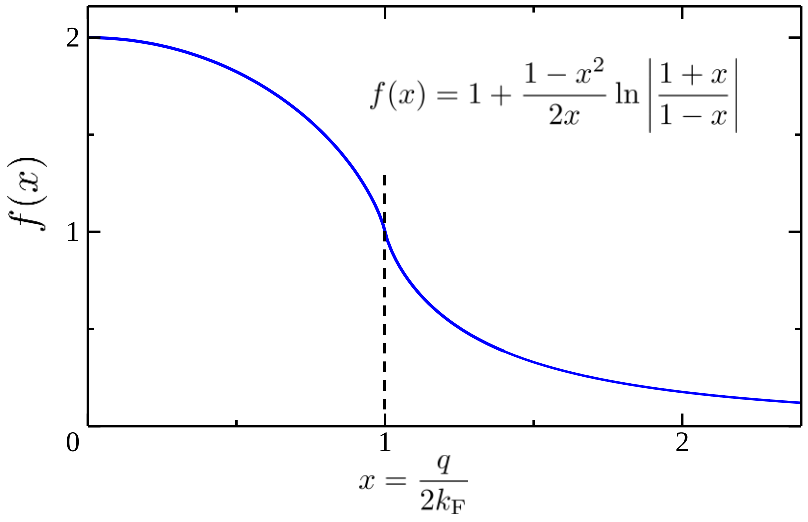
Fourier transformation:
$$\boldsymbol{B}_{\rm eff}(\boldsymbol{r}) = \frac{2J\delta(\boldsymbol{r})}{g_{\rm e}\mu_{\boldsymbol{B}}}\cdot\boldsymbol{S} = \int\frac{d\boldsymbol{q}}{(2\pi)^3\sqrt{V}}\boldsymbol{B}_{\boldsymbol{q}}e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$$

Magnetic moment spatial distribution and susceptibility in frequency space.
$$\boldsymbol{m}(\boldsymbol{r}) = \int\chi(\boldsymbol{q})\boldsymbol{B}_{\boldsymbol{q}}\frac{d\boldsymbol{q}}{(2\pi)^3\sqrt{V}}$$

Perturbation of $\mathscr{H}_{\rm scatt}$ on plane waves
$$\varphi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{\sqrt{V}} \pm \frac{JS}{V}\int\frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{E(\boldsymbol{k}+\boldsymbol{q})-E(\boldsymbol{k})}\frac{d\boldsymbol{q}}{(2\pi)^3\sqrt{V}}$$

$$\boldsymbol{m}_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{g_{\rm e}\mu_{\rm B}}{2}(\varphi^*_{\boldsymbol{k}-}\varphi_{\boldsymbol{k}-} - \varphi^*_{\boldsymbol{k}+}\varphi_{\boldsymbol{k}+})$$

RKKY interaction



$$\boldsymbol{m}_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{g_\mathrm{e}\mu_\mathrm{B}}{2}(\varphi^*_{\boldsymbol{k}-}\varphi_{\boldsymbol{k}-} - \varphi^*_{\boldsymbol{k}+}\varphi_{\boldsymbol{k}+})$$
$$= -\frac{g_\mathrm{e}\mu_\mathrm{B}JS}{V^2}\int\left(\frac{1}{E(\boldsymbol{k}+\boldsymbol{q})-E(\boldsymbol{k})}+\frac{1}{E(\boldsymbol{k}-\boldsymbol{q})-E(\boldsymbol{k})}\right)e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\frac{d\boldsymbol{q}}{(2\pi)^3}$$

$$\chi(\boldsymbol{q}) = \frac{g_\mathrm{e}^2\mu_\mathrm{B}^2}{2V}\int_{k\le k_\mathrm{F}}\left(\frac{1}{E(\boldsymbol{k}+\boldsymbol{q})-E(\boldsymbol{k})}+\frac{1}{E(\boldsymbol{k}-\boldsymbol{q})-E(\boldsymbol{k})}\right)\frac{d\boldsymbol{k}}{(2\pi)^3}$$
$$= \frac{3N}{8}\frac{(g_\mathrm{e}\mu_\mathrm{B})^2}{E_\mathrm{F}}\frac{1}{2}\left(1+\frac{4k_\mathrm{F}^2-q^2}{4qk_\mathrm{F}}\log\left|\frac{2k_\mathrm{F}+q}{2k_\mathrm{F}-q}\right|\right)$$

$$x = q/2k_\mathrm{F} \qquad f(x) = 1+\frac{1-x^2}{2x}\log\left|\frac{1+x}{1-x}\right|$$

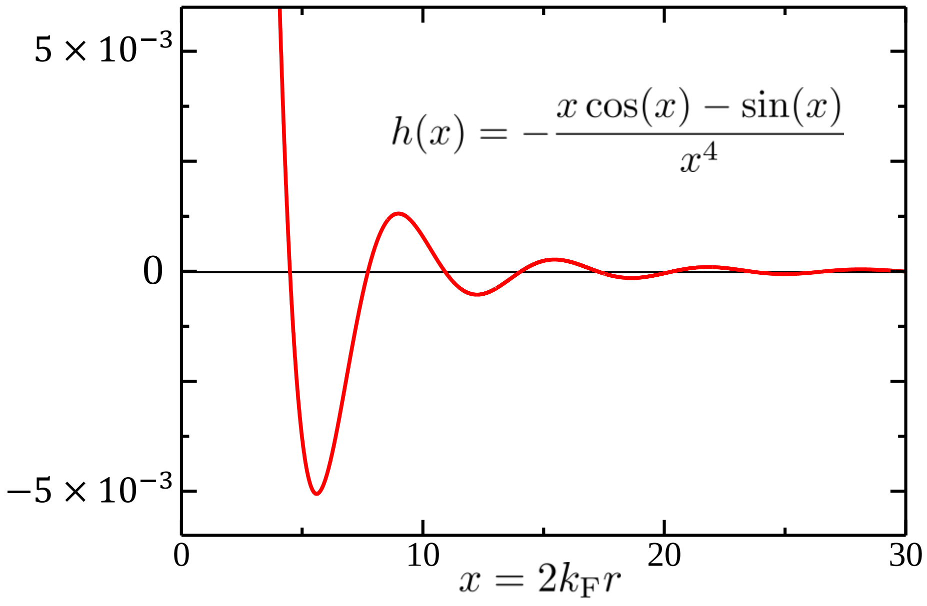
$$F(r) = \frac{1}{2\pi}\int d\boldsymbol{q}e^{i\boldsymbol{q}\cdot\boldsymbol{r}}f\left(\frac{q}{2k_\mathrm{F}}\right) = \frac{2}{r}\int_0^\infty q\sin(qr)f\left(\frac{q}{2k_\mathrm{F}}\right)dq$$
$$= \frac{1}{r}\int_{-\infty}^\infty q\sin(qr)f\left(\frac{q}{2k_\mathrm{F}}\right)dq$$

RKKY interaction (2)

$$\int_{-\infty}^{\infty} \frac{\sin[2k_\mathrm{F} r(1\pm x)]}{1\pm x}dx = \pi, \qquad \int_{-\infty}^{\infty} \frac{\cos[2k_\mathrm{F} r(1\pm x)]}{1\pm x}dx = 0$$

$$F(r) = -16\pi k_\mathrm{F}^3 \frac{2k_\mathrm{F} r\cos(2k_\mathrm{F} r) - \sin(2k_\mathrm{F} r)}{(2k_\mathrm{F} r)^4}$$

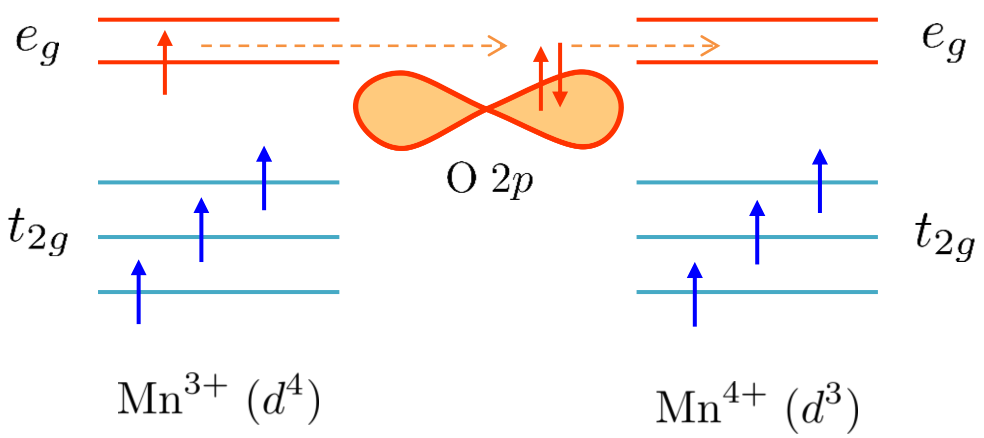
$$\boldsymbol{m}(\boldsymbol{r}) = -\frac{3}{32\pi^2}\frac{N g_\mathrm{e}\mu_\mathrm{B} F(r) J}{E_\mathrm{F}} S_z$$

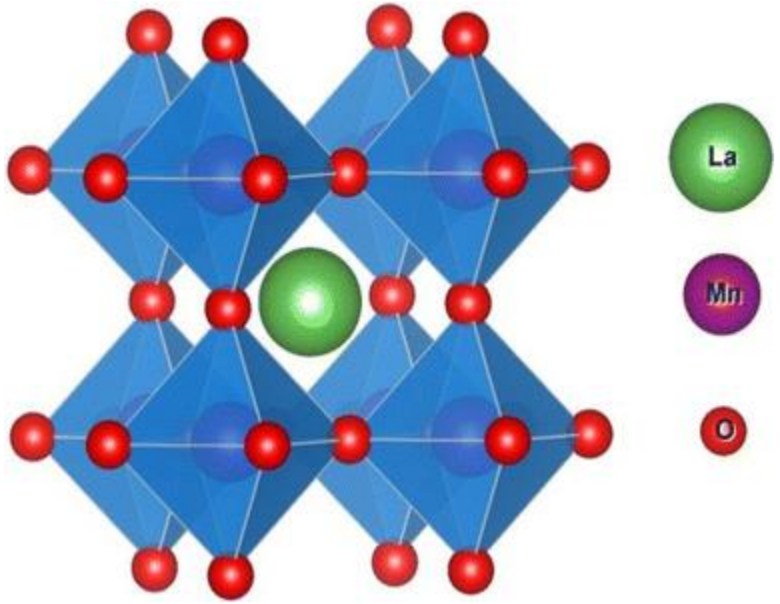


Second magnetic ion at $\boldsymbol{R}$

$$-\int \boldsymbol{m}(\boldsymbol{r})\boldsymbol{B}_\mathrm{eff}(\boldsymbol{r}-\boldsymbol{R})d\boldsymbol{r} = \frac{3N}{16\pi^2}\frac{J^2}{E_\mathrm{F}}F(R)S_{1z}S_{2z}$$

Double exchange interaction





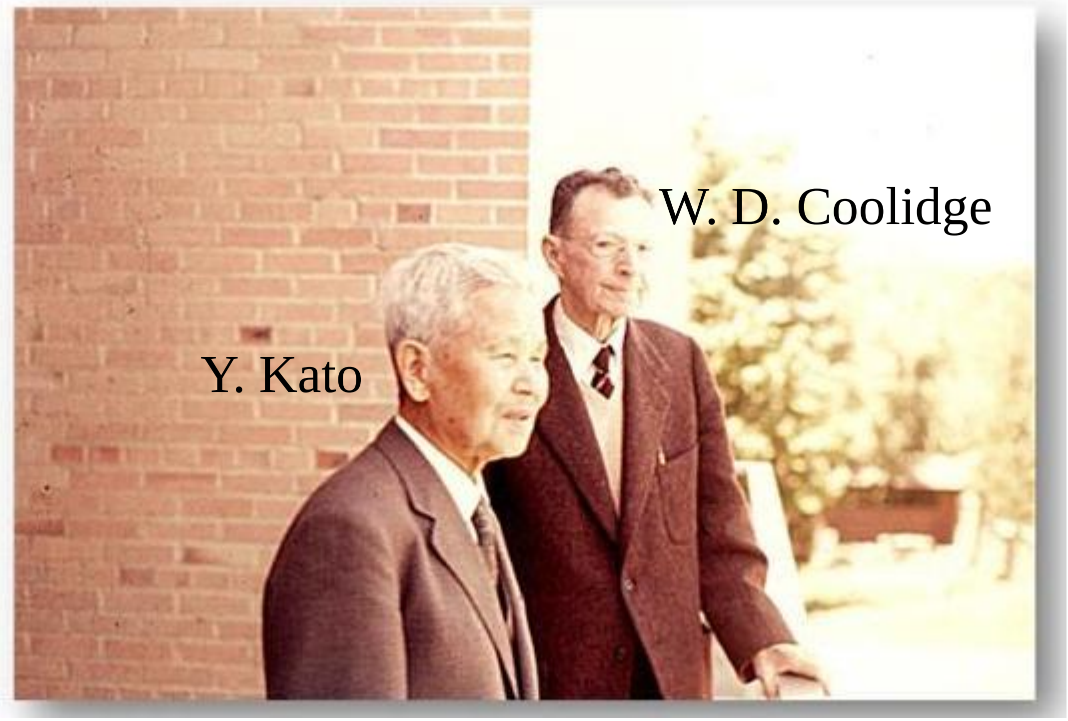
$LaMnO_3$

$LaMnO_3$ are anti-ferromagnetic insulator (Mott insulator). But when some La is replaced with Ca, Mn^{4+} ions appear. The system becomes metallic and at the same time this material shows ferromagnetism.

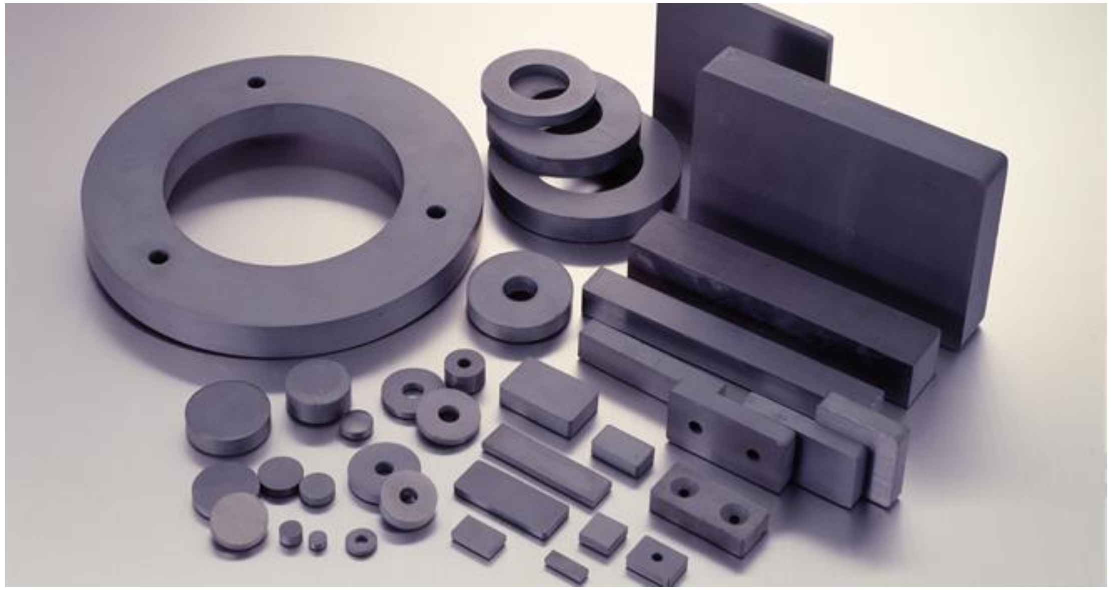
: Kind of kinetic exchange interaction.

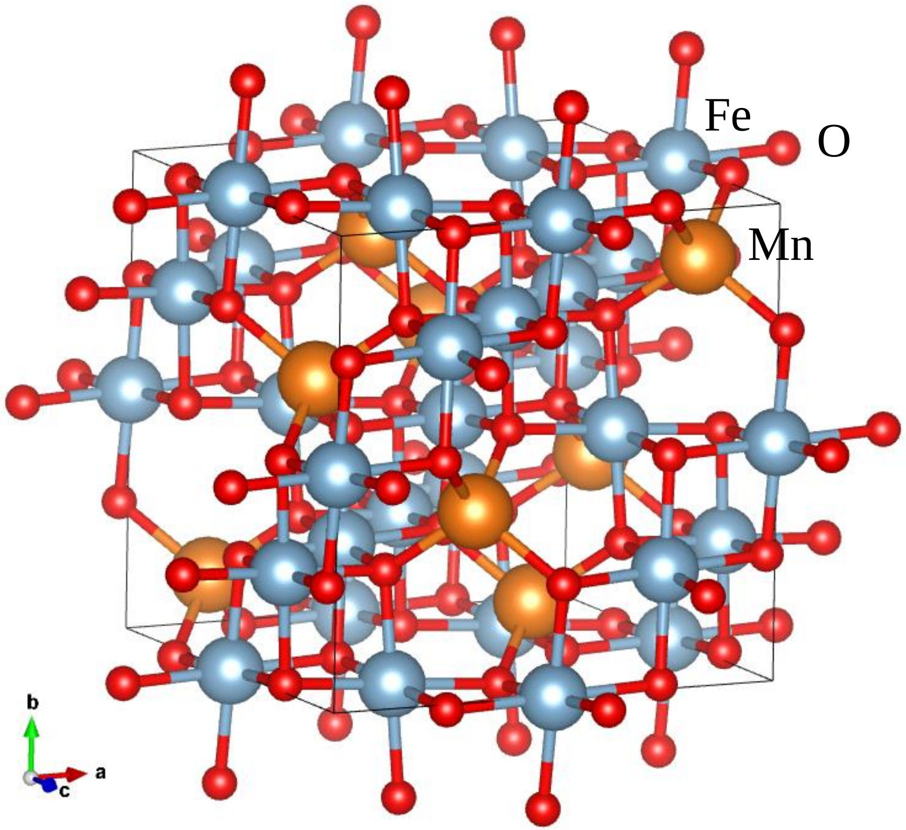
Chapter 5

Theories of Magnetic Insulators



http://teetokue.air-nifty.com/blog/2008/04/59_9f47.html





Molecular field approximation

Ferromagnetic Heisenberg Hamiltonian: $\mathscr{H} = -2J \sum_{\langle i,j \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - \mu \sum_i \boldsymbol{B} \cdot \boldsymbol{S}_i \qquad J,\ \mu > 0$

Average field approximation:
(molecular field approximation)

$$\mathscr{H}_{\text{eff}}(i) = -2J \sum_{\delta} \langle \boldsymbol{S}_{i+\delta} \rangle \cdot \boldsymbol{S}_i - \mu \boldsymbol{B} \cdot \boldsymbol{S}_i = -\mu \boldsymbol{B}_{\text{eff}} \cdot \boldsymbol{S}_i$$

$$\mu \boldsymbol{B}_{\text{eff}} = 2J \sum_{\delta} \langle \boldsymbol{S}_{i+\delta} \rangle + \mu \boldsymbol{B}$$

Remember $M = g_J \mu_{\text{B}} J B_J \left(\frac{g_J \mu_{\text{B}} J B}{k_{\text{B}} T} \right)$ replace $g_J \mu_{\text{B}} \to \mu,\ J \to S,\ B_J \to B_S$

then $M = \mu S B_S \left[\frac{\mu S}{k_{\text{B}} T} \left(B + \frac{2\alpha_z J}{\mu^2} M \right) \right]$

Brillouin function is expanded as $B_S(x) = \frac{S+1}{3S} x - \frac{1}{90} \frac{[(S+1)^2 + S^2](S+1)}{S^3} x^3 + \cdots$

Molecular field approximation (2)

then $$\left(1-\frac{2\alpha_z J}{\mu^2}\chi_0\right)M+\frac{1}{90}[(S+1)^2+S^2]\frac{1}{(k_\mathrm{B}T)^3}\left(\frac{2\alpha_z J}{\mu^2}\right)^2 M^3=\chi_0 B$$

with $\chi_0=\mu^2 S(S+1)/3$

The first order term drops at $k_\mathrm{B}T_\mathrm{C}=\dfrac{2}{3}S(S+1)\alpha_z J$ which gives the Curie temperature.

Curie-Weiss law $$\chi=\chi_0\left(1-\frac{2\alpha_z J}{\mu^2}\chi_0\right)^{-1}=\mu^2\frac{S(S+1)}{3k_\mathrm{B}(T-T_\mathrm{C})}$$

Summary

Spin Hamiltonian and quantum entanglement

Hubbard Hamiltonian

Superexchange interaction

RKKY interaction

Double exchange interaction

Theory of Magnetic insulators

Molecular field approximation

2022.6.01 Lecture 8

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Kanra Park Gunma Prefecture

- Spin Hamiltonian and quantum entanglement

➢ Hubbard Hamiltonian

➢ Superexchange interaction

➢ RKKY interaction

➢ Double exchange interaction

Ch. 5 Theory of Magnetic insulators

➢ Molecular field approximation

Outline

- Molecular field approximation
- Phenomenology of phase transition GL theory
    - Free energy
    - Spontaneous Symmetry Breaking
- Critical Exponent
- Theoretical models of magnetic materials
    - XY model
    - Ising model
- Antiferromagnetic Heisenberg model

Molecular-field approximation on ferromagnetic Heisenberg model

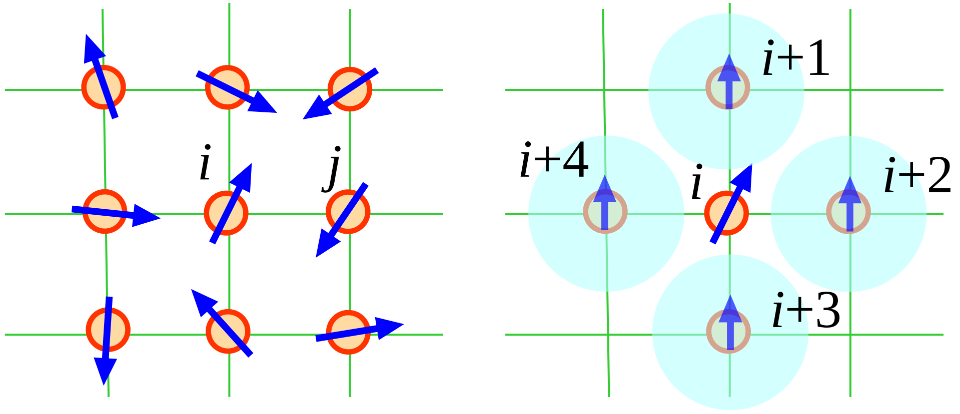
Ferromagnetic (J >0) Heisenberg model:

$$\mathscr{H} = -2J \sum_{\langle i,j \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - \mu \sum_i \boldsymbol{B} \cdot \boldsymbol{S}_i$$

nearest neighbor

Mean field (molecular-field) approximation:

Replace the neighboring spins with averaged one



$$\mathscr{H}_{\text{eff}}(i) = -2J \sum_{\delta} \langle \boldsymbol{S}_{i+\delta} \rangle \cdot \boldsymbol{S}_i - \mu \boldsymbol{B} \cdot \boldsymbol{S}_i = -\mu \boldsymbol{B}_{\text{eff}} \cdot \boldsymbol{S}_i$$

The averaged spins work as an effective field:

$$\mu \boldsymbol{B}_{\text{eff}} = 2J \sum_{\delta} \langle \boldsymbol{S}_{i+\delta} \rangle + \mu \boldsymbol{B}$$

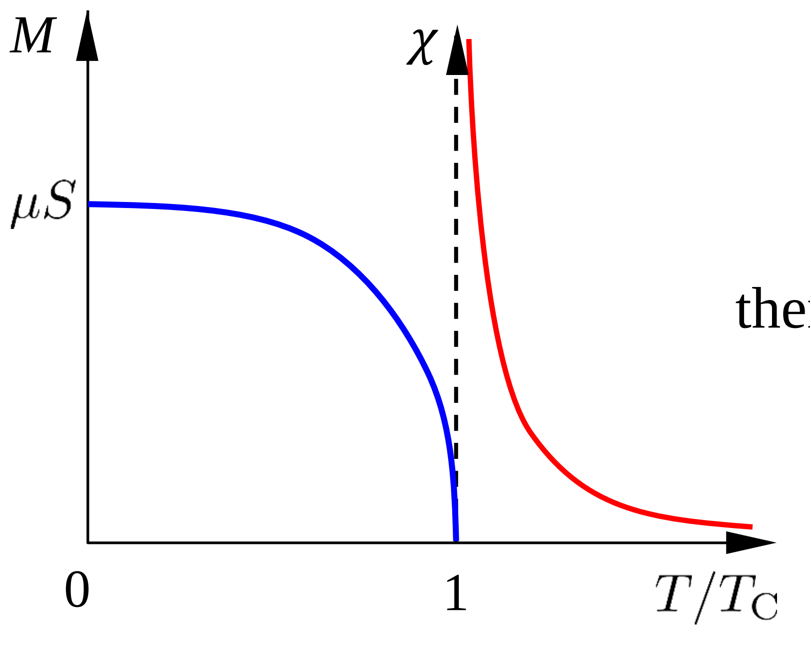
Remember paramagnetic representation of magnetization:

$$M = g_J \mu_{\text{B}} J B_J \left(\frac{g_J \mu_{\text{B}} J B}{k_{\text{B}} T} \right)$$

Replacement: $g_J \mu_{\text{B}} \to \mu,\ J \to S,\ B_J \to B_S \qquad B \to B_{\text{eff}}$

then $$M = \mu S B_S \left[\frac{\mu S}{k_{\text{B}} T} \left(B + \frac{2\alpha_z J}{\mu^2} M \right) \right]$$

Curie-Weiss law



Brillouin function is expanded as

$$B_S(x) = \frac{S+1}{3S}x - \frac{1}{90}\frac{[(S+1)^2+S^2](S+1)}{S^3}x^3 + \cdots$$

then $$\left(1-\frac{2\alpha_z J}{\mu^2}\chi_0\right)M + \frac{1}{90}[(S+1)^2+S^2]\frac{1}{(k_B T)^3}\left(\frac{2\alpha_z J}{\mu^2}\right)^2 M^3 = \chi_0 B$$

where $$\chi_0 = \frac{\mu^2 S(S+1)}{3k_B T}$$: the Curie law

The first order term drops at $k_B T_C = \frac{2}{3}S(S+1)\alpha_z J$

which gives the Curie temperature and the Curie-Weiss law

$$\boxed{\chi = \chi_0\left(1-\frac{2\alpha_z J}{\mu^2}\chi_0\right)^{-1} = \mu^2\frac{S(S+1)}{3k_B(T-T_C)}}$$

$T < T_C$

There exists non-zero solution for M, which has lower energy than M =0.

Solving the above we get

$$\boxed{M = \mu\sqrt{\frac{10}{3}\frac{S(S+1)}{\sqrt{(S+1)^2+S^2}}}\sqrt{1-\frac{T}{T_C}}}$$

$T \ll T_C$

$$x \gg 1 \qquad B_S(x) \sim 1 - \frac{1}{S}\exp\left(-\frac{x}{S}\right)$$

$$\boxed{M = \mu\left[S - \exp\left(-\frac{3}{S+1}\frac{T_C}{T}\right)\right]}$$

Ginzburg-Landau Theory(1)

The Curie-Weiss law $\chi \propto \dfrac{1}{1-(T_{\mathrm{C}}/T)} = 1 + \dfrac{T_{\mathrm{C}}}{T} + \left(\dfrac{T_{\mathrm{C}}}{T}\right)^2 + \left(\dfrac{T_{\mathrm{C}}}{T}\right)^3 + \cdots$

involves that the establishment of spontaneous magnetization is the result of a cooperative phenomenon.

Phenomenology: discuss the physical properties that do not depend on details of models.

The Ginzburg-Landau theory was developed for phenomenology of superconductivity.

Consider a symmetry of the Heisenberg model at B =0. $\mathscr{H} = -2J \sum_{\langle i,j \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j$

A symmetry operation: $\forall i \ \ \boldsymbol{S}_i \to -\boldsymbol{S}_i$

$\mathscr{H}$: unchanged

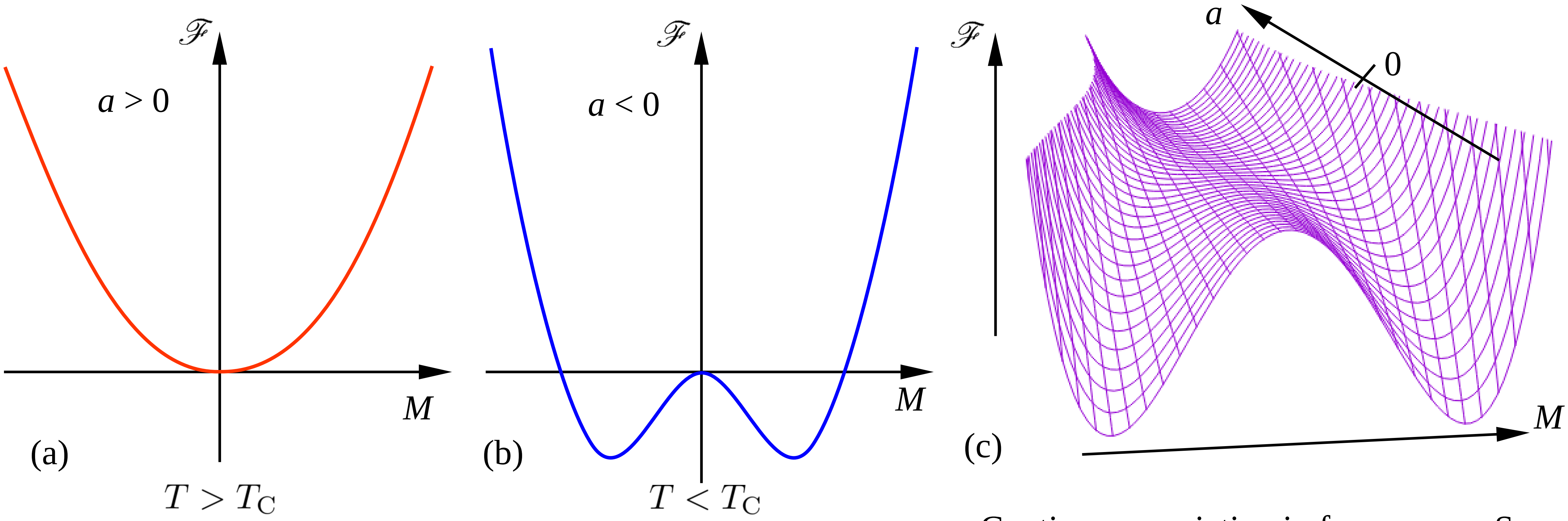
Free energy $\mathscr{F}$: unchanged

On the other hand $\boldsymbol{M} = \langle \boldsymbol{S}_i \rangle \to \langle -\boldsymbol{S}_i \rangle = -\boldsymbol{M}$ hence $\mathscr{F}(M) = \mathscr{F}(-M)$

Expansion to the series of power should be $\mathscr{F}(M) = \mathscr{F}_0 + aM^2 + bM^4$

To obtain stable (minimum) points $\dfrac{\partial \mathscr{F}}{\partial M} = 0 = 2aM + 4bM^3 = 2M(2bM^2 + a)$

Ginzburg-Landau Theory (2)



Continuous variation in free energy: Second order phase transition

$$\mathscr{F}(M) = \mathscr{F}_0 + aM^2 + bM^4$$

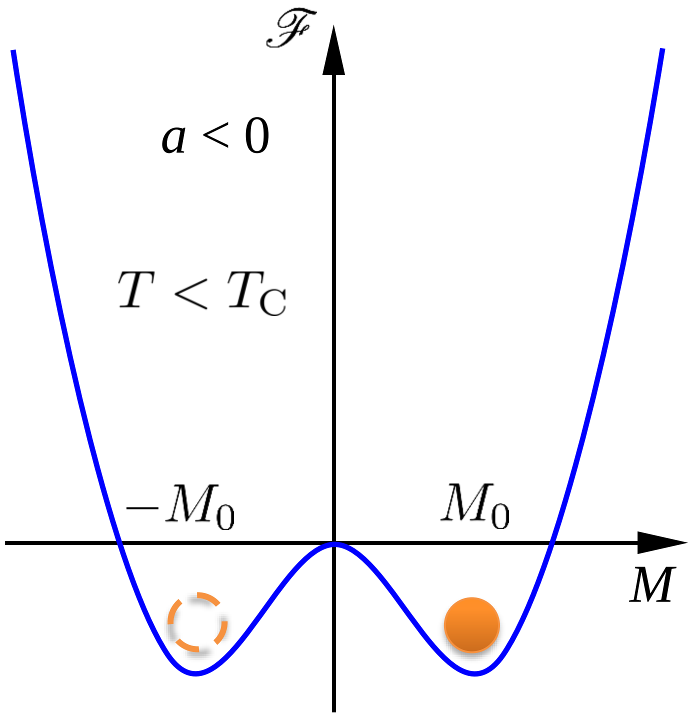
$a = k(T_C - T)/T_C$ T : relevant parameter

$$\frac{\partial \mathscr{F}}{\partial M} = 0 = 2aM + 4bM^3 = 2M(2bM^2 + a)$$

$$M_0 = \sqrt{-\frac{a}{2b}} = \sqrt{\frac{k(T_C - T)}{2bT_C}}$$

Magnetic equation of state

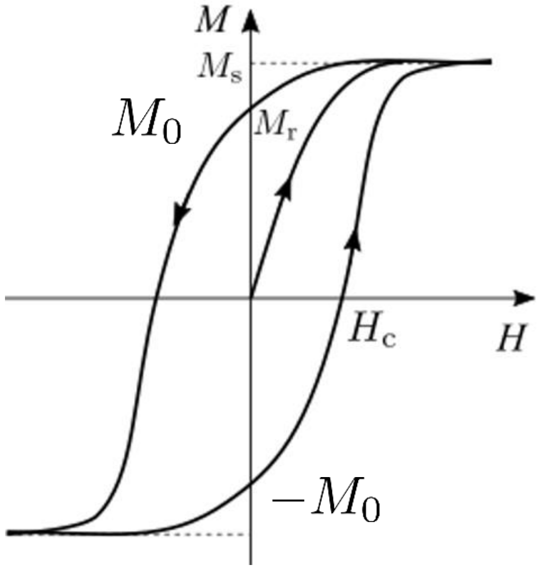
Spontaneous Symmetry Breaking



Spontaneous Symmetry Breaking

Spontaneous magnetization

$$M_0 = \sqrt{-\frac{a}{2b}} = \sqrt{\frac{k(T_C - T)}{2bT_C}}$$



MH curve

The symmetry of the system (Hamiltonian) is kept unchanged.

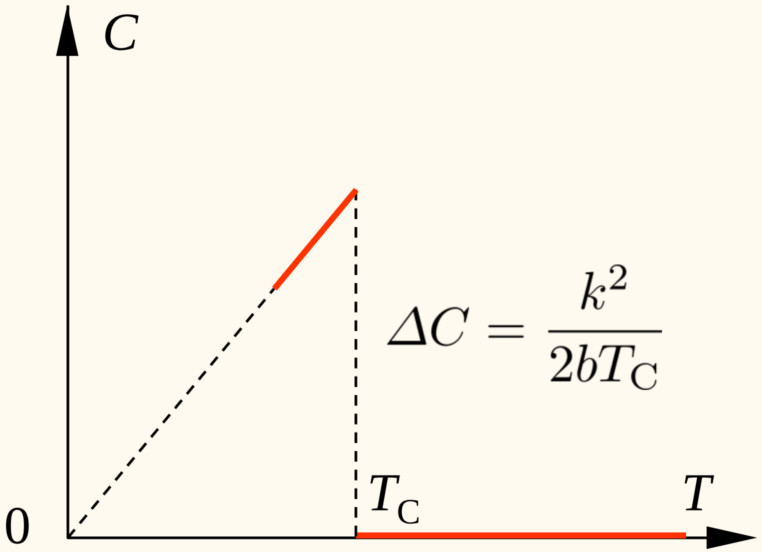
However the symmetry of the state is broken.

One of the central concepts in physics.

Phase transition, mass appearance, big bang, $\cdots$

Associated with appearance of Nambu-Goldstone mode

Critical exponent



In the presence of spontaneous magnetization, the free energy around the stable point is

$$\mathscr{F}(T) = \mathscr{F}_0 + aM_0^2 + bM_0^4 = \mathscr{F}_0 - \frac{a^2}{4b} = \mathscr{F}_0 - \frac{k^2(T_C - T)^2}{4bT_C^2}$$

Then the specific heat is obtained by

$$C = -T\frac{\partial^2 \mathscr{F}}{\partial T^2} = \frac{k^2 T}{2bT_C^2} \qquad T < T_C$$

$$\mathscr{F}(T) = \mathscr{F}_0 \qquad \therefore C = 0 \qquad T > T_C$$

$$\Delta C = \frac{k^2}{2bT_C}$$

Small B $\quad \mathscr{F}(M) = \mathscr{F}_0 + aM^2 + bM^4 - BM \qquad \frac{\partial \mathscr{F}}{\partial M} = 0 = 2aM + 4bM^3 - B$

$M^3 \propto B$
at the critical point

$$M \propto \begin{cases} B^{1/\delta} & (T = T_C), \\ (T_C - T)^\beta & (T < T_C), \end{cases} \qquad \chi \propto \begin{cases} (T - T_C)^{-\gamma} & (T > T_C), \\ (T_C - T)^{-\gamma'} & (T < T_C), \end{cases} \qquad C \propto \begin{cases} (T - T_C)^{-\alpha} & (T > T_C), \\ (T_C - T)^{-\alpha'} & (T < T_C). \end{cases}$$

Physical quantity that appears at the critical point $\quad A \propto (x - x_c)^\nu \quad$ Shift of a relevant parameter from the critical point

ν : Critical Exponent

Critical Exponent and Universality Class

Universality Class: Classification of the systems by symmetry, range of interaction, etc.
Each system which belongs to a universality class has the same set of critical exponents.

In the case of mean field approximation:

Critical exponent	α	β	γ	δ
Mean field approximation	0	$1/2$	1	3

One of the key features in analyzing phase transitions.

class	dimension	Symmetry	α	β	γ	δ	ν	η
3-state Potts	2	S_3	$\frac{1}{3}$	$\frac{1}{9}$	$\frac{13}{9}$	14	$\frac{5}{6}$	$\frac{4}{15}$
Ashkin-Teller (4-state Potts)	2	S_4	$\frac{2}{3}$	$\frac{1}{12}$	$\frac{7}{6}$	15	$\frac{2}{3}$	$\frac{1}{4}$
Ordinary percolation	1	1	1	0	1	∞	1	1
	2	1	$-\frac{2}{3}$	$\frac{5}{36}$	$\frac{43}{18}$	$\frac{91}{5}$	$\frac{4}{3}$	$\frac{5}{24}$
	3	1	−0.625(3)	0.4181(8)	1.793(3)	5.29(6)	0.87619(12)	0.46(8) or 0.59(9)
	4	1	−0.756(40)	0.657(9)	1.422(16)	3.9 or 3.198(6)	0.689(10)	−0.0944(28)
	5	1	≈ −0.85	0.830(10)	1.185(5)	3.0	0.569(5)	−0.075(20) or −0.0565
	6^+	1	−1	1	1	2	$\frac{1}{2}$	0
Directed percolation	1	1	0.159464(6)	0.276486(8)	2.277730(5)	0.159464(6)	1.096854(4)	0.313686(8)
	2	1	0.451	0.536(3)	1.60	0.451	0.733(8)	0.230
	3	1	0.73	0.813(9)	1.25	0.73	0.584(5)	0.12
	4^+	1	−1	1	1	2	$\frac{1}{2}$	0
Conserved directed percolation (Manna, or "local linear interface")	1	1		0.28(1)		0.14(1)	1.11(2)[1]	0.34(2)[1]
	2	1		0.64(1)	1.59(3)	0.50(5)	1.29(8)	0.29(5)
	3	1		0.84(2)	1.23(4)	0.90(3)	1.12(8)	0.16(5)
	4^+	1		1	1	1	1	0
Protected percolation	2	1		5/41[2]	86/41[2]			
	3	1		0.28871(15)[2]	1.3066(19)[2]			
Ising	2	$\mathbb{Z}_2$	0	$\frac{1}{8}$	$\frac{7}{4}$	15	1	$\frac{1}{4}$
	3	$\mathbb{Z}_2$	0.11008(1)	0.326419(3)	1.237075(10)	4.78984(1)	0.629971(4)	0.036298(2)
XY	3	$O(2)$	-0.01526(30)	0.34869(7)	1.3179(2)	4.77937(25)	0.67175(10)	0.038176(44)
Heisenberg	3	$O(3)$	−0.12(1)	0.366(2)	1.395(5)		0.707(3)	0.035(2)
Mean field	all	any	0	$\frac{1}{2}$	1	3	$\frac{1}{2}$	0
Molecular beam epitaxy[3]								
Gaussian free field								

Wikipedia

Models of magnetic systems (spin systems)

XY model: Spins are confined in a two-dimensional plane. $\boldsymbol{S}_i = (S_i^x, S_i^y)$

$$\mathscr{H} = -J \sum_{\langle i,j \rangle} \cos(\phi_i - \phi_j)$$

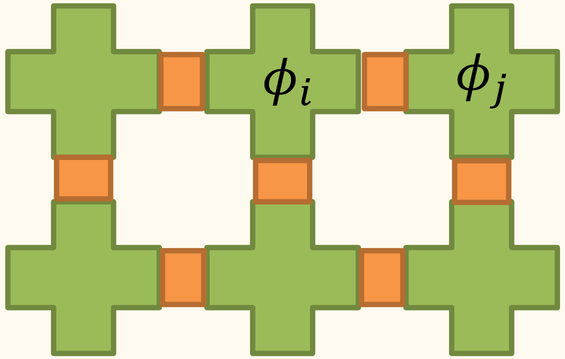
ϕ_i : Angle of each spin

Two-dimensional XY model: No long range order (Mermin-Wagner theorem)

Berezinskii-Kosterlitz-Thouless (BKT) transition

Quasi long range order (power decay)

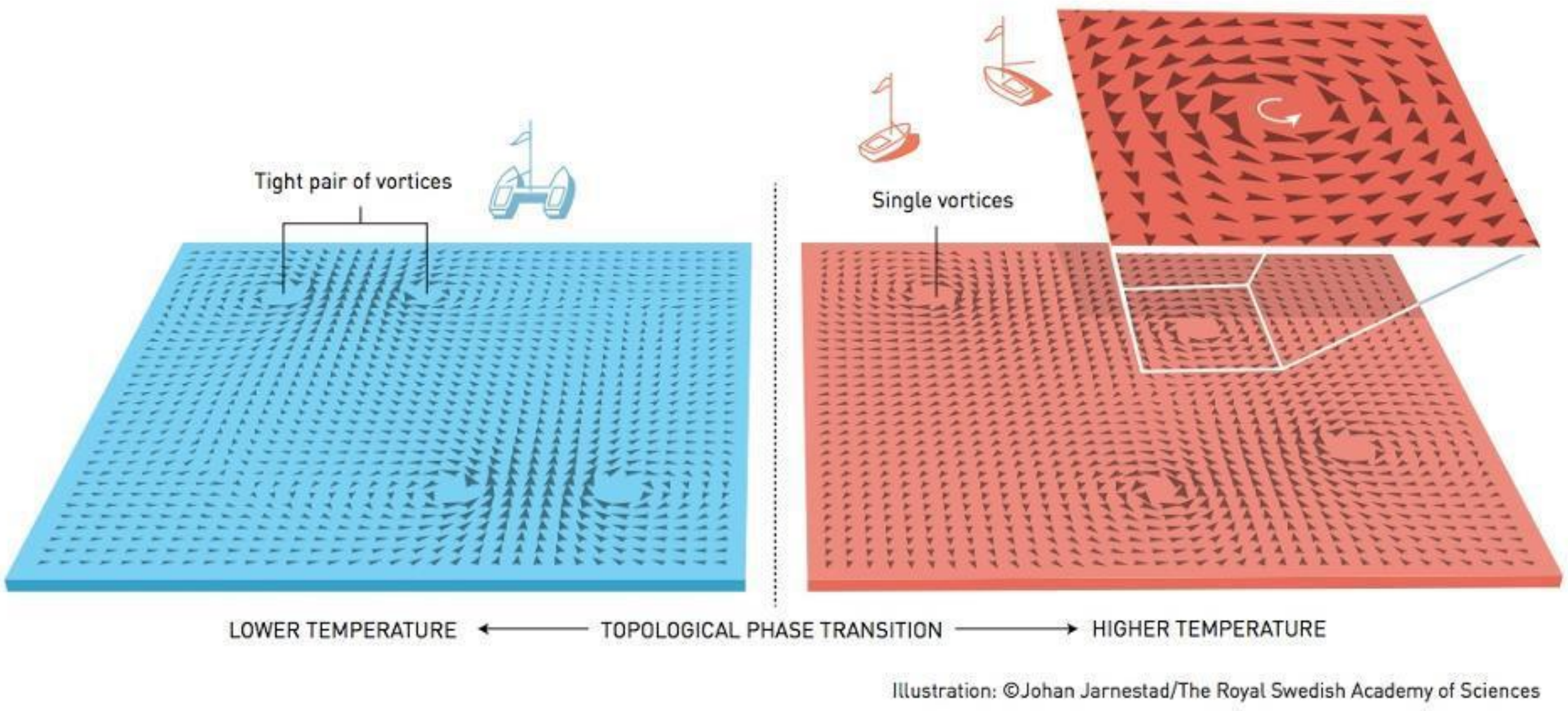
Realization of XY model: Josephson array



Josephson energy

$$E_{\mathrm{J}} = -E_0 \cos(\phi_i - \phi_j)$$

Berezinskii-Kosterlitz-Thouless Transition

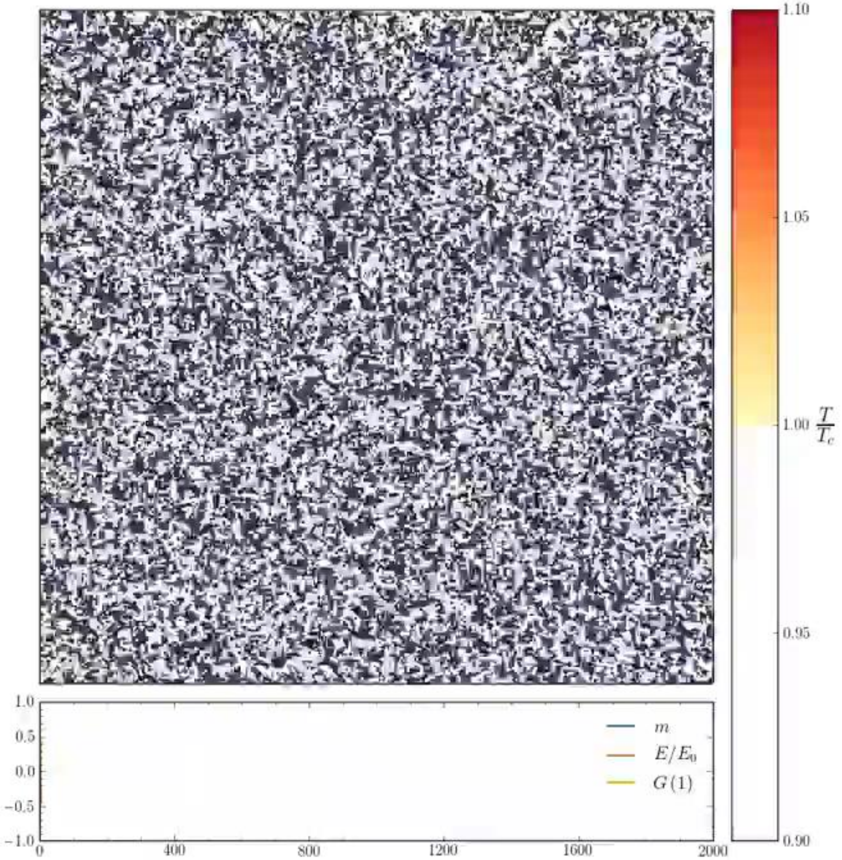


Ising model

Directions of spins are limited to *z*

$$\mathscr{H} = -J \sum_{\langle i,j \rangle} S_i S_j - h \sum_i S_i$$

Solution: 1d Ising, 2d Onsager



Model (Universality class)	α	β	γ	δ
2D Ising	0	1/8	7/4	15
3D Ising	0.115	0.324	1.239	4.82
3D XY	−0.01	0.34	1.32	4.9
3D Heisenberg	−0.11	0.36	1.39	4.9
Mean field approximation	0	1/2	1	3

https://www.youtube.com/watch?v=kjwKgpQ-l1s

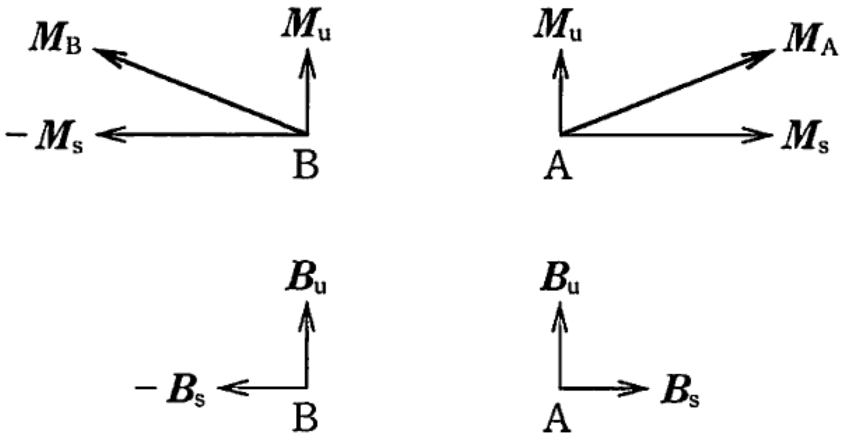
Antiferromagnetic Heisenberg model: Néel order and lattice partitioning

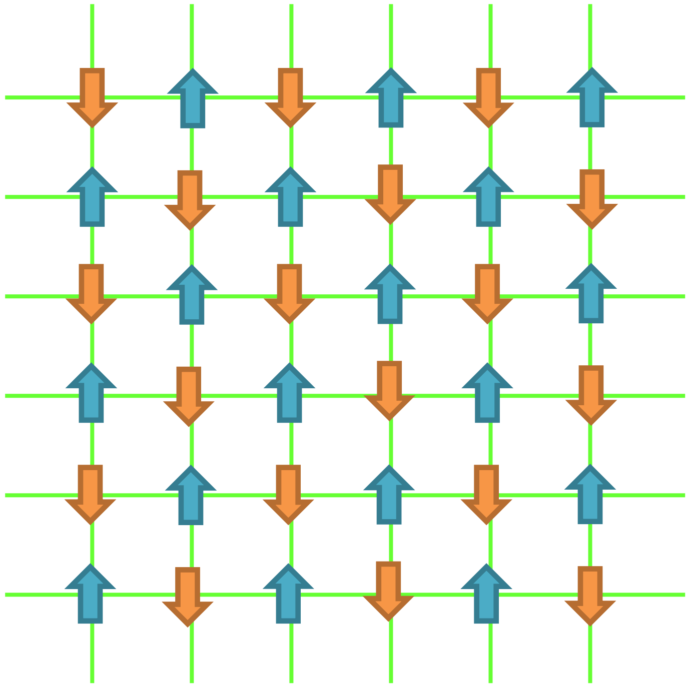
Antiferromagnetic
Heisenberg Hamiltonian

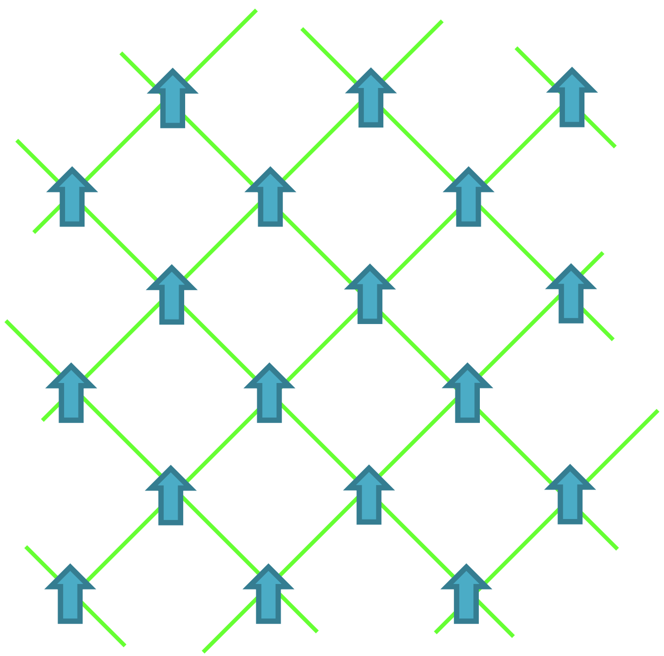
$$\mathscr{H} = -2J\sum_{\langle i,j\rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - \mu \sum_i \boldsymbol{B} \cdot \boldsymbol{S}_i$$

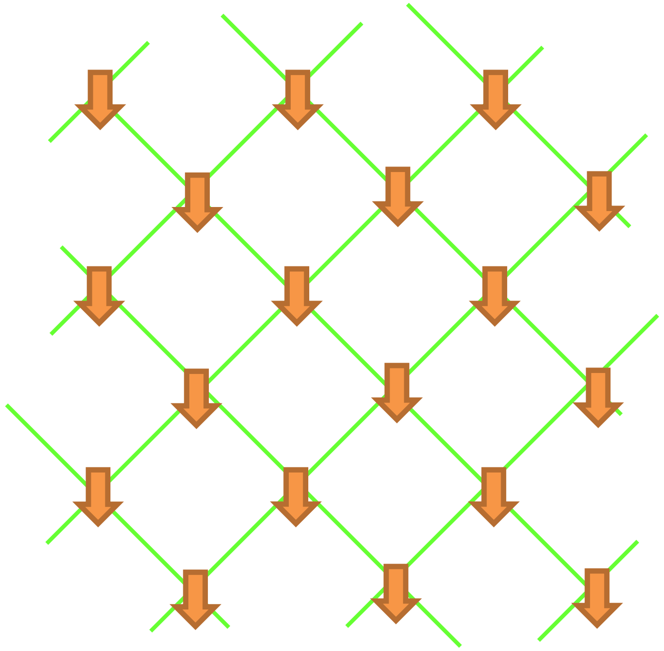
$J < 0$

$$\boldsymbol{B}_{\mathrm{A}} = \boldsymbol{B}_{\mathrm{u}} + \boldsymbol{B}_{\mathrm{s}}$$
$$\boldsymbol{B}_{\mathrm{B}} = \boldsymbol{B}_{\mathrm{u}} - \boldsymbol{B}_{\mathrm{s}}$$




Néel order in 2D square lattice


Partial Lattice A


Partial Lattice B

Antiferromagnetic Heisenberg model(2)

Molecular-field effective Hamiltonian

$$\mathscr{H}_{\text{eff}}(i) = -2J\sum_{\delta}\langle \boldsymbol{S}_{i+\delta}\rangle\cdot\boldsymbol{S}_i - \mu\boldsymbol{B}_{\text{A}}\cdot\boldsymbol{S}_i \quad (i\in\text{A})$$

$$\mathscr{H}_{\text{eff}}(j) = -2J\sum_{\delta}\langle \boldsymbol{S}_{j+\delta}\rangle\cdot\boldsymbol{S}_j - \mu\boldsymbol{B}_{\text{B}}\cdot\boldsymbol{S}_j \quad (j\in\text{B})$$

Averaged moments

$$\begin{cases} \boldsymbol{M}_{\text{A}} = \mu\langle\boldsymbol{S}_i\rangle = \boldsymbol{M}_{\text{u}} + \boldsymbol{M}_{\text{s}} \\ \boldsymbol{M}_{\text{B}} = \mu\langle\boldsymbol{S}_j\rangle = \boldsymbol{M}_{\text{u}} - \boldsymbol{M}_{\text{s}} \end{cases}$$

Vector Brillouin function

$$\vec{B}_S(\boldsymbol{x}) = B_S(x)\frac{\boldsymbol{x}}{x}$$

Self-consistent equation

$$\boldsymbol{M}_{\text{u}} + \boldsymbol{M}_{\text{s}} = \mu S\vec{B}_S\left\{\frac{\mu S}{k_{\text{B}}T}\left[\boldsymbol{B}_{\text{u}} + \boldsymbol{B}_{\text{s}} + \frac{2\alpha_z J}{\mu^2}(\boldsymbol{M}_{\text{u}} - \boldsymbol{M}_{\text{s}})\right]\right\}$$

Uniform susceptibility

$$\chi_{\text{u}} = \lim_{B_{\text{u}}\to 0}\frac{M_{\text{u}}}{B_{\text{u}}} = \chi_0\left(1 - \frac{2\alpha_z J}{\mu^2}\chi_0\right)^{-1}$$

Alternative susceptibility

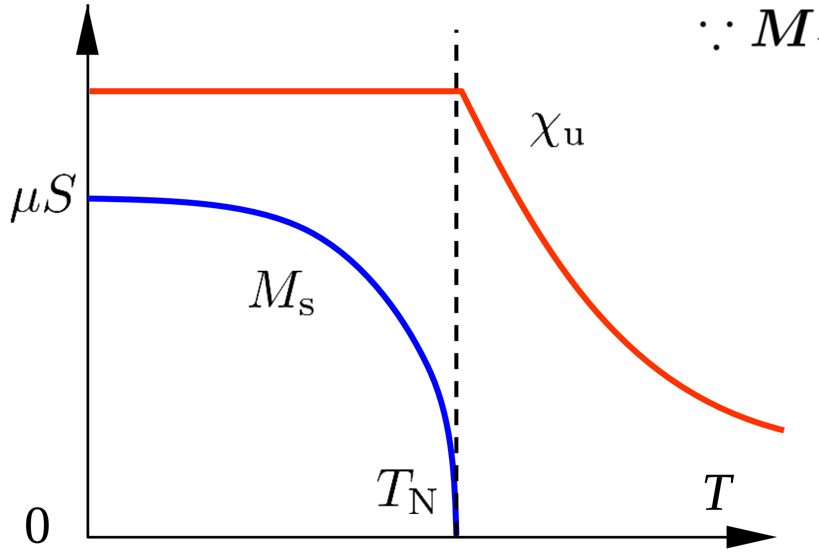
$$\chi_{\text{s}} = \lim_{B_{\text{s}}\to 0}\frac{M_{\text{s}}}{B_{\text{s}}} = \chi_0\left(1 + \frac{2\alpha_z J}{\mu^2}\chi_0\right)^{-1}$$

Antiferromagnetic Heisenberg model

Around stable points

$$\boldsymbol{M}_\mathrm{u}+\boldsymbol{M}_\mathrm{s}=\mu S\left[\vec{B}_S\left(\frac{\mu S}{k_\mathrm{B}T}\frac{-2\alpha_z J}{\mu^2}\boldsymbol{M}_\mathrm{s}\right)+\frac{d}{dM_\mathrm{s}}B_S\left(\frac{\mu S}{k_\mathrm{B}T}\frac{-2\alpha_z J}{\mu^2}\boldsymbol{M}_\mathrm{s}\right)\left(-\boldsymbol{M}_\mathrm{u}-\frac{\mu^2}{2\alpha_z J}\boldsymbol{B}_\mathrm{u}\right)\right]$$

$$\because \boldsymbol{M}_\mathrm{u}\perp\boldsymbol{M}_\mathrm{s}$$



Self-consistent equation for M_S

$$M_\mathrm{s}=\mu S B_S\left(\frac{\mu S}{k_\mathrm{B}T}\frac{-2\alpha_z J}{\mu^2}M_\mathrm{s}\right)$$

$$1=\mu S\frac{d}{dM_\mathrm{s}}B_S\left(\frac{\mu S}{k_\mathrm{B}T}\frac{-2\alpha_z J}{\mu^2}M_\mathrm{s}\right)$$

$$\boldsymbol{M}_\mathrm{u}=-\boldsymbol{M}_\mathrm{u}-\frac{\mu^2}{2\alpha_z J}\boldsymbol{B}_\mathrm{u}$$

$$\chi_\mathrm{u}=\lim_{B_\mathrm{u}\to 0}\frac{M_\mathrm{u}}{B_\mathrm{u}}=-\frac{\mu^2}{-4\alpha_z J}$$

Summary

- Molecular field approximation
- Phenomenology of phase transition GL theory
  - Free energy
  - Spontaneous Symmetry Breaking
- Critical Exponent
- Theoretical models of magnetic materials
  - XY model
  - Ising model
- Antiferromagnetic Heisenberg model

2022.6.8 Lecture 9

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Review

- Molecular field approximation
- Phenomenology of phase transition GL theory
  - Free energy
  - Spontaneous Symmetry Breaking
- Critical Exponent
- Theoretical models of magnetic materials
  - XY model
  - Ising model
- Antiferromagnetic Heisenberg model

Outline

- Anti-ferromagnetic Heisenberg model : parallel field susceptibility
- Spin flop and metamagnetic transition

- Ferrimagnetism
- Molecular-field approximation

- Helimagnetism

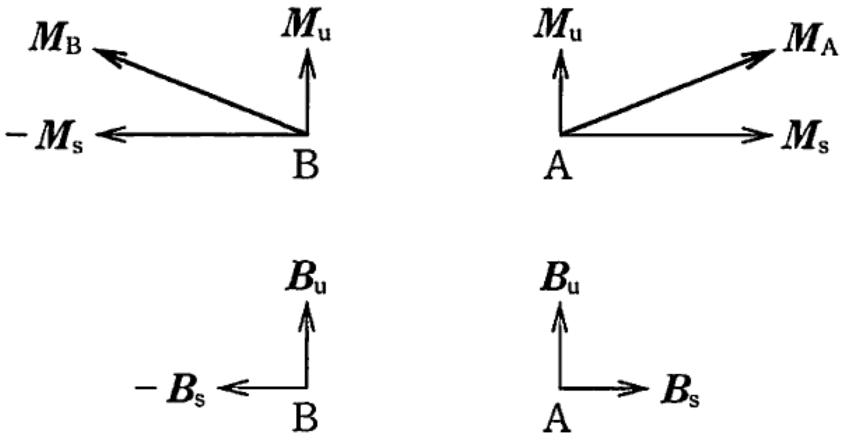
- Spin wave

Antiferromagnetic Heisenberg model

Antiferromagnetic Heisenberg Hamiltonian

$$\mathscr{H} = -2J\sum_{\langle i,j\rangle}\boldsymbol{S}_i\cdot\boldsymbol{S}_j - \mu\sum_i \boldsymbol{B}\cdot\boldsymbol{S}_i$$

$J < 0$

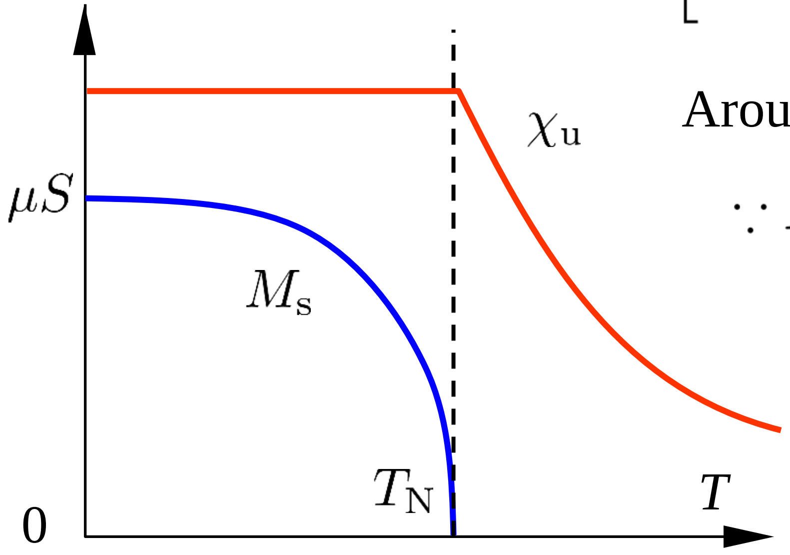


Sublattice magnetic field

$$\boldsymbol{B}_{\rm A} = \boldsymbol{B}_{\rm u} + \boldsymbol{B}_{\rm s}$$
$$\boldsymbol{B}_{\rm B} = \boldsymbol{B}_{\rm u} - \boldsymbol{B}_{\rm s}$$

Self-consistent equation $\longrightarrow$ spontaneous sublattice magnetization

$$\boldsymbol{M}_{\rm u} + \boldsymbol{M}_{\rm s} = \mu S\left[\vec{B}_S\left(\frac{\mu S}{k_{\rm B}T}\frac{-2\alpha_z J}{\mu^2}\boldsymbol{M}_{\rm s}\right) + \frac{d}{dM_{\rm s}}B_S\left(\frac{\mu S}{k_{\rm B}T}\frac{-2\alpha_z J}{\mu^2}\boldsymbol{M}_{\rm s}\right)\left(-\boldsymbol{M}_{\rm u} - \frac{\mu^2}{2\alpha_z J}\boldsymbol{B}_{\rm u}\right)\right]$$



Around stable points

$\because\ \boldsymbol{M}_{\rm u} \perp \boldsymbol{M}_{\rm s}$

Self-consistent equation for M_S

$$M_{\rm s} = \mu S B_S\left(\frac{\mu S}{k_{\rm B}T}\frac{-2\alpha_z J}{\mu^2}M_{\rm s}\right)$$

$$1 = \mu S\frac{d}{dM_{\rm s}}B_S\left(\frac{\mu S}{k_{\rm B}T}\frac{-2\alpha_z J}{\mu^2}M_{\rm s}\right) \qquad \boldsymbol{M}_{\rm u} = -\boldsymbol{M}_{\rm u} - \frac{\mu^2}{2\alpha_z J}\boldsymbol{B}_{\rm u}$$

$$\chi_{\rm u} = \lim_{B_{\rm u}\to 0}\frac{M_{\rm u}}{B_{\rm u}} = -\frac{\mu^2}{-4\alpha_z J}$$

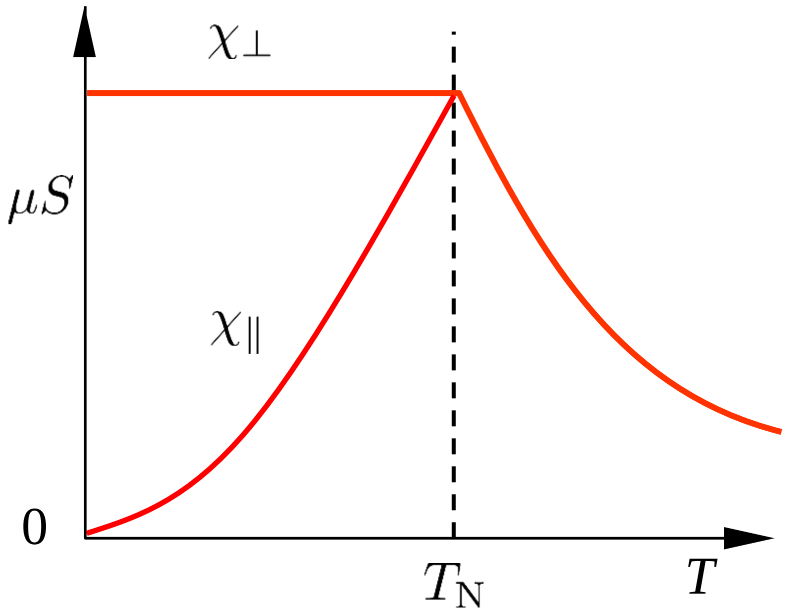
Antiferromagnetic Heisenberg model: parallel field

Consider sublattice-dependent effective magnetic field $\begin{cases} B_{\text{eff}}(\text{A}) = B + B_{\text{sub}}(\text{A}), \\ B_{\text{eff}}(\text{B}) = B + B_{\text{sub}}(\text{B}) \end{cases}$

Set of self-consistent equations for sublattice-dependent magnetic field

$$\langle M_{\text{A}} \rangle = \mu S \mathcal{B}_S \left[\frac{\mu S}{k_{\text{B}} T} \left(B + \frac{2\alpha_z J}{\mu^2} \langle M_{\text{B}} \rangle \right) \right],$$
$$\langle M_{\text{B}} \rangle = \mu S \mathcal{B}_S \left[\frac{\mu S}{k_{\text{B}} T} \left(B + \frac{2\alpha_z J}{\mu^2} \langle M_{\text{A}} \rangle \right) \right]$$

$\mathcal{B}_S(x)$: Brillouin function



This set of equations should be solved numerically.

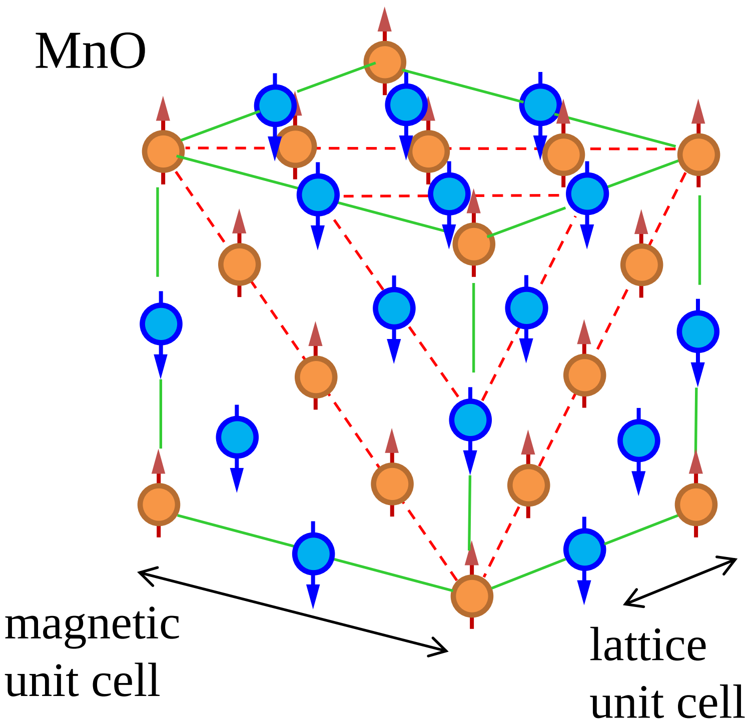
Then the parallel susceptibility is given by $\chi_\parallel = \lim_{B \to 0} \dfrac{M_A + M_B}{B}$

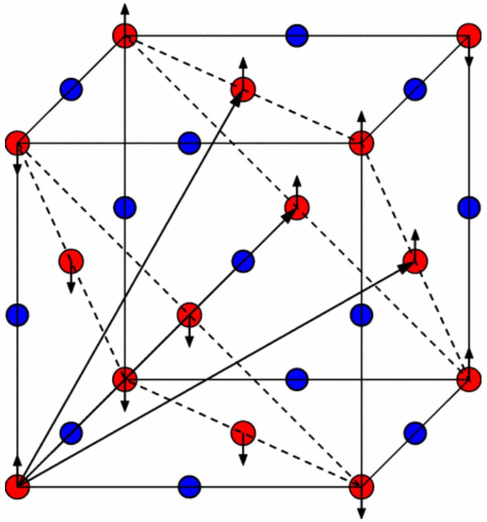
$T \to 0$ $\quad M_{\text{A}} = -M_{\text{B}} = \mu S$ $\quad$ then $\quad \chi_\parallel \to 0$

On the other hand, at $T = T_{\text{N}}$ $\quad \chi_\parallel = \chi_\perp$

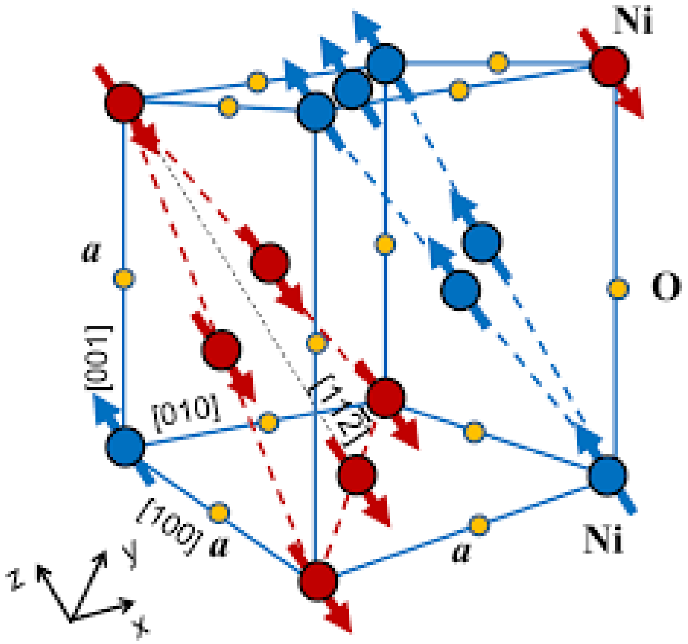
Examples of spin configuration in metal-oxide antiferromagnets

MnO

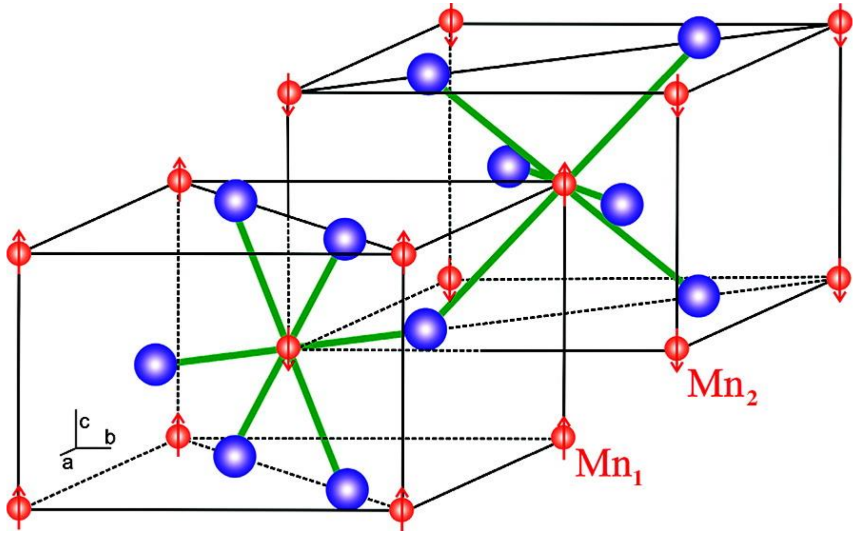




FeO

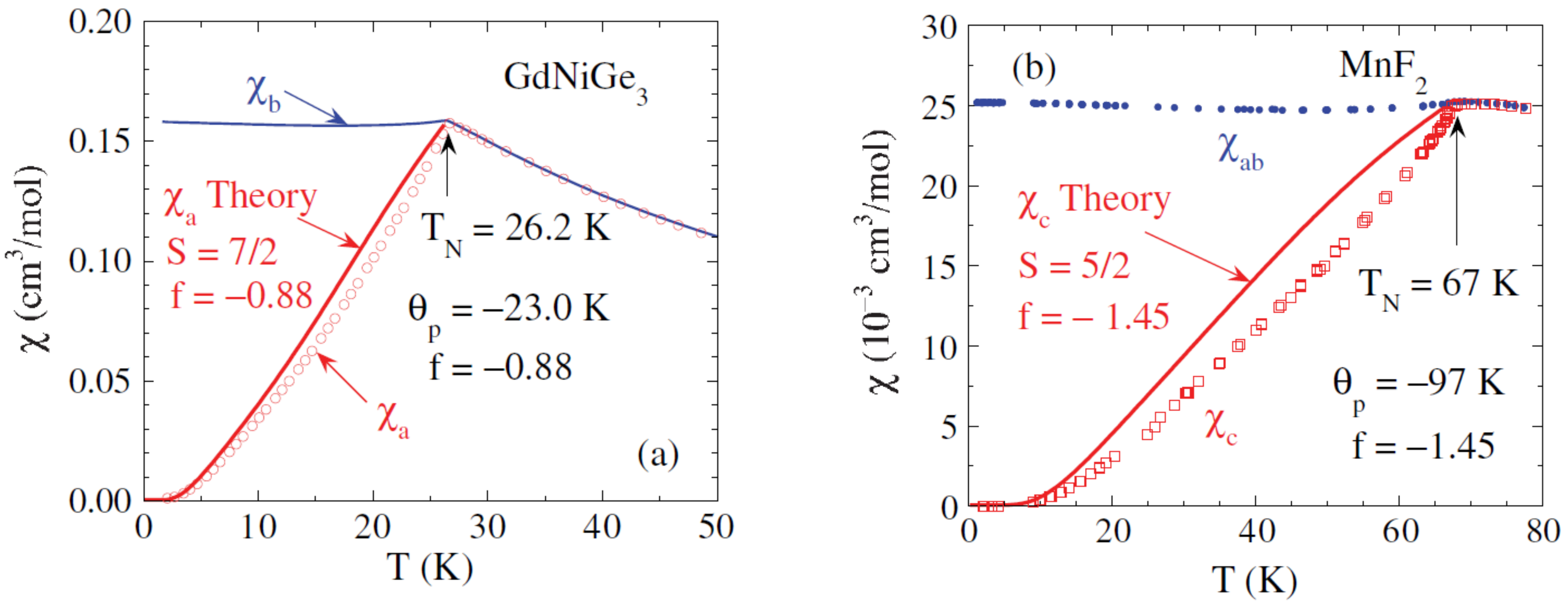


NiO



MnF_2

Temperature dependence of susceptibility



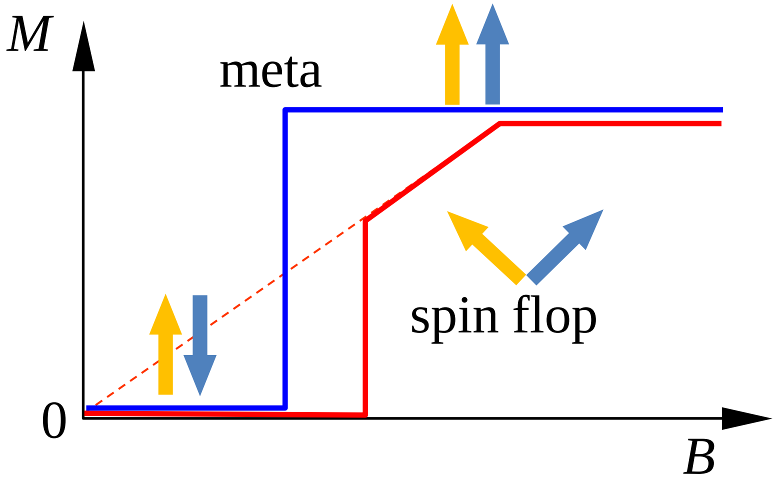
High temperature side ($T > T_{\mathrm{N}}$) $\quad \chi_{\mathrm{u}} \propto \dfrac{1}{T+\theta}$ $\quad \theta$: Weiss temperature

$$\left.\begin{aligned} \chi_{\mathrm{u}} &= \lim_{B_{\mathrm{u}}\to 0}\frac{M_{\mathrm{u}}}{B_{\mathrm{u}}} = \chi_0\left(1-\frac{2\alpha_z J}{\mu^2}\chi_0\right)^{-1} \\ \chi_{\mathrm{s}} &= \lim_{B_{\mathrm{s}}\to 0}\frac{M_{\mathrm{s}}}{B_{\mathrm{s}}} = \chi_0\left(1+\frac{2\alpha_z J}{\mu^2}\chi_0\right)^{-1} \end{aligned}\right\} \quad \theta = T_{\mathrm{N}}$$

Typical anti-ferromagnets Néel and Weiss temperatures

Material	Lattice-type of magnetic ions	Néel temperature (K)	Weiss temperature (K)
MnO	fcc	116	610
MnS	fcc	160	528
MnTe	hexagonal	307	690
MnF_2	bct	67	82
FeF_2	bct	79	117
$FeCl_2$	hexagonal	24	48
FeO	fcc	198	570
$CoCl_2$	hexagonal	25	38
CoO	fcc	291	330
$NiCl_2$	hexagonal	50	62
NiO	fcc	525	~ 2000
Cr	fcc	308	

Spin phase transition at higher fields in antiferromagnets



Consider a material with susceptibility χ

With applying magnetic field B the energy lowering in the material is

$$E_{\mathrm{m}} = -\int_0^B \frac{M(B')}{\mu_0}\frac{dB'}{\mu_0} - \chi\int_0^B \frac{B'}{\mu_0}\frac{dB'}{\mu_0} = -\frac{\chi}{2\mu_0^2}B^2$$

$T < T_{\mathrm{N}} \qquad \chi_\perp > \chi_\parallel$

$\longrightarrow$ States under vertical magnetic field is more stable

However crystals often have magnetic anisotropy. Let *K* be the anisotropic energy.

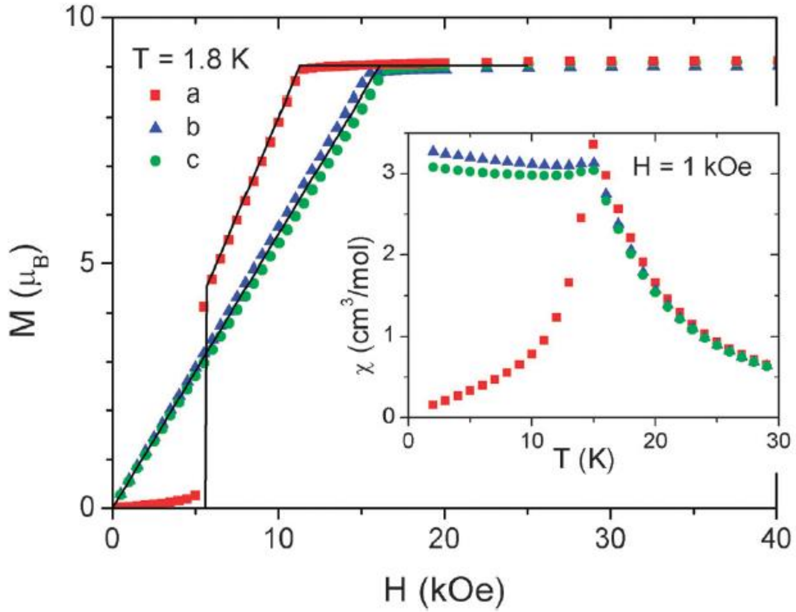
The anisotropic energy is overcome by the Zeeman energy at $\frac{\chi_\perp - \chi_\parallel}{2\mu_0^2}B_{\mathrm{c}}^2 = K$ Spin flop transition

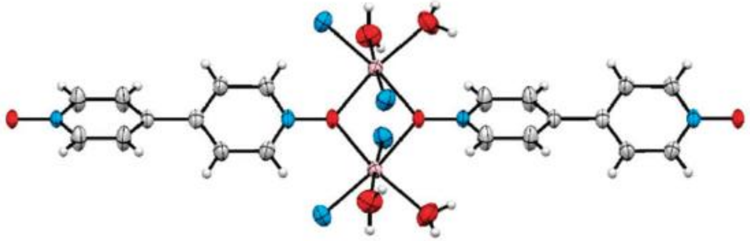
$$B_{\mathrm{c}} = \mu_0\sqrt{\frac{2K}{\chi_\perp - \chi_\parallel}}$$

Meta magnetism transition: antiferromagnetic interaction is overcome by the Zeeman energy

Spin flop transition, metamagnetic transition

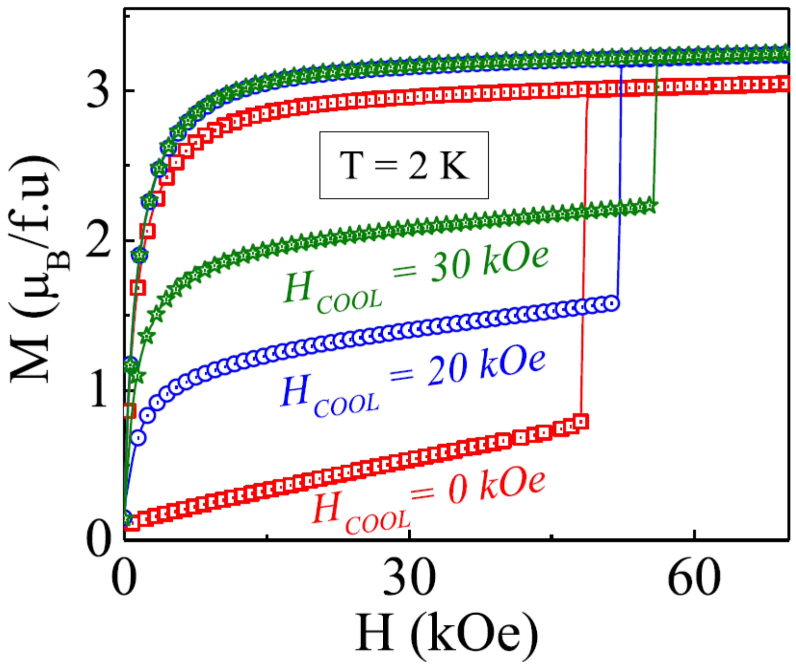
Metamagnetic transition



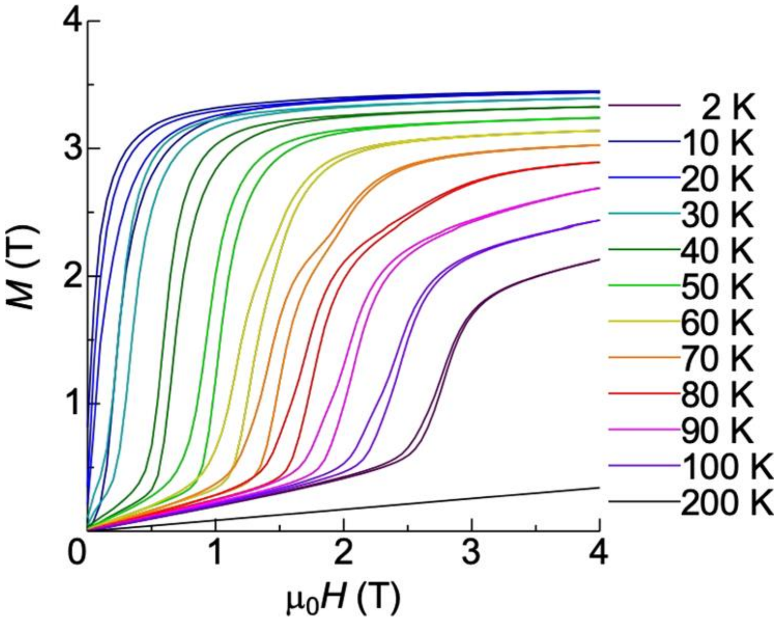


$\{[Mn_2(bpdo)(H_2O)_4][Nb(CN)_8] \cdot 6H_2O\}_n$

Spin flop transition in polymer anti-ferromagnet



$Sm_{0.5}Ca_{0.25}Sr_{0.25}Mn_3$



Helical magnet Ho single crystal

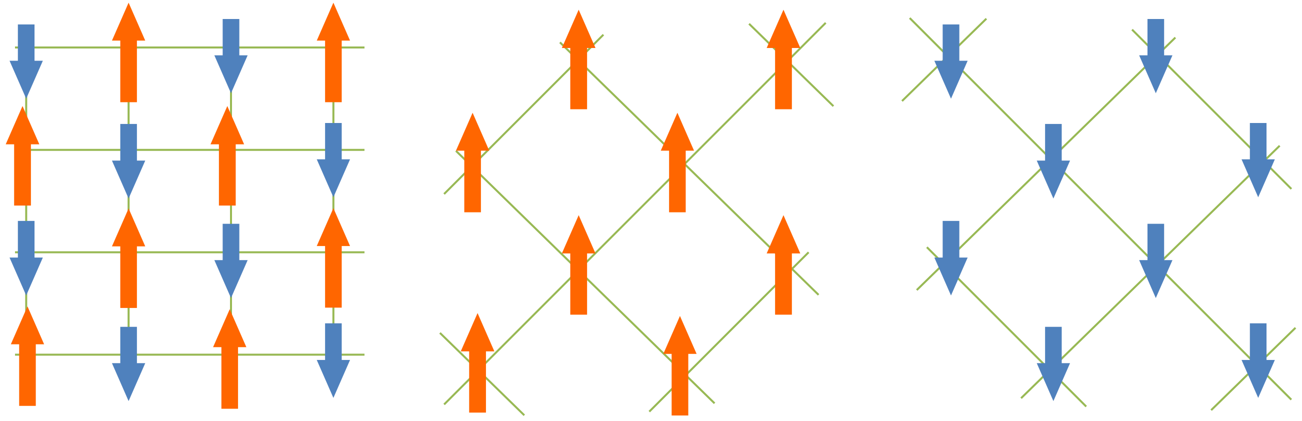
Remember in magnetic refrigeration, to have a good efficiency

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$$ should be large.

Because the metamagnetic transition is temperature sensitive, very high efficiency may be attainable.

Ferrimagnetism

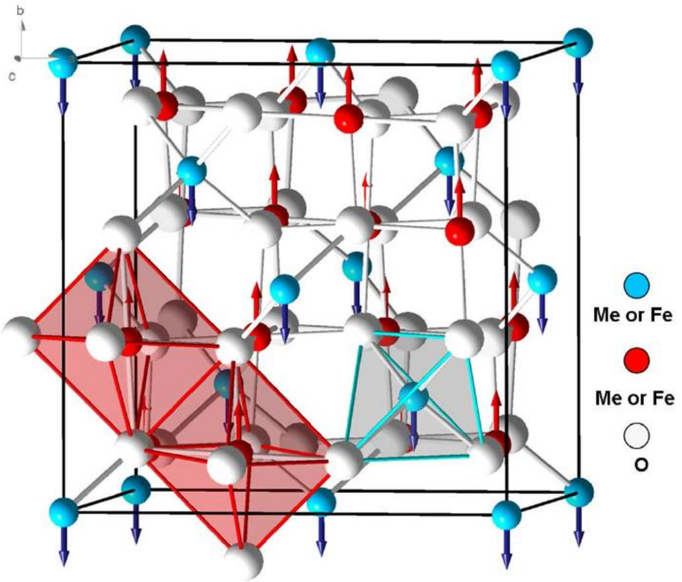
Ferrimagnetism ⟵ Magnetism in ferrites



Anti-ferromagnetic exchange interaction between the two sublattices: the same as anti-ferromagnetism

However the amplitudes of magnetization (the magnetic moments) are not the same.

Spontaneous magnetizations do not cancel out.



spinel ferrite

Molecular field approximation

$$\begin{cases} B_{\mathrm{A}} = \alpha M_{\mathrm{A}} + (-\gamma)(-M_{\mathrm{B}}) = \alpha M_{\mathrm{A}} + \gamma M_{\mathrm{B}}, \\ B_{\mathrm{B}} = \gamma M_{\mathrm{A}} + \beta M_{\mathrm{B}} \end{cases}$$

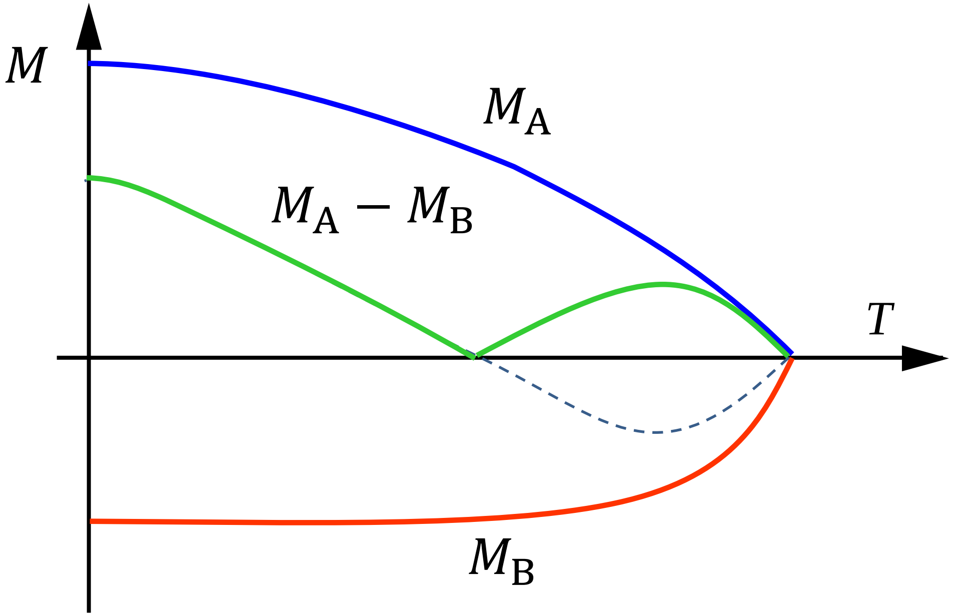
Molecular fields: intra-sublattice interaction is included

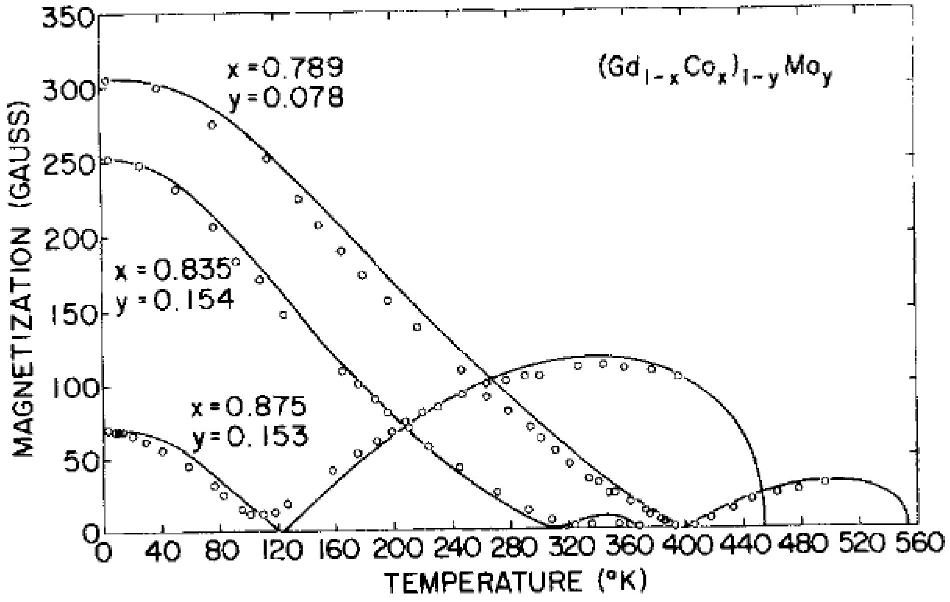
$$\begin{cases} M_{\mathrm{A}} = \mu S_{\mathrm{A}} \mathcal{B}_{S_{\mathrm{A}}} \left[\dfrac{\mu S_{\mathrm{A}}}{k_{\mathrm{B}} T} (\alpha M_{\mathrm{A}} + \gamma M_{\mathrm{B}}) \right], \\ M_{\mathrm{B}} = \mu S_{\mathrm{B}} \mathcal{B}_{S_{\mathrm{B}}} \left[\dfrac{\mu S_{\mathrm{B}}}{k_{\mathrm{B}} T} (\gamma M_{\mathrm{A}} + \beta M_{\mathrm{B}}) \right]. \end{cases}$$

Self-consistent set of equations

$\mathcal{B}_S(x)$: Brillouin function

Compensated ferrimagnetism

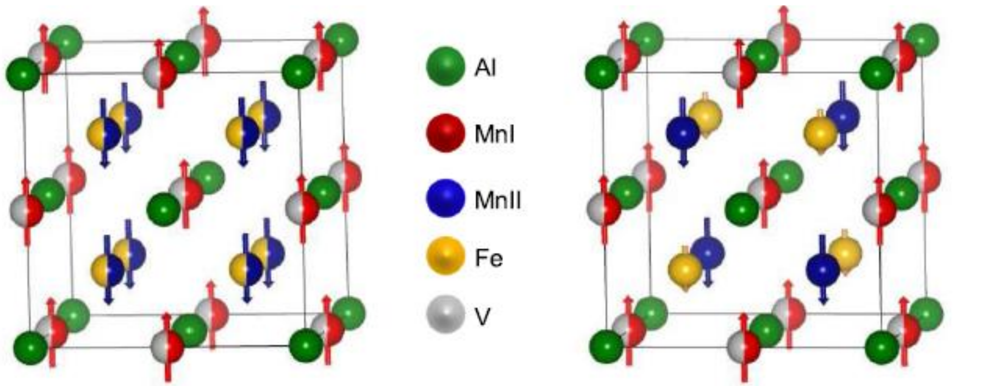




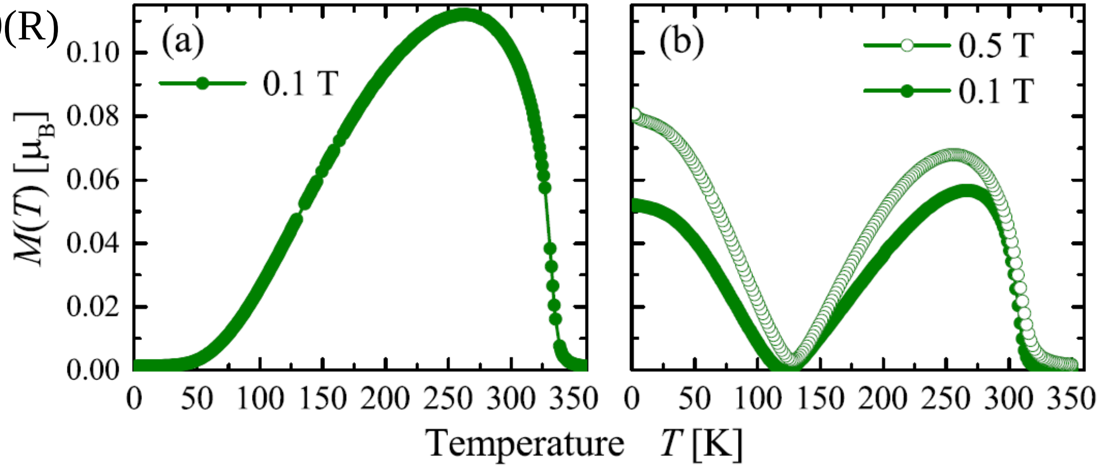
Hasegawa et al. AIP conf. proc. **24**, 110 (`75).

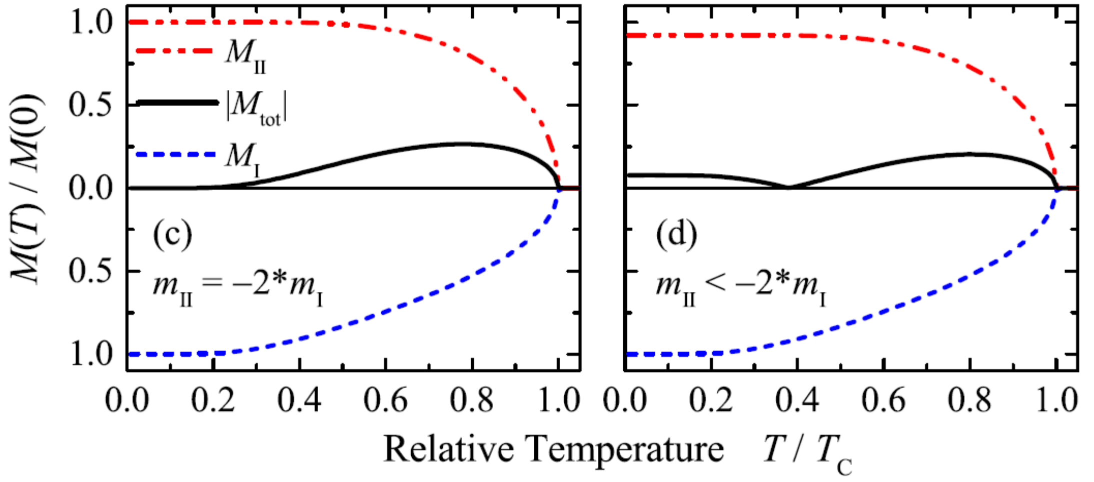
$Mn_{1.5}V_{0.5}FeAl$
Cubic Heusler
$L2_1$
$Fm\bar{3}m$

Stinshoff et al.
PRB **95**, 060410(R) (`17)



X
$F\bar{4}3m$





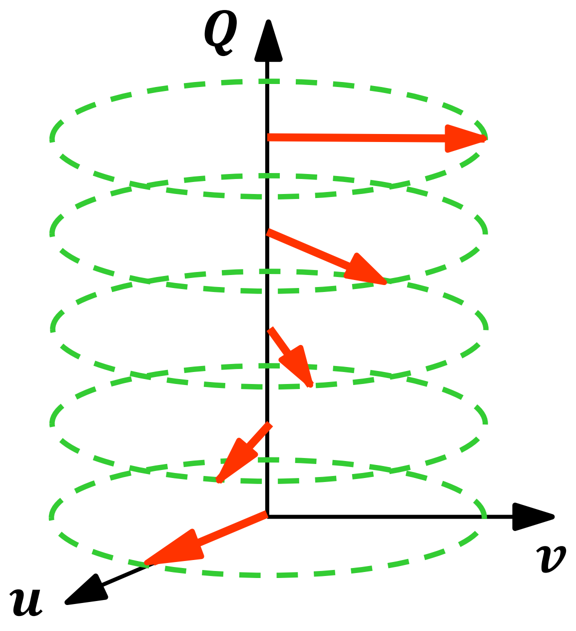
Helimagnetism

Heisenberg model (again!) $$\mathscr{H} = -\sum_{\langle i,j\rangle} J_{ij}\boldsymbol{S}_i\cdot\boldsymbol{S}_j - \mu\sum_i \boldsymbol{B}_i\cdot\boldsymbol{S}_i$$

Remember the agenda of molecular field approximation. $\boldsymbol{B}_i = \boldsymbol{0}$ in the first place

1. Find classical ground state
2. Consider the field configuration to stabilize the classical ground state
3. Write down the self consistent equation

Look for a stable state.



Fourier expansion $$\langle\boldsymbol{S}_i\rangle = \frac{1}{\sqrt{N}}\sum_{\boldsymbol{q}}\langle\boldsymbol{S}_{\boldsymbol{q}}\rangle\exp(i\boldsymbol{q}\cdot\boldsymbol{r}_i)$$

Then $$|\langle\boldsymbol{S}_i\rangle|^2 = S^2 = \frac{1}{N}\sum_{\boldsymbol{q},\boldsymbol{q}'}\langle\boldsymbol{S}_{\boldsymbol{q}}\rangle\cdot\langle\boldsymbol{S}_{\boldsymbol{q}'}\rangle\exp(i(\boldsymbol{q}+\boldsymbol{q}')\cdot\boldsymbol{r}_i)$$

The expectation value of the Hamiltonian is written as $$\langle\mathscr{H}\rangle = -\sum_{\langle i,j\rangle} J_{ij}\langle\boldsymbol{S}_i\rangle\cdot\langle\boldsymbol{S}_j\rangle = -\sum_{\boldsymbol{q}} J_{\boldsymbol{q}}\langle\boldsymbol{S}_{\boldsymbol{q}}\rangle\cdot\langle\boldsymbol{S}_{-\boldsymbol{q}}\rangle$$

where $$J_{\boldsymbol{q}} = \sum_j J_{ij}\exp[-i\boldsymbol{q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)]$$

Helimagnetism (2)

In $$|\langle \boldsymbol{S}_i\rangle|^2 = S^2 = \frac{1}{N}\sum_{\boldsymbol{q},\boldsymbol{q}'}\langle \boldsymbol{S}_{\boldsymbol{q}}\rangle\cdot\langle \boldsymbol{S}_{\boldsymbol{q}'}\rangle \exp(i(\boldsymbol{q}+\boldsymbol{q}')\cdot\boldsymbol{r}_i)$$

the summation on *i* in the right hand side can be carried out as
$$\frac{1}{N}\sum_i\sum_{\boldsymbol{q},\boldsymbol{q}'}\langle \boldsymbol{S}_{\boldsymbol{q}}\rangle\cdot\langle \boldsymbol{S}_{\boldsymbol{q}'}\rangle \exp(i(\boldsymbol{q}+\boldsymbol{q}')\cdot\boldsymbol{r}_i) = \sum_{\boldsymbol{q},\boldsymbol{q}'}\langle \boldsymbol{S}_{\boldsymbol{q}}\rangle\cdot\langle \boldsymbol{S}_{\boldsymbol{q}'}\rangle\,\delta_{\boldsymbol{q},-\boldsymbol{q}'}$$

Then $$NS^2 = \sum_{\boldsymbol{q}}\langle \boldsymbol{S}_{\boldsymbol{q}}\rangle\cdot\langle \boldsymbol{S}_{-\boldsymbol{q}}\rangle$$ this should be a constraint.

Let $\pm\boldsymbol{Q}$ be wavenumbers at which $J_{\boldsymbol{q}}$ take the maxima

$\boldsymbol{Q}=0$: Ferromagnetism
$\boldsymbol{Q}=\boldsymbol{K}-\boldsymbol{Q}$: Antiferromagnetism

Then we assume $$\langle \boldsymbol{S}_{\boldsymbol{Q}}\rangle \neq 0,\quad \langle \boldsymbol{S}_{-\boldsymbol{Q}}\rangle \neq 0,\quad (\text{others}) = 0$$

The equation on the top is
$$NS^2 = \langle \boldsymbol{S}_{\boldsymbol{Q}}\rangle\cdot\langle \boldsymbol{S}_{\boldsymbol{Q}}\rangle\exp(2i\boldsymbol{Q}\cdot\boldsymbol{r}_i) + \langle \boldsymbol{S}_{-\boldsymbol{Q}}\rangle\cdot\langle \boldsymbol{S}_{-\boldsymbol{Q}}\rangle\exp(-2i\boldsymbol{Q}\cdot\boldsymbol{r}_i) + 2\langle \boldsymbol{S}_{\boldsymbol{Q}}\rangle\cdot\langle \boldsymbol{S}_{-\boldsymbol{Q}}\rangle$$

From the constraint $$\langle \boldsymbol{S}_{\boldsymbol{Q}}\rangle\cdot\langle \boldsymbol{S}_{\boldsymbol{Q}}\rangle = \langle \boldsymbol{S}_{-\boldsymbol{Q}}\rangle\cdot\langle \boldsymbol{S}_{-\boldsymbol{Q}}\rangle = 0$$

$$\mathrm{Re}[\langle \boldsymbol{S}_{\boldsymbol{Q}}\rangle] = \boldsymbol{a},\ \mathrm{Im}[\langle \boldsymbol{S}_{\boldsymbol{Q}}\rangle] = \boldsymbol{b} \longmapsto |\boldsymbol{a}|^2 - |\boldsymbol{b}|^2 = 0,\ \boldsymbol{a}\cdot\boldsymbol{b} = 0$$

Helimagnetism (3)

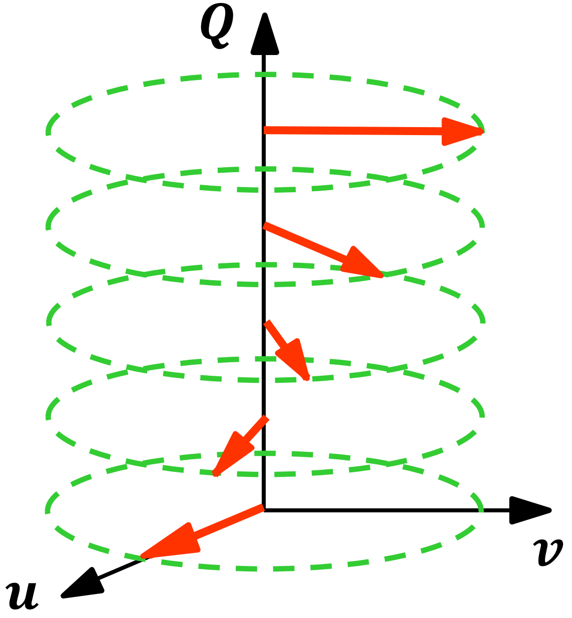
Then we can write with taking ***u*** and ***v*** as orthogonal unit vectors as

$$\langle \boldsymbol{S}_{\boldsymbol{Q}} \rangle = \frac{\sqrt{N}}{2} S(\boldsymbol{u} - i\boldsymbol{v})$$

Then the ground state spin configuration is given by

$$\langle \boldsymbol{S}_i \rangle = S[\boldsymbol{u}\cos(\boldsymbol{Q}\cdot\boldsymbol{r}_i) + \boldsymbol{v}\sin(\boldsymbol{Q}\cdot\boldsymbol{r}_i)]$$

This represents the helical structure.



Molecular field approximation

Stabilization field
$$\boldsymbol{B}_i = B_q[\boldsymbol{u}\cos(\boldsymbol{q}\cdot\boldsymbol{r}_i) + \boldsymbol{v}\sin(\boldsymbol{q}\cdot\boldsymbol{r}_i)]$$

Molecular field
$$\langle \boldsymbol{S}_i \rangle = m_q[\boldsymbol{u}\cos(\boldsymbol{q}\cdot\boldsymbol{r}_i) + \boldsymbol{v}\sin(\boldsymbol{q}\cdot\boldsymbol{r}_i)]$$

Effective Hamiltonian
$$\mathscr{H}_{\rm eff}(i) = -(2m_qJ_q + \mu B_q)[\boldsymbol{u}\cos(\boldsymbol{q}\cdot\boldsymbol{r}_i) + \boldsymbol{v}\sin(\boldsymbol{q}\cdot\boldsymbol{r}_i)]\cdot\boldsymbol{S}_i$$

Self consistent equation
$$m_q = S\mathcal{B}_S\left[\frac{S}{k_{\rm B}T}(2m_qJ_q + \mu B_q)\right]$$

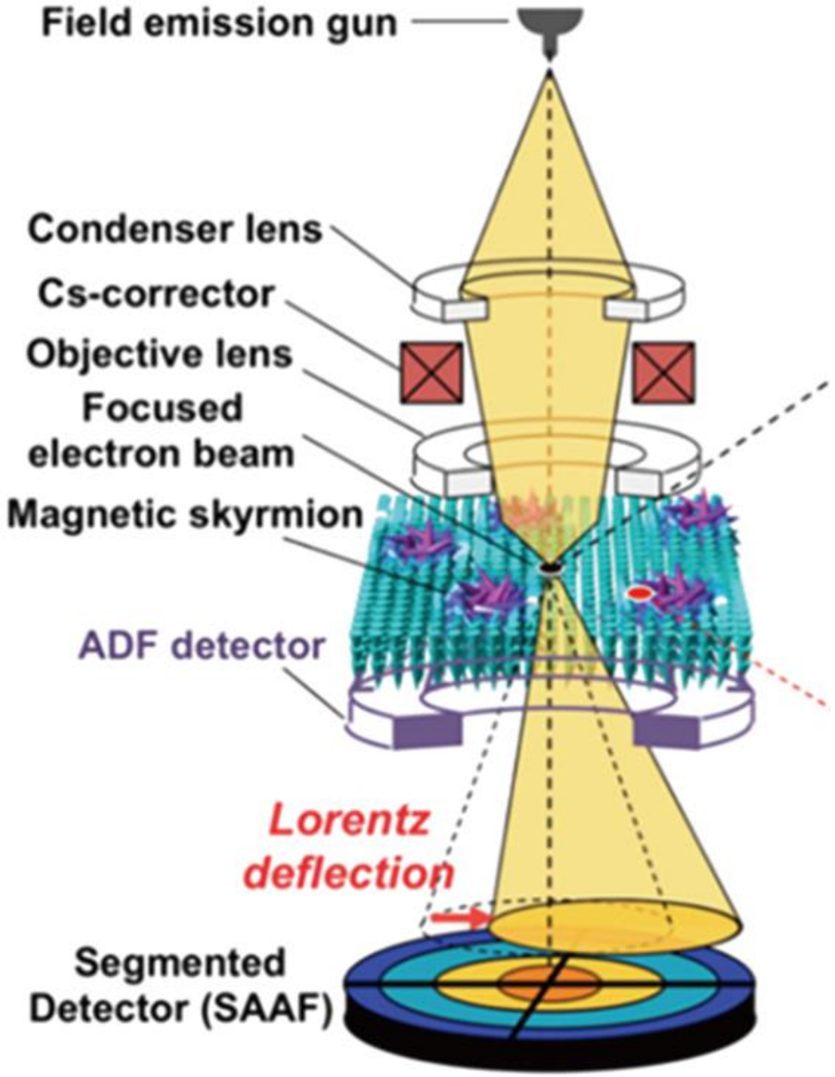
Helical susceptibility
$$\chi_q = \lim_{B_q\to 0}\frac{\mu m_q}{B_q} = \chi_0\left(1 - \frac{2J_q}{\mu^2}\chi_0\right)^{-1}$$

Helical order temperature
$$k_{\rm B}T_{\boldsymbol{Q}} = \frac{2}{3}S(S+1)J_{\boldsymbol{Q}}$$

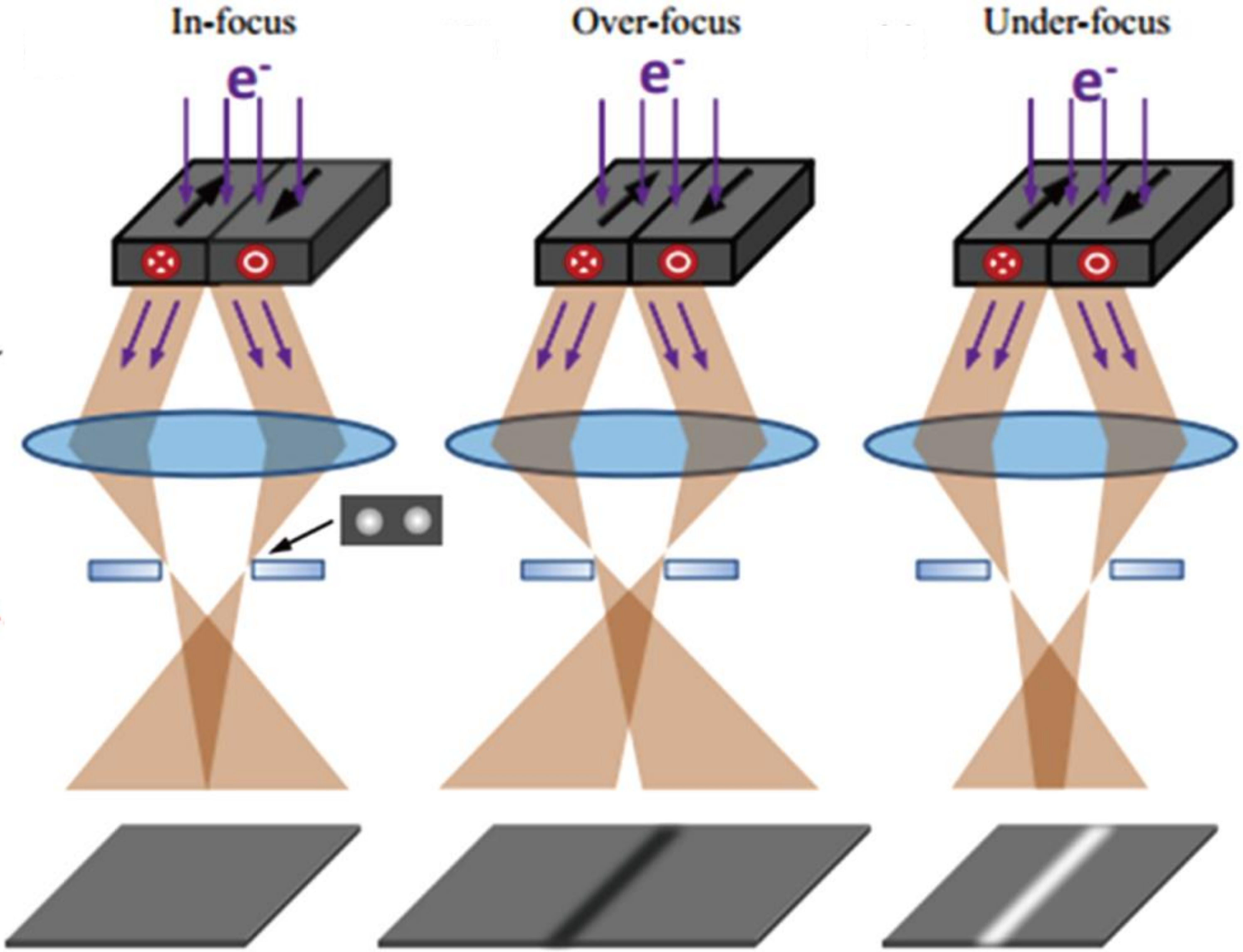
Lorentz transmission microscope

Li-cong et al. Ch. Phys. B **27**, 066802 (`18)

Overview

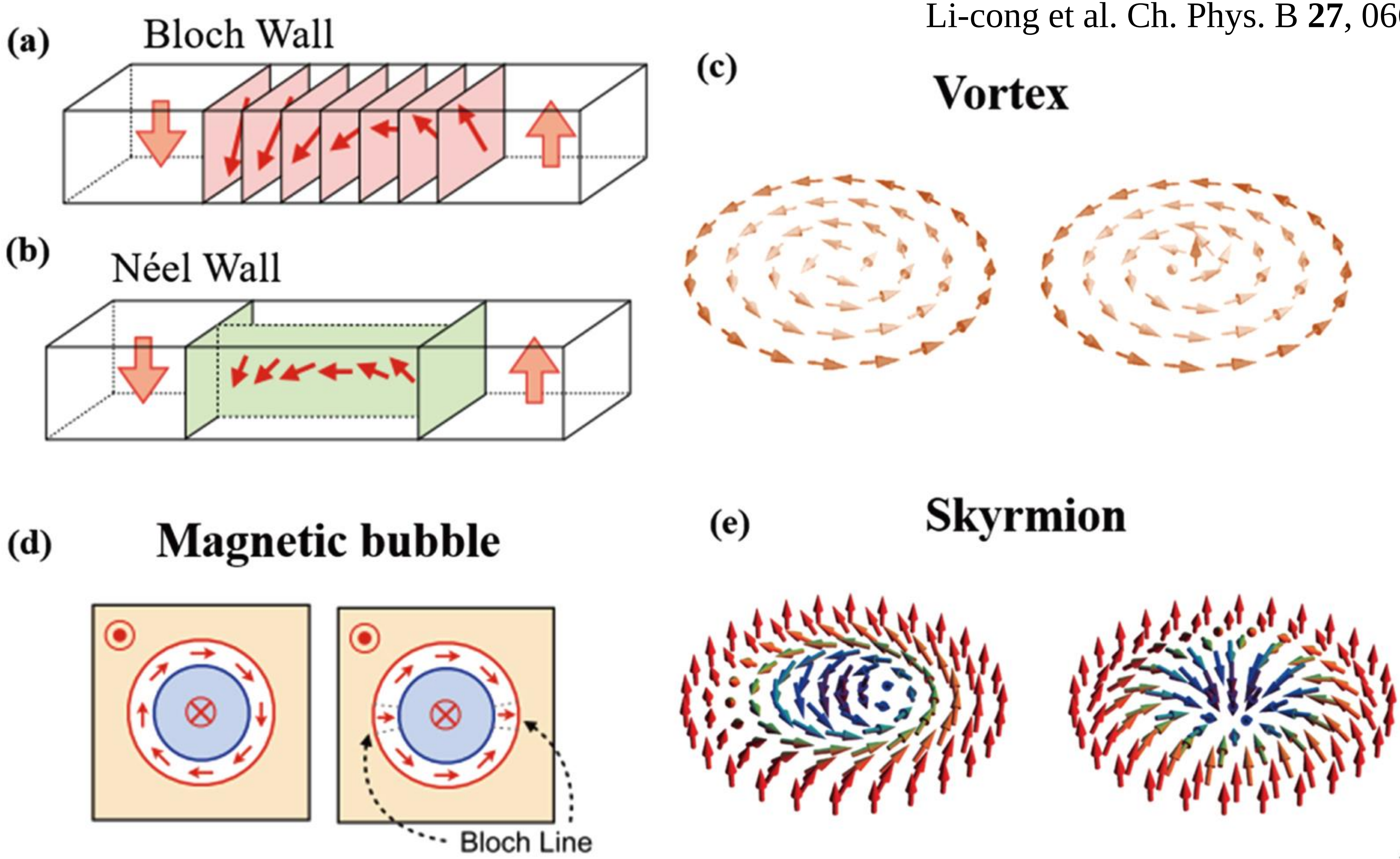


Effect of defocusing

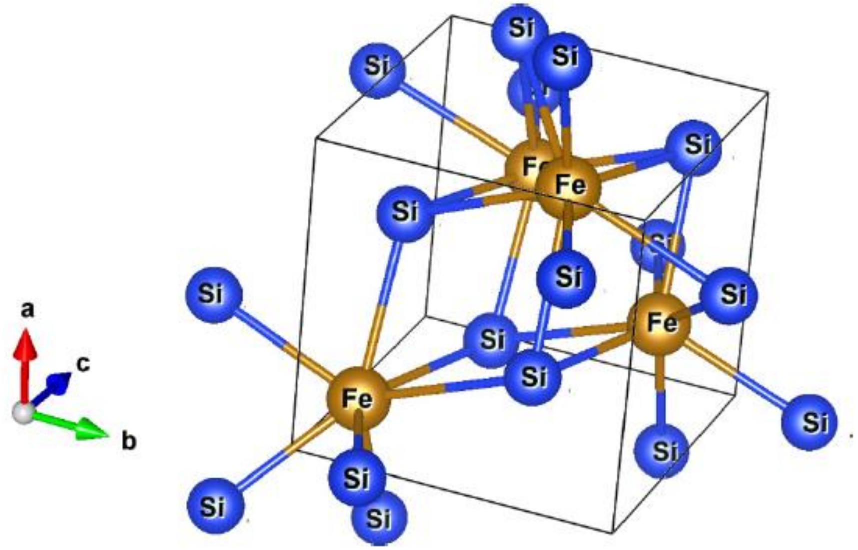


Spatially localized magnetic structures

Li-cong et al. Ch. Phys. B **27**, 066802 (`18)



Real space observations of spin structures by Lorentz microscope



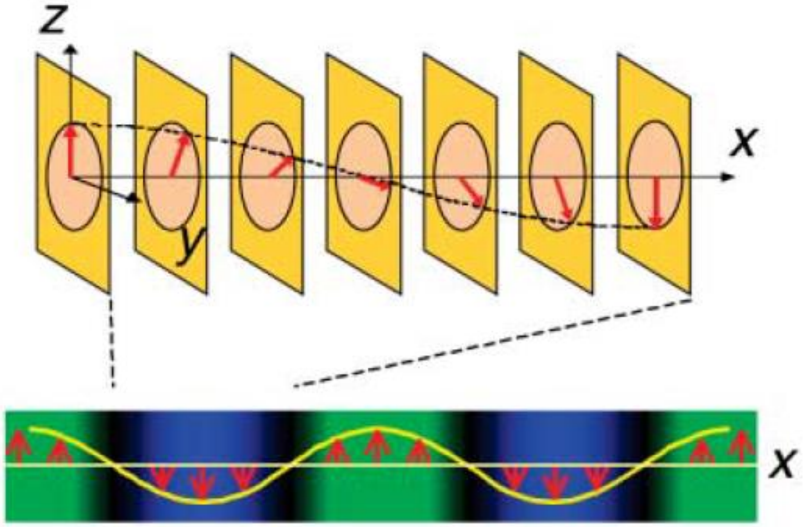
ε-FeSi B20-type cubic non-centro-symmetric lattice

↓

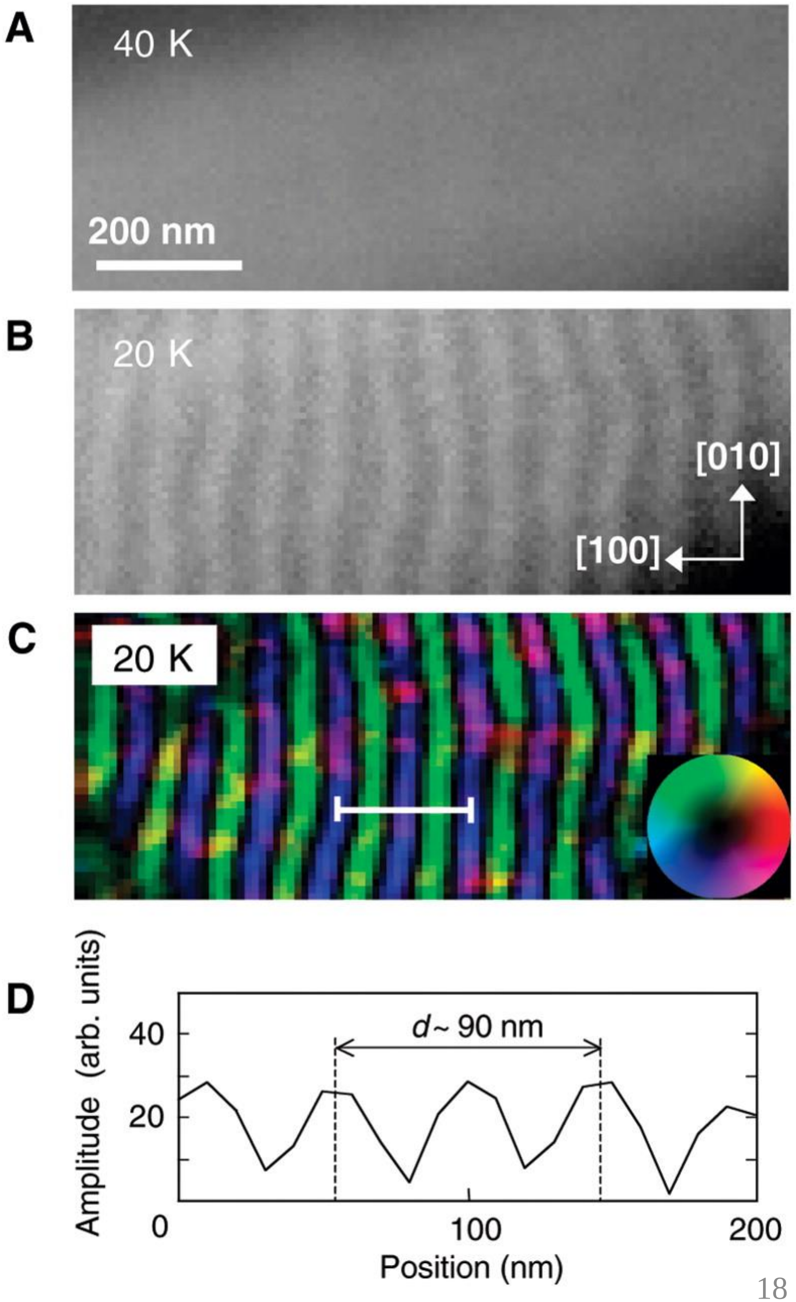
Dzyalosinsky-Moriya interaction causes helimagnetism

Uchida et al., Science **311**, 359 (`06)

$Fe_{1-x}Co_xSi$



Helical structure can be detected in the Fresnel mode of Lorentz microscope.

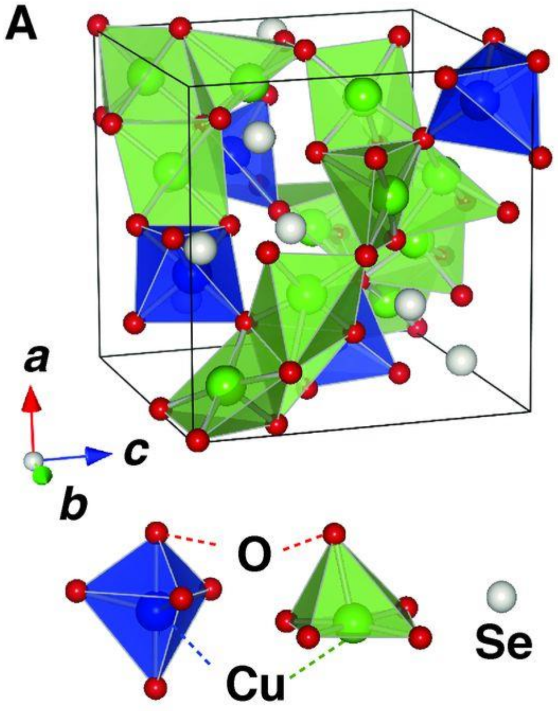


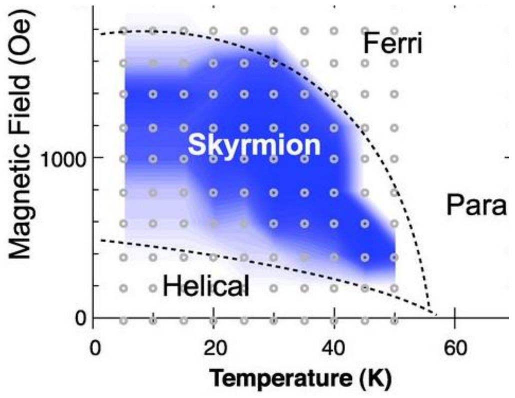
Observation of skyrmions by Lorentz microscope

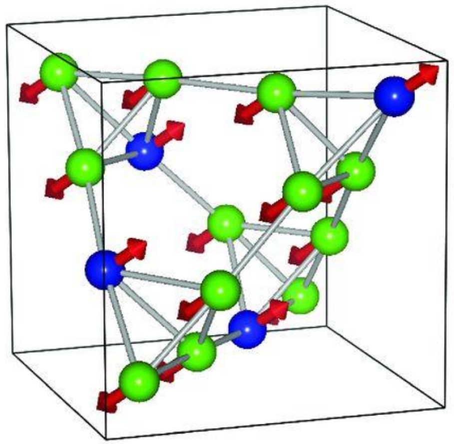
Cu_2OSeO_3

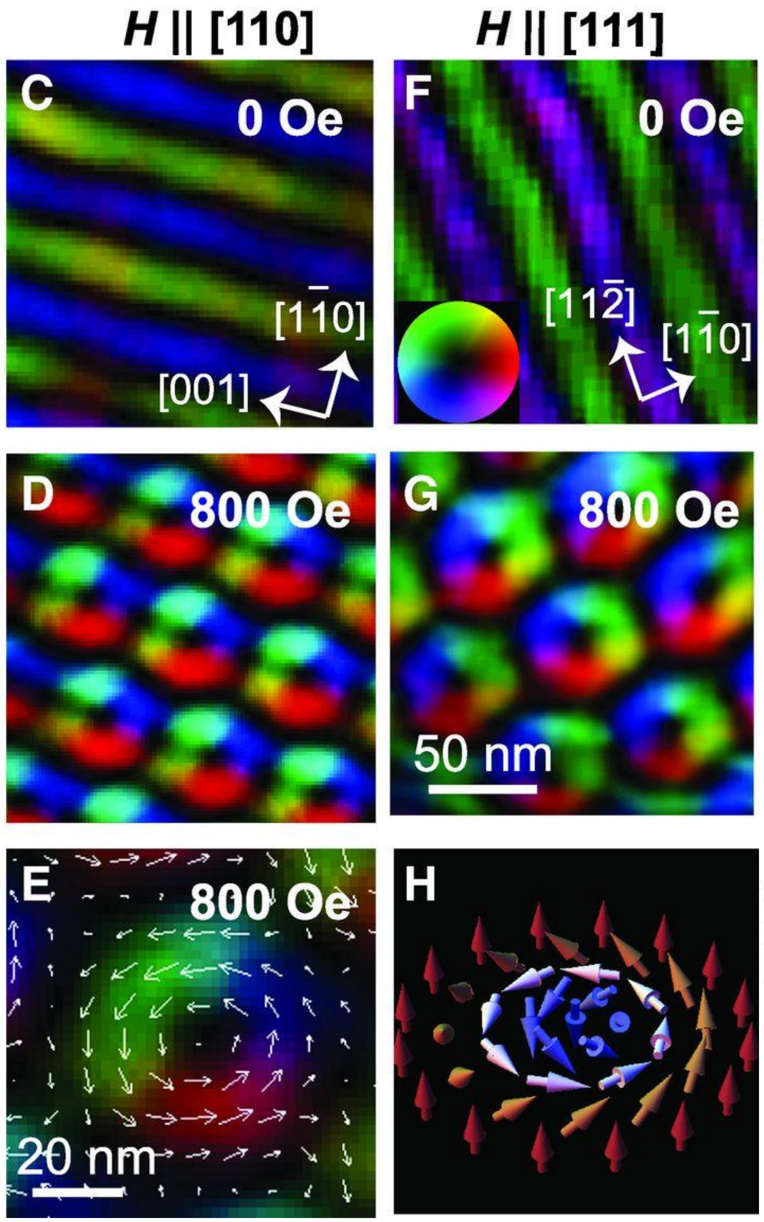
The DM interaction causes helimagnetism.

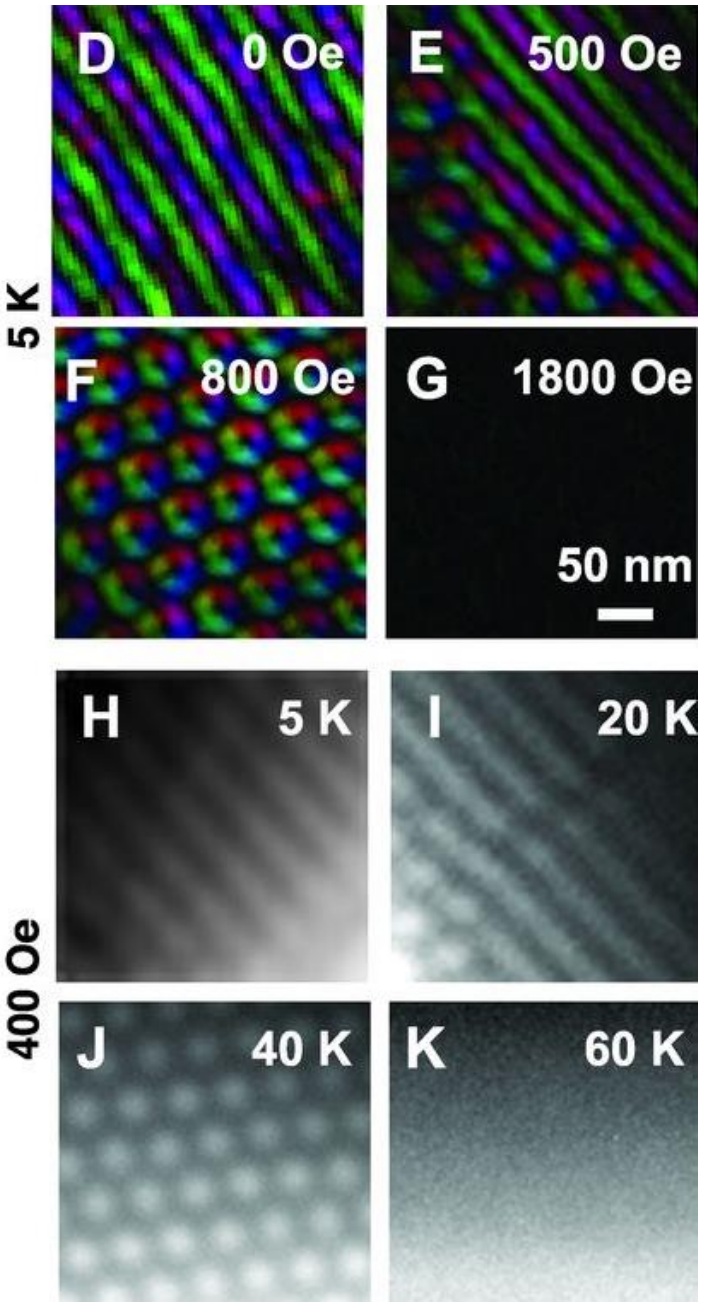
Seki et al.
Science **336**, 198 (`12)











Spin wave (ferromagnetic)

Ferromagnetic Heisenberg model $\mathscr{H} = -2J\sum_{\langle i,j\rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - \mu \sum_i \boldsymbol{B} \cdot \boldsymbol{S}_i$

Heisenberg equation of motion can be re-written as a torque equation

$$\hbar \frac{d\boldsymbol{S}_i}{dt} = \frac{1}{i}[\boldsymbol{S}_i, \mathscr{H}] = -2J\sum_\delta \boldsymbol{S}_{i+\delta} \times \boldsymbol{S}_i - \mu \boldsymbol{B} \times \boldsymbol{S}_i$$

$$\left[\begin{array}{l} [S^\alpha, S^\beta] = iS^\gamma, (\alpha, \beta, \gamma) = (x, y, z; \text{cyclic}) \\ [S_i^x, S_i^x S_j^x + S_i^y S_j^y + S_i^z S_j^z] = [S_i^x, S_i^y S_j^y] + [S_i^x, S_i^z S_j^z] = i(S_i^z S_j^y - S_i^y S_j^z) = i(\boldsymbol{S}_j \times \boldsymbol{S}_i)_x \end{array} \right]$$

$$\boldsymbol{S}_{\boldsymbol{q}} = \frac{1}{\sqrt{N}} \sum_i \boldsymbol{S}_i \exp(-i\boldsymbol{q} \cdot \boldsymbol{r}_i), \quad J_{\boldsymbol{q}} = \sum_\delta J \exp[-i\boldsymbol{q} \cdot (\boldsymbol{r}_i - \boldsymbol{r}_{i+\delta})]$$

Fourier transformed equation of motion $\hbar \frac{d\boldsymbol{S}_{\boldsymbol{q}}}{dt} = -\frac{2}{\sqrt{N}} \sum_{\boldsymbol{q}'} J_{\boldsymbol{q}'} \boldsymbol{S}_{\boldsymbol{q}'} \times \boldsymbol{S}_{\boldsymbol{q}-\boldsymbol{q}'} - \mu \boldsymbol{B} \times \boldsymbol{S}_{\boldsymbol{q}}$

$\langle \boldsymbol{S}_{\boldsymbol{0}} \rangle = \sqrt{N} S \boldsymbol{e}_z$ has much larger value than others.

Then we can approximate $\hbar \frac{d\boldsymbol{S}_{\boldsymbol{q}}}{dt} = -[2(J_{\boldsymbol{0}} - J_{\boldsymbol{q}})S + \mu B]\boldsymbol{e}_z \times \boldsymbol{S}_{\boldsymbol{q}}$

Spin wave (ferromagnetic) (2)

These equation represents precession around z-axis (in Fourier space)

$$\begin{cases} \hbar \dfrac{dS_{\boldsymbol{q}x}}{dt} = \quad [2(J_{\boldsymbol{0}} - J_{\boldsymbol{q}})S + \mu B]S_{\boldsymbol{q}y}, \\ \hbar \dfrac{dS_{\boldsymbol{q}y}}{dt} = -[2(J_{\boldsymbol{0}} - J_{\boldsymbol{q}})S + \mu B]S_{\boldsymbol{q}x}, \\ \hbar \dfrac{dS_{\boldsymbol{q}z}}{dt} = 0 \end{cases}$$

Hence we write $S_{\boldsymbol{q}x} + iS_{\boldsymbol{q}y} \propto \exp[-i\epsilon_{\boldsymbol{q}} t/\hbar]$

to obtain the excitation energy $\epsilon_{\boldsymbol{q}} = 2(J_{\boldsymbol{0}} - J_{\boldsymbol{q}})S + \mu B$

Holstein-Primakoff transformation

Summary

- Anti-ferromagnetic Heisenberg model : parallel field susceptibility
- Spin flop and metamagnetic transition
- Ferrimagnetism
- Molecular-field approximation
- Helimagnetism
- Spin wave

2022.06.15 Lecture 10

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Review

- Anti-ferromagnetic Heisenberg model : parallel field susceptibility
- Spin flop and metamagnetic transition

- Ferrimagnetism
- Molecular-field approximation

- Helimagnetism

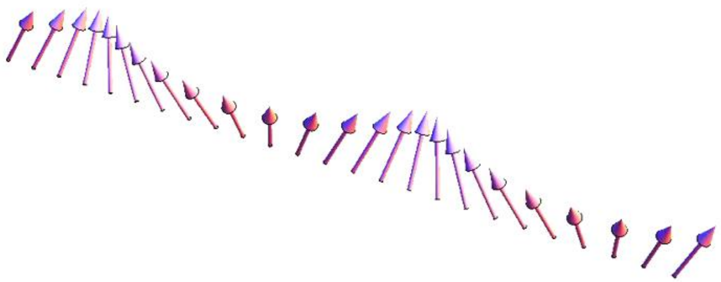
- Spin wave

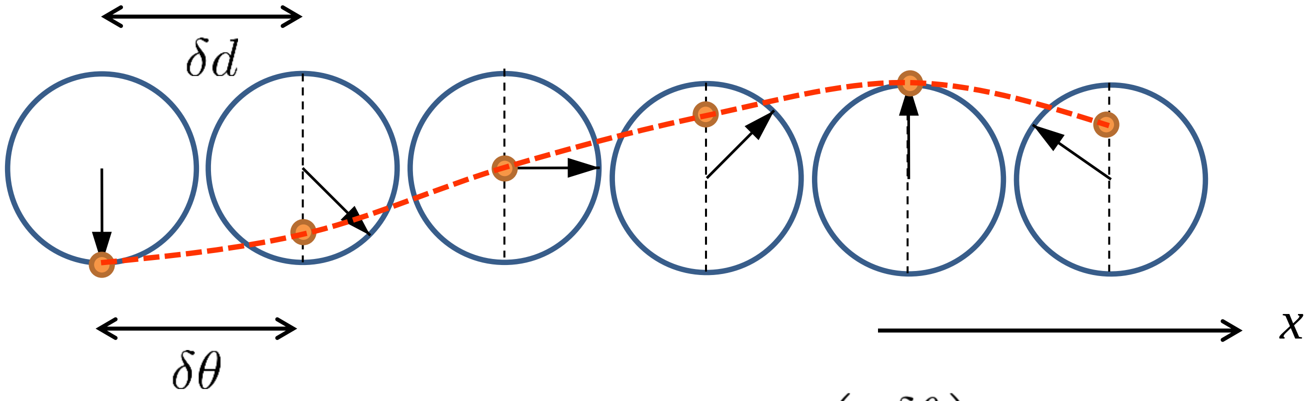
Outline

- Spin wave (classical) in a ferromagnet
- Quantization of spin wave (magnon)
- Magnons in an anti-ferromagnet
- Magnon approximation for weak excitations in ferro- and anti-ferromagnets
- Nambu-Goldstone mode in phase transition
- Experiments on magnons

Spin wave from phase shift of spin precessions

https://www.youtube.com/watch?v=pWQ3r-2Xjeo





snapshot $$S_x = S_0 \cos(n\delta\theta) = S_0 \cos\left(x\frac{\delta\theta}{\delta d}\right) = S_0 \cos kx$$

$$S = S_x + iS_y = S_0 \exp(ikx)$$

cf. Bloch electrons → Magnons can be described in magnetic Brillouin zone.

Total spin $\boldsymbol{S} = \sum_i \boldsymbol{S}_i$ Heisenberg equation: $i\hbar\frac{\partial \boldsymbol{S}}{\partial t} = [\boldsymbol{S}, \mathscr{H}]$

Such a motion of macroscopic magnetic moment can be confirmed by Ferromagnetic resonance (FMR)

Phase shifts of precessions with sites:

$$S_{ix} = A\cos(\omega_0 t + \theta_i), \quad S_{iy} = A\sin(\omega_0 t + \theta_i)$$

Then a snapshot should be expressed in a Fourier form.

However for ω_0 we need to consider the spin-spin interaction.

Equations of motion in the momentum space

Fourier transform, inverse Fourier transform:

$$S_{\boldsymbol{q}x} = \frac{1}{\sqrt{N}} \sum_j S_{jz} \exp(-i\boldsymbol{q}\cdot\boldsymbol{r}_j), \quad S_{jx} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{q}} S_{\boldsymbol{q}x} \exp(i\boldsymbol{q}\cdot\boldsymbol{r}_j)$$

Heisenberg Hamiltonian, equation of motion:

$$\mathscr{H} = -2J \sum_{\langle i,j\rangle} \hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j \ , \qquad i\hbar\frac{\partial \boldsymbol{S}}{\partial t} = [\boldsymbol{S}, \mathscr{H}]$$

Substituting the above Fourier transforms into equation of motion, we obtain a set of equations of motion in the momentum space as:

$$\begin{cases} i\hbar\dfrac{\partial S_{\boldsymbol{q}x}}{\partial t} = \dfrac{4i}{\sqrt{N}} J \displaystyle\sum_{\langle i,j\rangle} S_{iy}S_{jz}\exp(-i\boldsymbol{q}\cdot\boldsymbol{r}_i)\{1-\exp[i\boldsymbol{q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)]\} \\ i\hbar\dfrac{\partial S_{\boldsymbol{q}y}}{\partial t} = -\dfrac{4i}{\sqrt{N}} J \displaystyle\sum_{\langle i,j\rangle} S_{ix}S_{jz}\exp(-i\boldsymbol{q}\cdot\boldsymbol{r}_i)\{1-\exp[i\boldsymbol{q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)]\}. \end{cases}$$

Fourier transform of interaction *J*:

$$J_{\boldsymbol{q}} = \sum_j J\exp[i\boldsymbol{q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)]$$

(*i* can be taken somewhere)

Nearest neighbor approximation:

Small angle approximation, i.e., replace S_{jz} with S:

$$\begin{cases} \hbar\dfrac{\partial S_{\boldsymbol{q}x}}{\partial t} = 2[J_0 - J_{\boldsymbol{q}}]SS_{\boldsymbol{q}y}, \\ \hbar\dfrac{\partial S_{\boldsymbol{q}y}}{\partial t} = -2[J_0 - J_{\boldsymbol{q}}]SS_{\boldsymbol{q}x}. \end{cases}$$

Spin wave (ferromagnetic)

These are the equation we obtained in the last lecture but B:

$$\hbar \frac{d\boldsymbol{S}_{\boldsymbol{q}}}{dt} = -[2(J_{\boldsymbol{0}} - J_{\boldsymbol{q}})S + \mu B]\boldsymbol{e}_z \times \boldsymbol{S}_{\boldsymbol{q}}$$

These equation represents precession around z-axis (in Fourier space)

$$\begin{cases} \hbar \dfrac{dS_{\boldsymbol{q}x}}{dt} = \quad [2(J_{\boldsymbol{0}} - J_{\boldsymbol{q}})S + \mu B]S_{\boldsymbol{q}y}, \\ \hbar \dfrac{dS_{\boldsymbol{q}y}}{dt} = -[2(J_{\boldsymbol{0}} - J_{\boldsymbol{q}})S + \mu B]S_{\boldsymbol{q}x}, \\ \hbar \dfrac{dS_{\boldsymbol{q}z}}{dt} = 0 \end{cases}$$

Hence we write

$$S_{\boldsymbol{q}x} + iS_{\boldsymbol{q}y} \propto \exp[-i\epsilon_{\boldsymbol{q}} t/\hbar]$$

to obtain the excitation energy

$$\epsilon_{\boldsymbol{q}} = 2(J_{\boldsymbol{0}} - J_{\boldsymbol{q}})S + \mu B$$

Remember the message:

$$\left[\begin{array}{l} S_{ix} = A\cos(\omega_0 t + \theta_i), \quad S_{iy} = A\sin(\omega_0 t + \theta_i) \\ \text{However for } \omega_0 \text{ we need to consider the spin-spin interaction.} \end{array} \right]$$

Holstein-Primakoff transformation

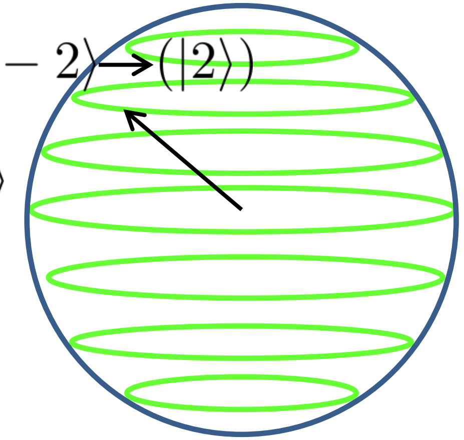
Let us consider the quantization of the spin wave.

Spin operator: $\boldsymbol{S}$ $\quad |m\rangle$: eigenfunction of S_z with eigenvalue of m.

We define up/down operator as: $S_\pm = S_x \pm S_y$

Then from the properties of spin operator:
$$\left.\begin{aligned} S_+ |m\rangle &= \sqrt{S(S+1) - m(m+1)}\, |m+1\rangle \\ S_- |m\rangle &= \sqrt{S(S+1) - m(m-1)}\, |m-1\rangle \end{aligned}\right\}$$

This is as if we are treating number states $|n\rangle$.



Let us introduce boson creation/annihilation operators: $a^\dagger,\ a$
$$\begin{cases} a_j |n_j\rangle = \sqrt{n_j}\, |n_j - 1\rangle \\ a_j^\dagger |n_j\rangle = \sqrt{n_j + 1}\, |n_j + 1\rangle \end{cases}$$

"Vacuum" of the boson: $|S\rangle \quad (S_z = S)$

n-boson state: $|S - n\rangle$

Then as is for ordinary boson operators, we obtain: $a|S\rangle = 0, \quad |S-n\rangle = \dfrac{1}{\sqrt{n!}}(a^\dagger)^n |S\rangle$

With number operator $\hat{n} = a^\dagger a$ we can write
$$\left.\begin{aligned} S_z &= S - \hat{n}, \\ S_+ &= \sqrt{2S - \hat{n}}\, a, \\ S_- &= a^\dagger \sqrt{2S - \hat{n}} \end{aligned}\right\}$$
Holstein-Primakoff transformation

Non-interacting spin wave approximation

In Holstein-Primakoff transformation we have nonlinear terms. → Interaction between the bosons.

Expand the square roots in Holstein-Primakoff transformation

$$\left.\begin{aligned}\hat{S}_{j+} &= \sqrt{2S}\left(1-\frac{a_j^\dagger a_j}{4S}+\cdots\right)a_j,\\ \hat{S}_{j-} &= \sqrt{2S}a_j^\dagger\left(1-\frac{a_j^\dagger a_j}{4S}+\cdots\right)\end{aligned}\right\}$$

Then the Hamiltonian is expanded as

$$\begin{aligned}\mathscr{H} &= -2\sum_{\langle i,j\rangle} J_{ij}\hat{\boldsymbol{S}}_i\cdot\hat{\boldsymbol{S}}_j = -2\sum_{\langle i,j\rangle} J_{ij}\{\hat{S}_{iz}\hat{S}_{jz}+(\hat{S}_{i+}\hat{S}_{j-}+\hat{S}_{i-}\hat{S}_{j+})/2\}\\ &= -2\sum_{\langle i,j\rangle} J_{ij}\left[S^2-S(\hat{n}_i+\hat{n}_j)+S(a_i^\dagger a_j+a_j^\dagger a_i)+\hat{n}_i\hat{n}_j-\frac{1}{4}a_i^\dagger a_j^\dagger a_j a_j-\frac{1}{4}a_j^\dagger a_j^\dagger a_j a_i+\cdots\right].\end{aligned}$$

Take up to quadratic terms

$$\mathscr{H} = -2\sum_{\langle i,j\rangle} J_{ij}[S^2-S(\hat{n}_i+\hat{n}_j)+S(a_i^\dagger a_j+a_j^\dagger a_i)]$$

Ferromagnetic spin wave: ferromagnetic magnon

Fourier transform of creation/annihilation operators:

$$a_{\boldsymbol{q}} = \frac{1}{\sqrt{N}} \sum_j a_j \exp(i\boldsymbol{q}\cdot\boldsymbol{r}),$$
$$a_{\boldsymbol{q}}^\dagger = \frac{1}{\sqrt{N}} \sum_j a_j \exp(-i\boldsymbol{q}\cdot\boldsymbol{r})$$

Substitute these to the approximated Hamiltonian

Magnon Hamiltonian

$$\mathscr{H} = -2\sum_{\langle i,j\rangle} J_{ij}S^2 + 2\sum_{\boldsymbol{q}}[J_{\boldsymbol{0}} - J_{\boldsymbol{q}}]S a_{\boldsymbol{q}}^\dagger a_{\boldsymbol{q}}$$
$$= E_0 + \sum_{\boldsymbol{q}} \hbar\omega_{\boldsymbol{q}} a_{\boldsymbol{q}}^\dagger a_{\boldsymbol{q}}$$

Total magnetization: $M = \mu\left\langle \sum_i S_{iz}\right\rangle = \mu SN - \mu\sum_i \langle a_i^\dagger a_i\rangle = \mu SN - \mu \sum_{\boldsymbol{q}} n(\epsilon_{\boldsymbol{q}})$

with Bose distribution function: $n(\epsilon) = \left(\exp\frac{\epsilon}{k_{\mathrm{B}}T} - 1\right)^{-1}$

Magnon dispersion

$$\hbar\epsilon_{\boldsymbol{q}} = 2S(J_{\boldsymbol{0}} - J_{\boldsymbol{q}}) = 2SJ\{2 - [\exp(iqa) + \exp(-iqa)]\} \simeq 2SJ\left[2 - 2\left(1 - \frac{(qa)^2}{2}\right)\right] = \underline{2SJ(qa)^2}$$

Then we obtain $M = \mu N\left[S - \zeta\left(\frac{3}{2}\right)\left(\frac{k_{\mathrm{B}}T}{8\pi JS}\right)^{3/2}\right]$ $\zeta(z) = \sum_{n=1}^{\infty}\frac{1}{n^2}$ $\zeta\left(\frac{3}{2}\right) \approx 2.612$

Why we have introduced the concept: Magnon?

Low temperature Magnetic moment: $$M = \mu N \left[S - \zeta\left(\frac{3}{2}\right)\left(\frac{k_{\mathrm{B}}T}{8\pi JS}\right)^{3/2} \right] \qquad \zeta(z) = \sum_{n=1}^{\infty} \frac{1}{n^2} \qquad \zeta\left(\frac{3}{2}\right) \approx 2.612$$

The internal energy is: $$U = E_0 + \sum_{\boldsymbol{q}} n(\epsilon_{\boldsymbol{q}}) = E_0 + 12\pi JSN\zeta\left(\frac{5}{2}\right)\left(\frac{k_{\mathrm{B}}T}{8\pi JS}\right)^{5/2}.$$

Then low temperature specific heat is obtained by $$C = \frac{\partial U}{\partial T} = \frac{15}{4} N k_{\mathrm{B}} \zeta\left(\frac{5}{2}\right)\left(\frac{k_{\mathrm{B}}T}{8\pi JS}\right)^{3/2}$$

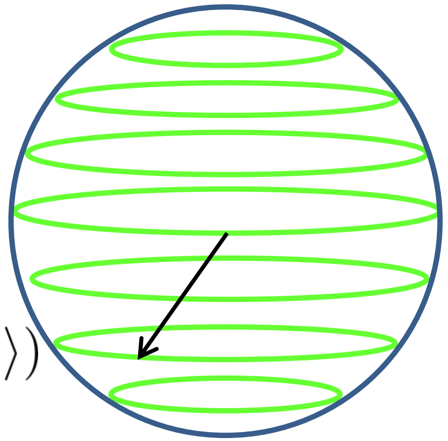
As above, by considering magnons we can calculate low energy excitations and obtain important quantities.

Magnons: Low temperature model of ferro (anti-ferro) magnets.

Spin wave modeling of anti-ferromagnets

Anti-ferromagnet → Decompose into A, B sublattices

A sublattice: we can consider magnon model



$|-S+2\rangle \rightarrow (|2\rangle)$

$|-S\rangle \rightarrow (|0\rangle)$

vacuum

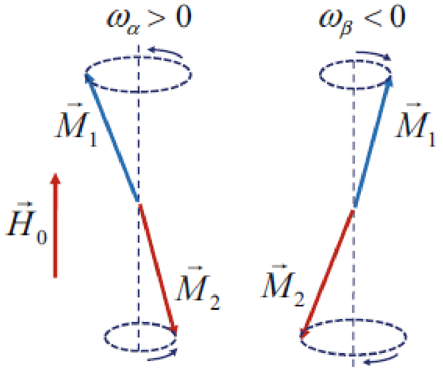
B sublattice: Magnetization is reversed

Take the vacuum as $|0\rangle_{\mathrm{B}} = |-S\rangle$

Boson creation/annihilation operators $b_j^\dagger, \quad b_j$

Then the Holstein-Primakoff transform is

$$\left.\begin{aligned} S_{jz} &= -S + b_j^\dagger b_j, \\ S_{j+} &= b_j^\dagger \sqrt{2S - b_j^\dagger b_j}, \\ S_{j-} &= \sqrt{2S - b_j^\dagger b_j}\, b_j \end{aligned}\right\}$$



Quadratic Hamiltonian : $\mathscr{H} = -\alpha_z |J| N S^2 + 2|J|S \sum_{\langle i,j \rangle} (a_i^\dagger a_i + b_j^\dagger b_j + a_i b_j + a_i^\dagger b_j^\dagger) \qquad i \in \mathrm{A}, \quad j \in \mathrm{B}$

Spin wave modeling of anti-ferromagnets (2)

Fourier transformation of creation/annihilation operators

$$\left.\begin{aligned} a_i &= \sqrt{\frac{2}{N}} \sum_{\boldsymbol{q}} a_{\boldsymbol{q}} \exp(-i\boldsymbol{q}\cdot\boldsymbol{r}_i), \\ b_j &= \sqrt{\frac{2}{N}} \sum_{\boldsymbol{q}} b_{\boldsymbol{q}} \exp(-i\boldsymbol{q}\cdot\boldsymbol{r}_j) \end{aligned}\right\}$$

Momentum representation of the Hamiltonian

$$\mathscr{H} = -\alpha_z|J|NS^2 + 2\alpha_z|J|S\sum_{\boldsymbol{q}}[a^\dagger_{\boldsymbol{q}}a_{\boldsymbol{q}} + b^\dagger_{\boldsymbol{q}}b_{\boldsymbol{q}} + \gamma(\boldsymbol{q})(a^\dagger_{\boldsymbol{q}}b^\dagger_{\boldsymbol{q}} + a_{\boldsymbol{q}}b_{\boldsymbol{q}})]$$

with nearest neighbor summation

$$\gamma(\boldsymbol{q}) = \alpha_z^{-1}\sum_{\boldsymbol{\rho}}\exp(-i\boldsymbol{q}\cdot\boldsymbol{\rho})$$

But the above Hamiltonian is still not diagonalized. (Néel ordered state is not true ground state.)

Bogoluibov transformation

$(a_{\boldsymbol{q}}, b_{\boldsymbol{q}}) \to (\alpha_{\boldsymbol{q}}, \beta_{\boldsymbol{q}})$

$$\left.\begin{aligned} a_{\boldsymbol{q}} &= \cosh\theta_{\boldsymbol{q}}\alpha_{\boldsymbol{q}} - \sinh\theta_{\boldsymbol{q}}\beta^\dagger_{\boldsymbol{q}}, \\ b_{\boldsymbol{q}} &= \cosh\theta_{\boldsymbol{q}}\beta_{\boldsymbol{q}} - \sinh\theta_{\boldsymbol{q}}\alpha^\dagger_{\boldsymbol{q}}. \end{aligned}\right\}$$

Bosonic commutation relations

$$[\alpha_{\boldsymbol{q}}, \alpha^\dagger_{\boldsymbol{q}}] = 1, \quad [\beta_{\boldsymbol{q}}, \beta^\dagger_{\boldsymbol{q}}] = 1, \quad [\alpha_{\boldsymbol{q}}, \beta_{\boldsymbol{q}}] = [\alpha^\dagger_{\boldsymbol{q}}, \beta^\dagger_{\boldsymbol{q}}] = 0$$

Spin wave modeling of anti-ferromagnets (3)

$$\mathscr{H} = -\alpha_z|J|NS^2 + 2\alpha_z|J|S\sum_{\boldsymbol{q}}[(\cosh 2\theta_{\boldsymbol{q}} - \gamma(\boldsymbol{q})\sinh\theta_{\boldsymbol{q}})(\alpha^\dagger_{\boldsymbol{q}}\alpha_{\boldsymbol{q}} + \beta^\dagger_{\boldsymbol{q}}\beta_{\boldsymbol{q}} + 1) - 1$$
$$- (\sinh 2\theta_{\boldsymbol{q}} - \gamma(\boldsymbol{q})\cosh 2\theta_{\boldsymbol{q}})(\alpha_{\boldsymbol{q}}\beta_{\boldsymbol{q}} + \alpha^\dagger_{\boldsymbol{q}}\beta^\dagger_{\boldsymbol{q}})]$$

Condition for diagonalization: $\sinh 2\theta_{\boldsymbol{q}} / \cosh 2\theta_{\boldsymbol{q}} = \tanh 2\theta_{\boldsymbol{q}} = \gamma(\boldsymbol{q})$

Diagonalized Hamiltonian: $\mathscr{H} = -\alpha_z|J|NS^2 + 2\alpha_z|J|S\sum_{\boldsymbol{q}}[(\sqrt{1-\gamma(\boldsymbol{q})^2} - 1) + \sqrt{1-\gamma(\boldsymbol{q})^2}(\alpha^\dagger_{\boldsymbol{q}}\alpha_{\boldsymbol{q}} + \beta^\dagger_{\boldsymbol{q}}\beta_{\boldsymbol{q}})]$

Ground state energy: $-\alpha_z|J|NS^2 + 2\alpha_z|J|S\sum_{\boldsymbol{q}}[(\sqrt{1-\gamma(\boldsymbol{q})^2} - 1)$

Néel ordered state energy

Energy lowering due to hybridization of $S, S-1, \cdots, -S$ states

⇓

$\langle S_{jz}\rangle$ is shorter than S

How? $\langle S_{jz}\rangle = S - \frac{2}{N}\sum_{\boldsymbol{q}}\sinh\theta_{\boldsymbol{q}} = S - \frac{1}{N}\sum_{\boldsymbol{q}}\left(\frac{1}{\sqrt{1-\gamma(\boldsymbol{q})^2}} - 1\right)$

Spin wave modeling of anti-ferromagnets (4)

$$\langle S_{jz}\rangle = S - \Delta \qquad E_0 = N|J|\alpha_z S(S+\epsilon)$$

Lattice	Square	Simple Cubic	Body Centered Cubic
Δ	0.917	0.078	0.0593
ϵ	$0.158+0.0062S^{-1}$	$0.097+0.0024S^{-1}$	$0.073+0.0013S^{-1}$

Magnon dispersion $\epsilon_{\boldsymbol{q}} = 2\alpha_z|J|S\sqrt{1-\gamma(\boldsymbol{q})^2}$ Simple cubic case $\gamma(\boldsymbol{q}) = \cos\frac{q_x}{2}\cos\frac{q_y}{2}\cos\frac{q_z}{2}$

Asymptotic form $q \to 0$ $\epsilon_{\boldsymbol{q}} = 2\sqrt{2\alpha_z}|J|Saq$

Internal energy $U = E_0 + \frac{\pi^2}{15}N\left(\frac{k_\mathrm{B}T}{2\sqrt{2\alpha_z}|J|S}\right)^3 k_\mathrm{B}T$

Results

Lattice	1D Chain	2D Square Lattice	3D Simple Cubic
$-\frac{E_0}{\alpha_z|J|NS^2}$	$1+0.363S^{-1}$	$1+0.158S^{-1}$	$1+0.097S^{-1}$
$\frac{C}{Nk_\mathrm{B}}$	$\frac{2\pi}{3}\left(\frac{k_\mathrm{B}T}{2\alpha_z|J|S}\right)$	$\frac{14.42}{\pi}\left(\frac{k_\mathrm{B}T}{2\alpha_z|J|S}\right)^2$	$4\sqrt{3}\frac{\pi^2}{5}\left(\frac{k_\mathrm{B}T}{2\alpha_z|J|S}\right)^3$
ΔS	Diverge	0.197	0.078

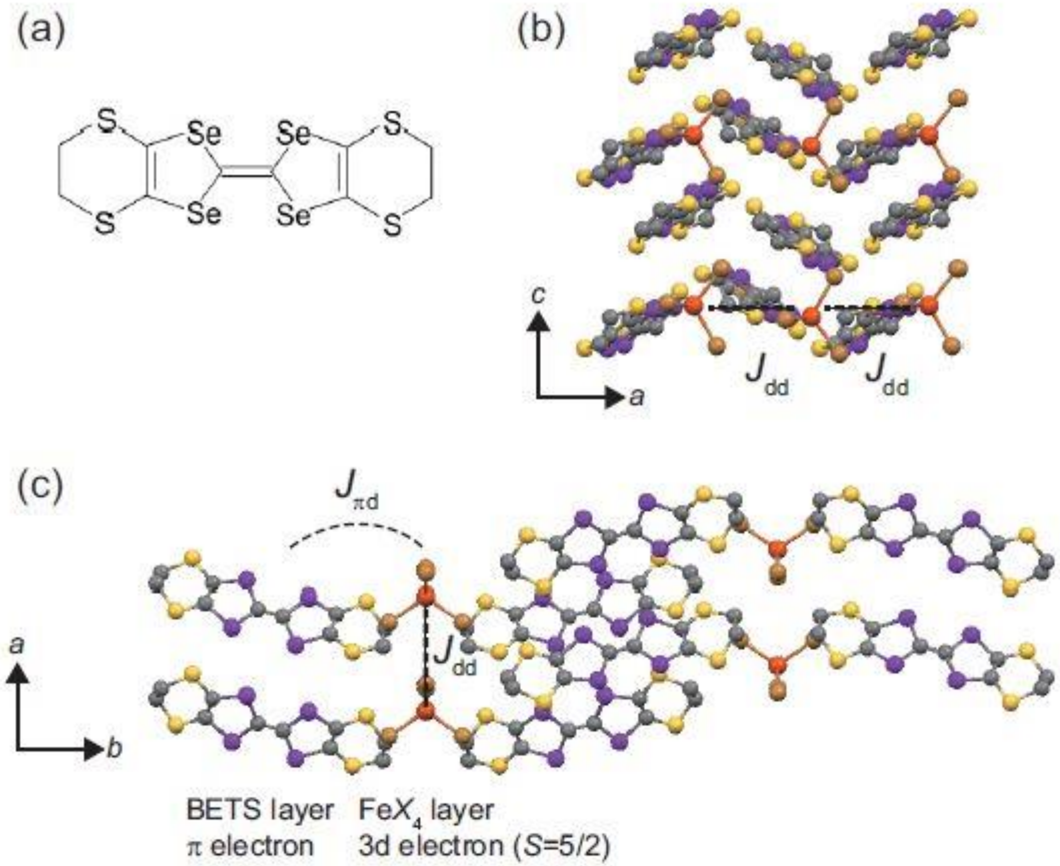
Specific heat of an organic anti-ferromagnet

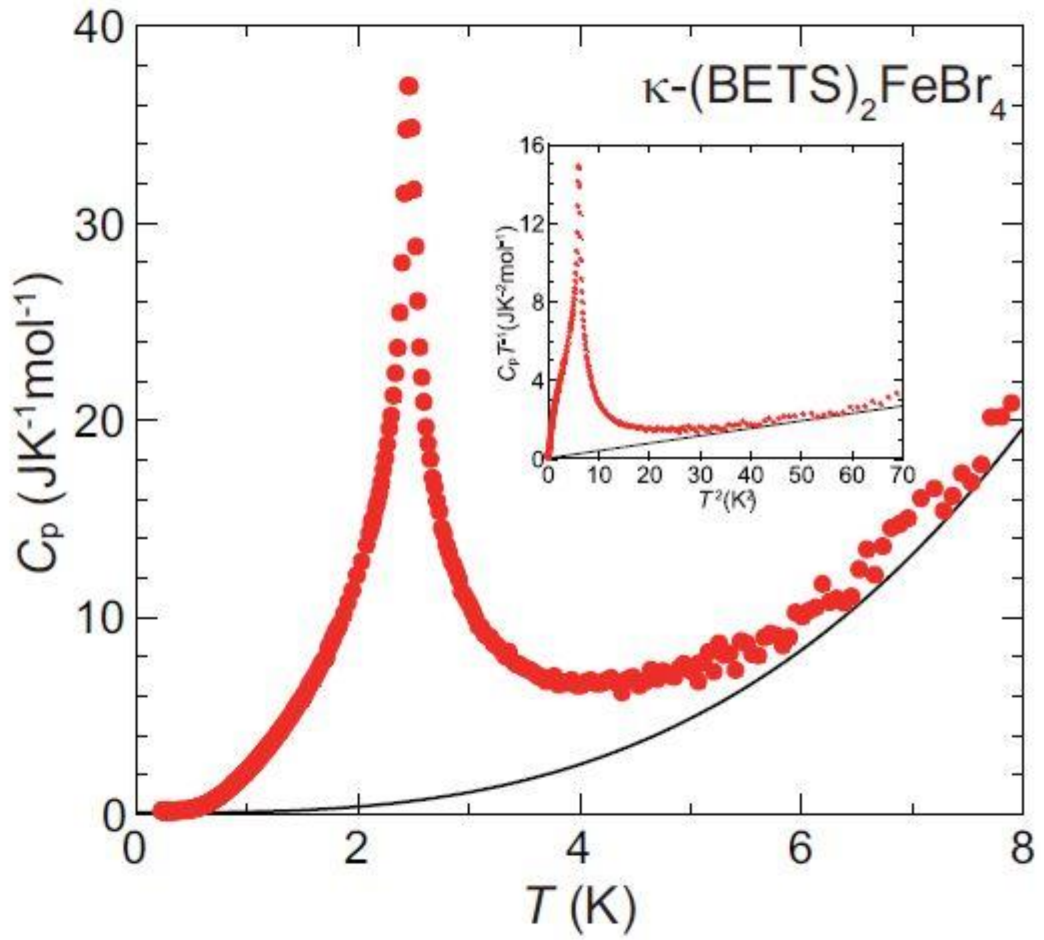
κ-$(\mathrm{BETS})_2\mathrm{FeBr}_4$

Anti-ferromagnetic T_N : 2.5 K

Superconducting T_c : 1.1 K

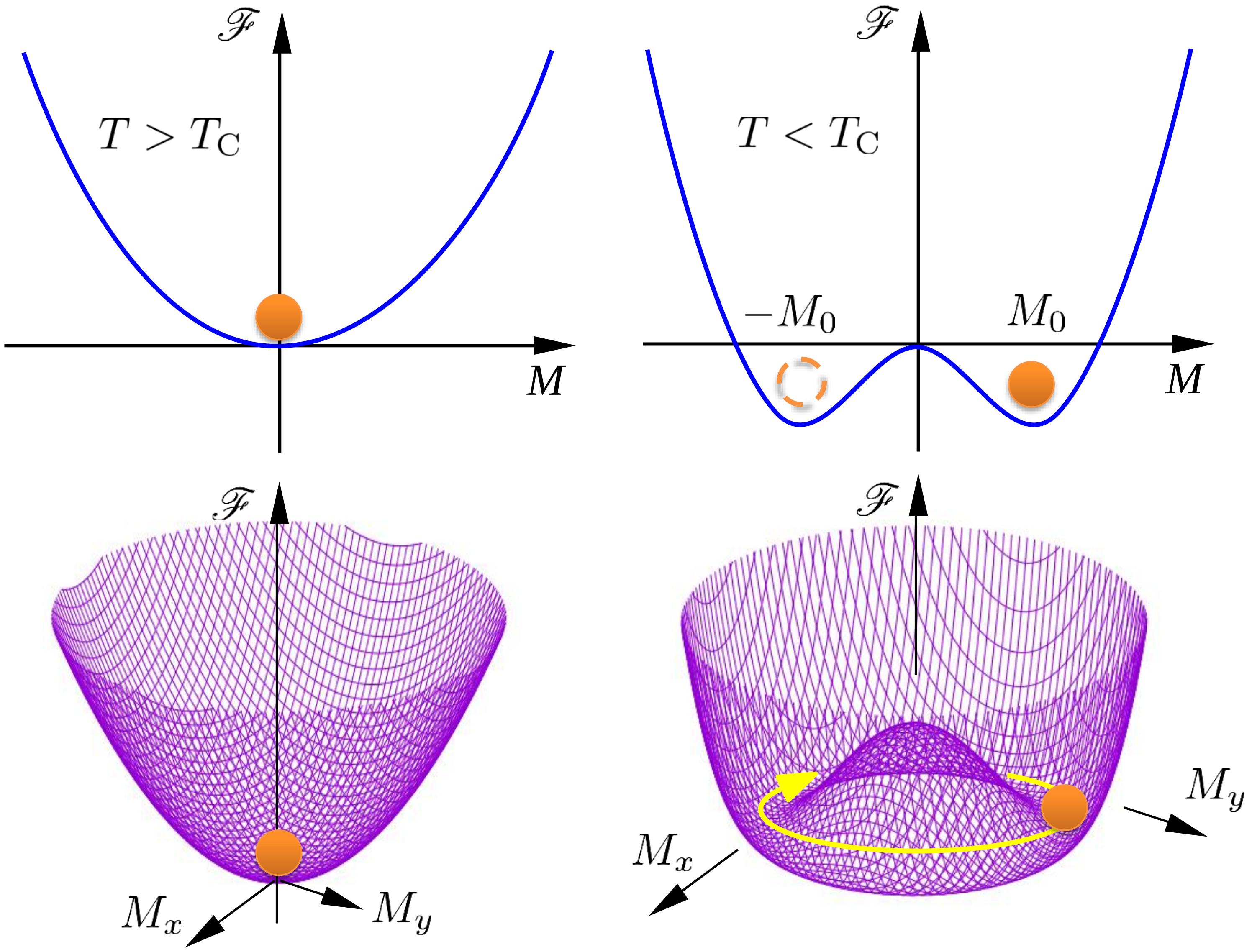
Normal metal specific heat: $C_\mathrm{m} = AT + BT^3$





Fukuoka et al., PRB **93**, 245136 (2016)

Spontaneous Symmetry Breaking and Nambu-Goldstone mode



Spontaneous symmetry breaking

Nambu-Goldstone theorem

When a spontaneous symmetry breaking takes place, a mode with zero energy at long wavelength limit appears.

$$E = mc^2$$
$$\downarrow \quad \downarrow$$
$$0 \quad 0$$ massless

Nambu-Goldston mode

(Nambu-Goldston boson)

Magnons in the case of ferromagnets (type-B) and anti-ferromagnets (type-A).

Generalization of Nambu-Goldstone theorem (column)

Nambu-Goldstone mode, Higgs mode → Birth of particle mass; Standard theory of elementary particles

The theories based on the principle prevail all over the physics.

However, there still have been many open questions!

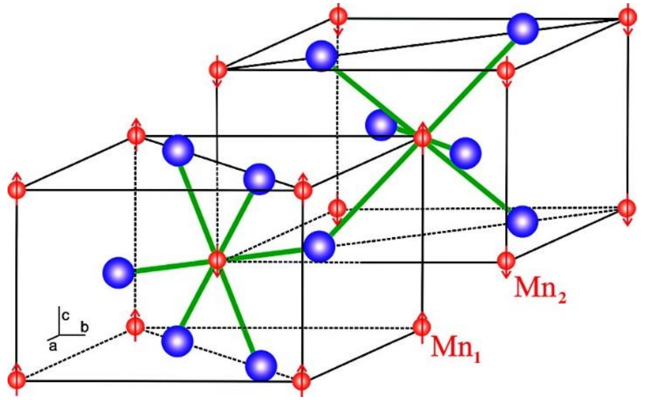
An example: According to the primitive statement, the number of NG mode should be the same as that of broken symmetries.

	Broken symmetry	**Number of NG modes**	**Number of broken symmetry**
N-G theorem		x	$y = x$
Crystal	Translational symmetry	3	3
3D Ferromagnet	Rotational symmetry	1	2
Spinor BEC	Rotational symmetry	2	3
Skymion crystal	Translational symmetry	1	2

Extended theorem (2012) : $x = y - \mathrm{rank} \langle [Q_a, Q_b] \rangle / 2$

Watanabe, Murayama PRL **108**, 25162 (2012); Hidaka PRL **110**, 091601 (2013); Hidaka, Minami PTEP 2020, 033A01

Magnon dispersion relation measurement in MnF_2



Neutron time-of-flight (TOF) measurement

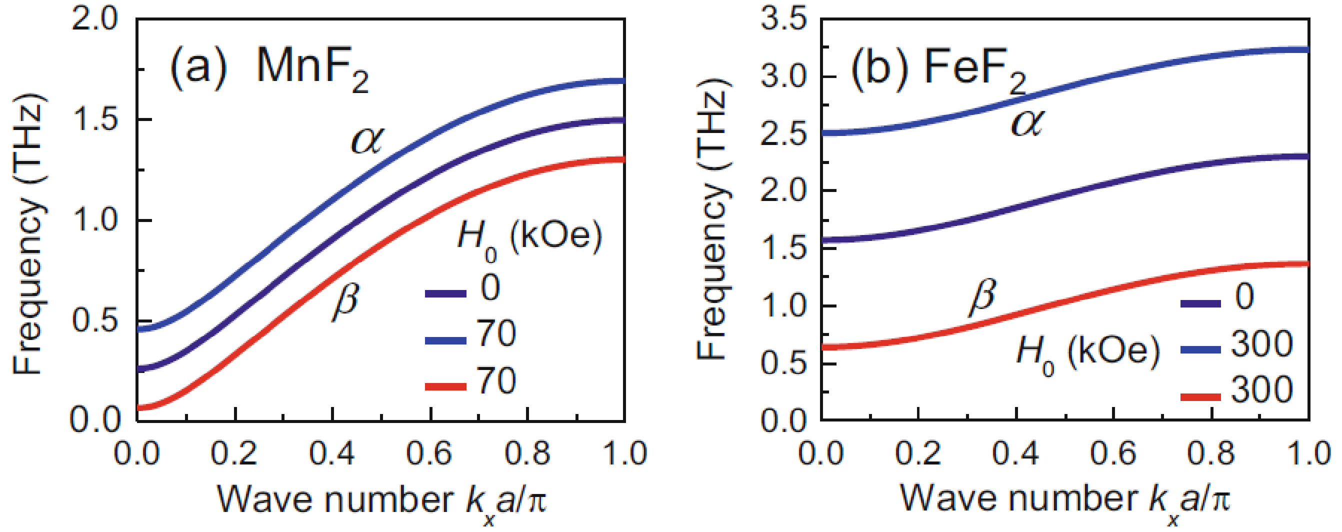
$$\mathscr{H}_{\rm int} = -\boldsymbol{\mu}_{\rm e} \cdot \boldsymbol{B}_{\rm n} \qquad \boldsymbol{B}_{\rm n} = {\rm rot}\left(\boldsymbol{\mu}_{\rm n} \times \frac{\boldsymbol{r}}{r^3}\right)$$

neutron magnetic field

electron moment

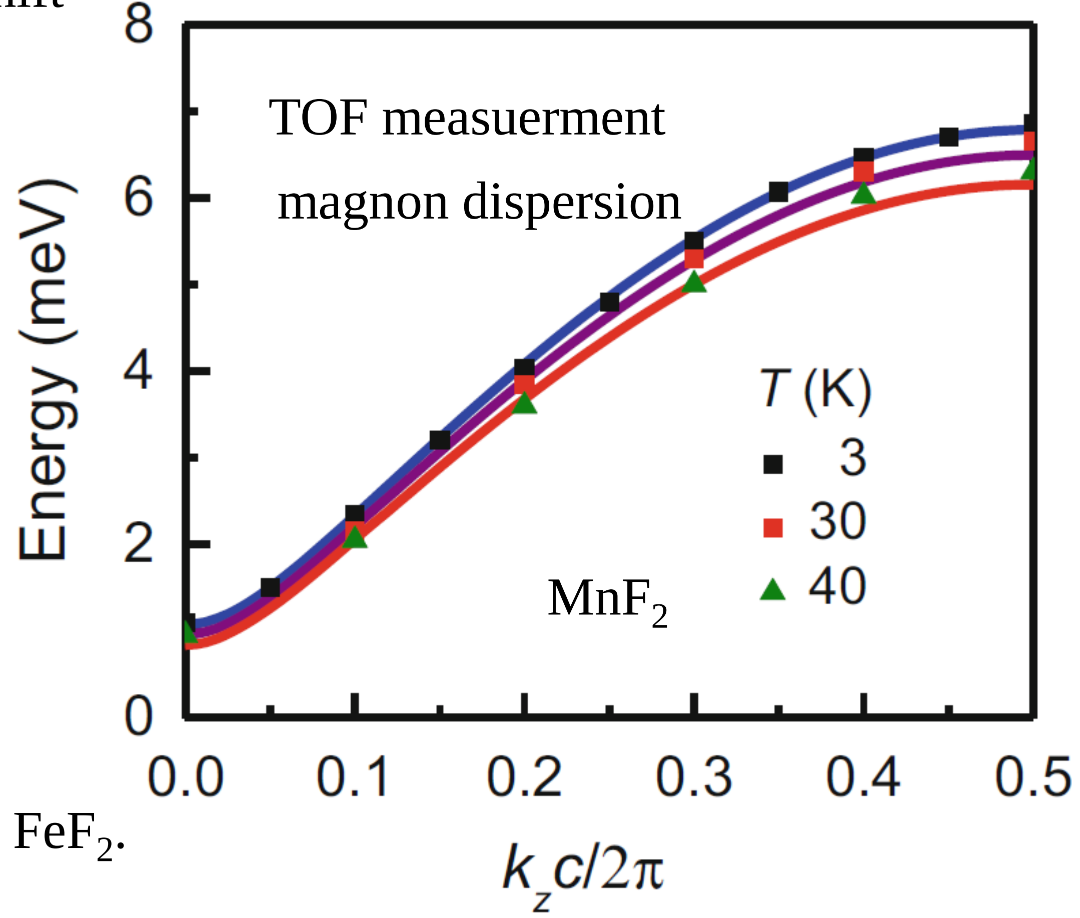
neutron inelastic scattering

$$\begin{cases} \hbar \boldsymbol{k} \longrightarrow \hbar(\boldsymbol{k} - \boldsymbol{q}) & \text{momentum shift} \\ \Delta E = \dfrac{\hbar^2}{2M}(-2\boldsymbol{k}\cdot\boldsymbol{q} + \boldsymbol{q}^2) & \text{energy loss} \end{cases}$$



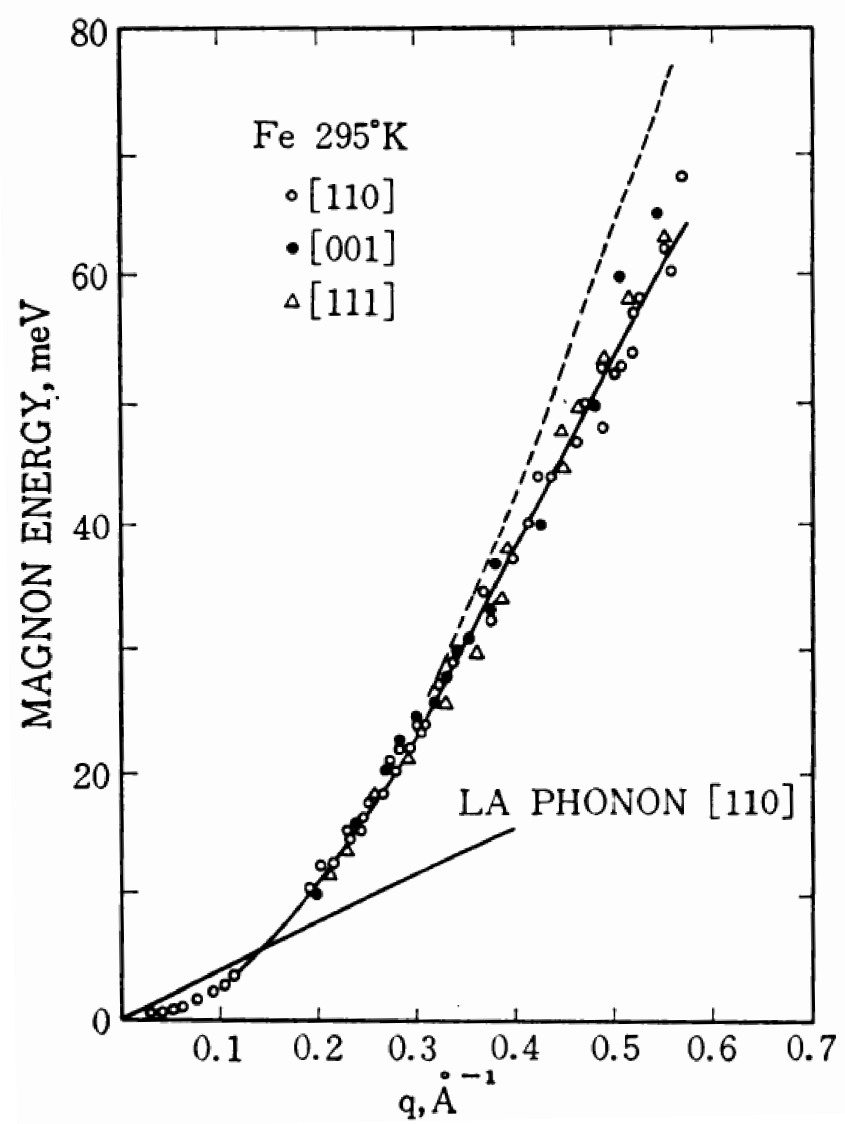
Calculated dispersions of anti-ferromagnetic magnons in MnF_2 and FeF_2.

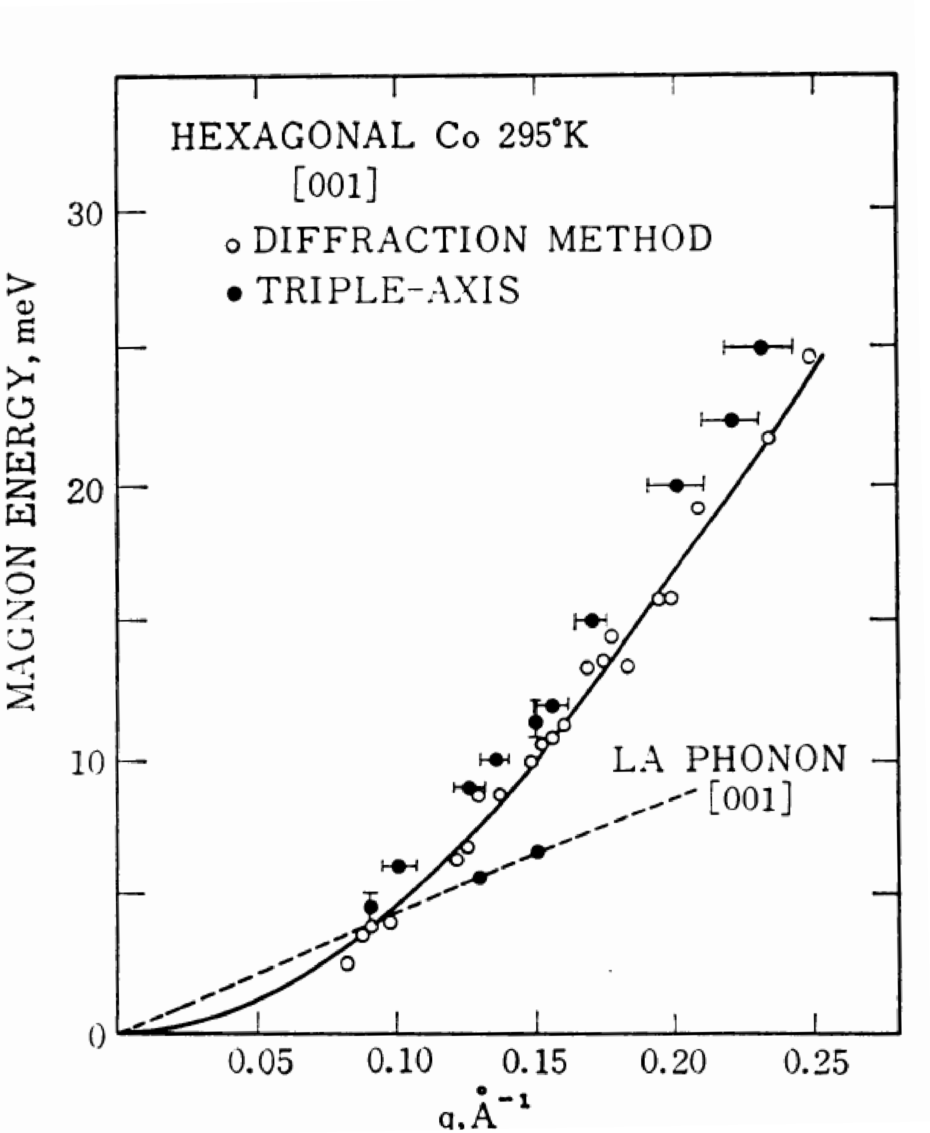
(Taken from *Fundamentals of Magnonics*.)



Low et al., JAP **35**, 998 (1964).

Magnon dispersions in metallic ferromagnets

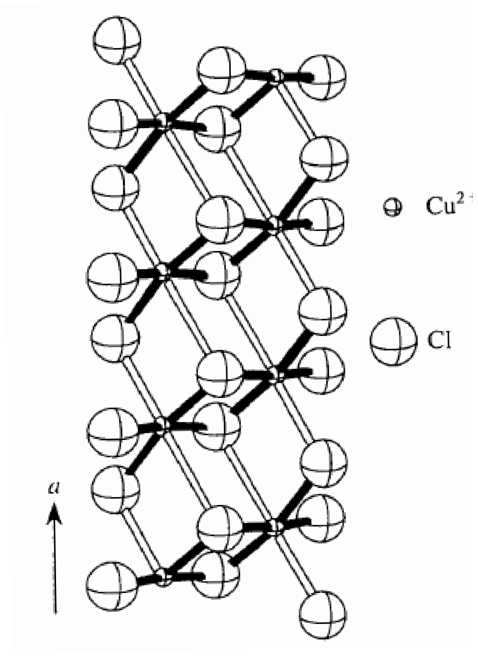


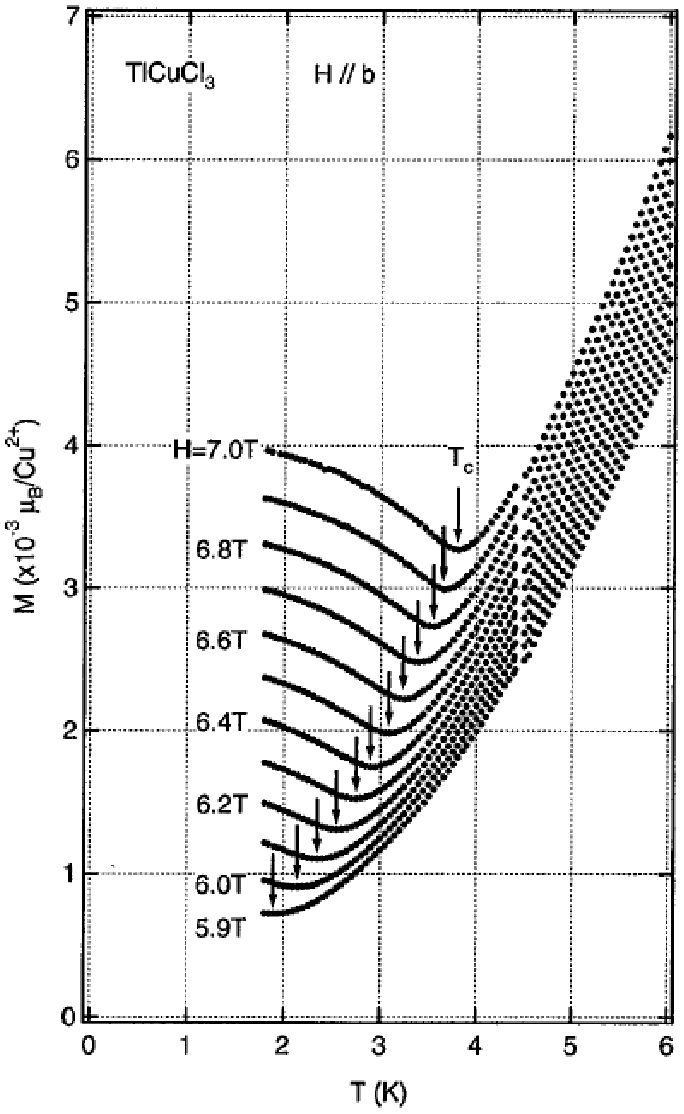


Bose-Einstein condensation of magnons

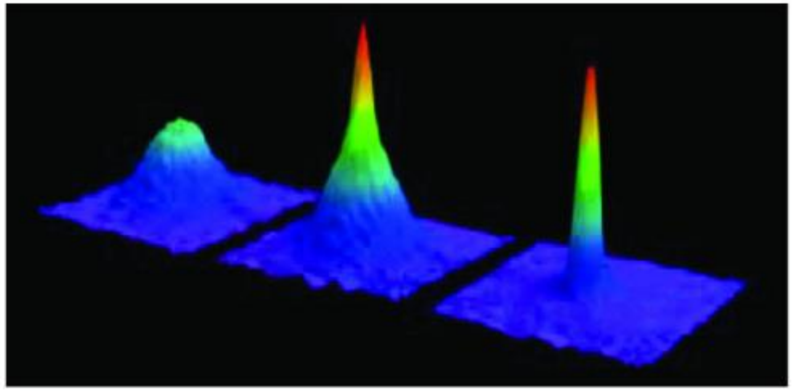
Magnons: not completely bosons (para statistics) however can be treated as "hard core" bosons

$TlCuCl_3$





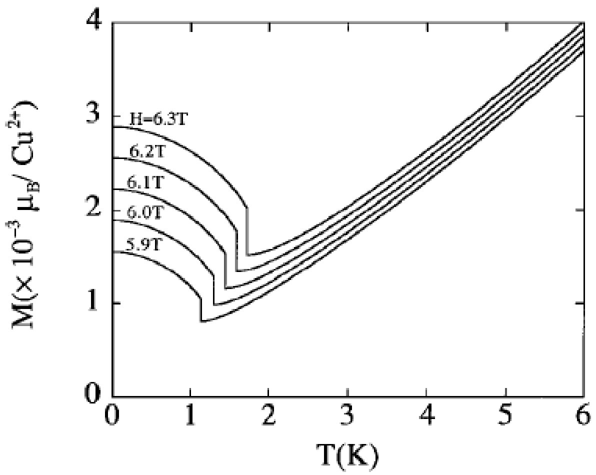
Sharp enhancement of magnetization

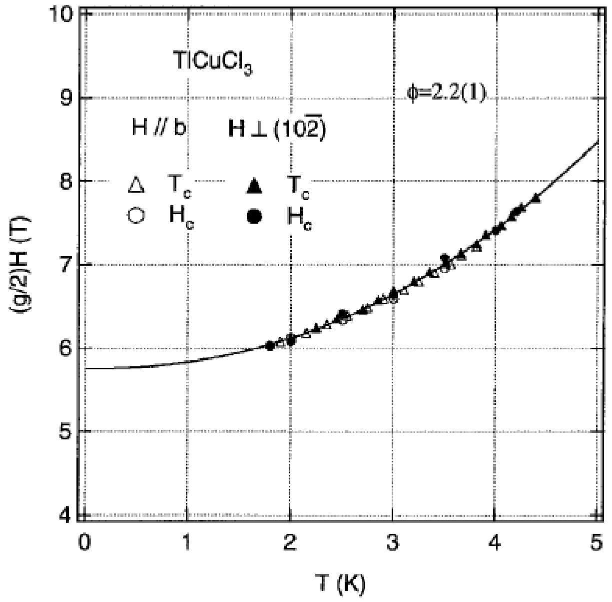


BEC in cold Rb atom ensemble

Sharp increase in particle density

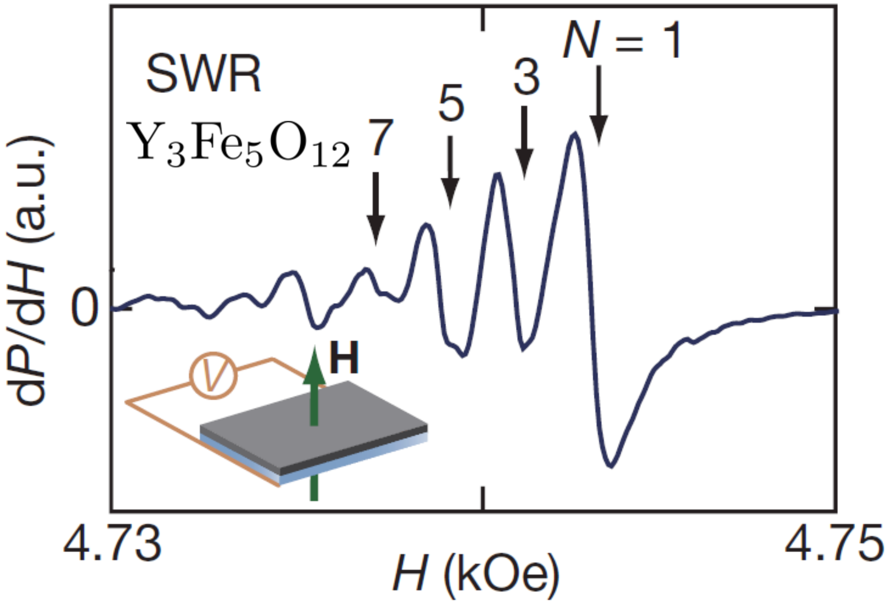
Theory





Nikuni et al., PRL **84**, 5868 (2000)

Magnon (spin wave) resonance in thin films



Kajiwara et al., Nature **464**, 262 (2010)

Spin wave resonance in a thin film

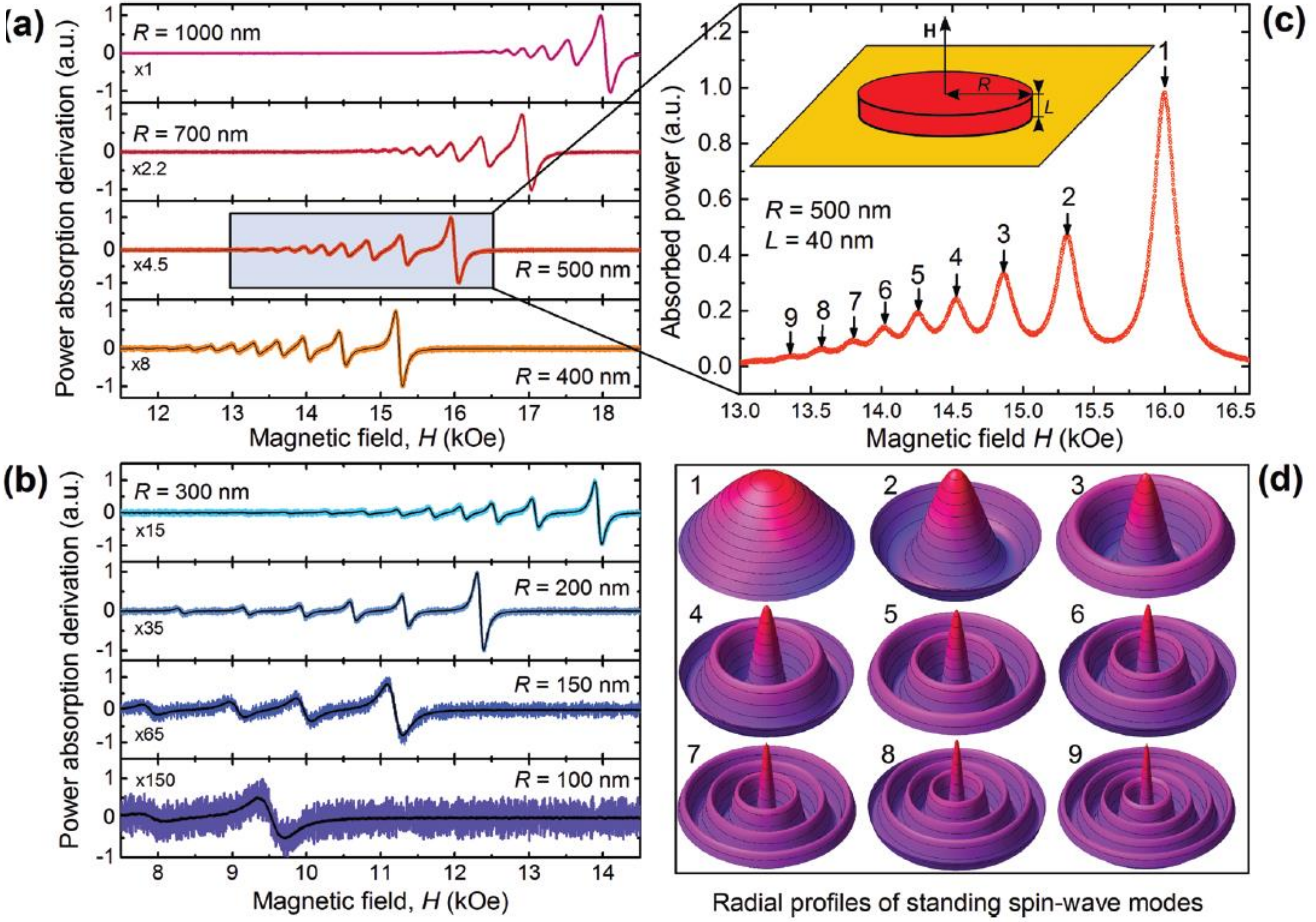
$$\frac{m}{\gamma} = \frac{B}{\mu_0} - 4\pi M_S + \frac{2Ak^2}{M_S}$$

$$k = \frac{p\pi}{L} \quad p: \text{odd number},$$

$$L: \text{ film thickness} \qquad A = \frac{\alpha_z S^2 J}{a}$$

Kittel Phys. Rev. **110**, 1295 (1958)

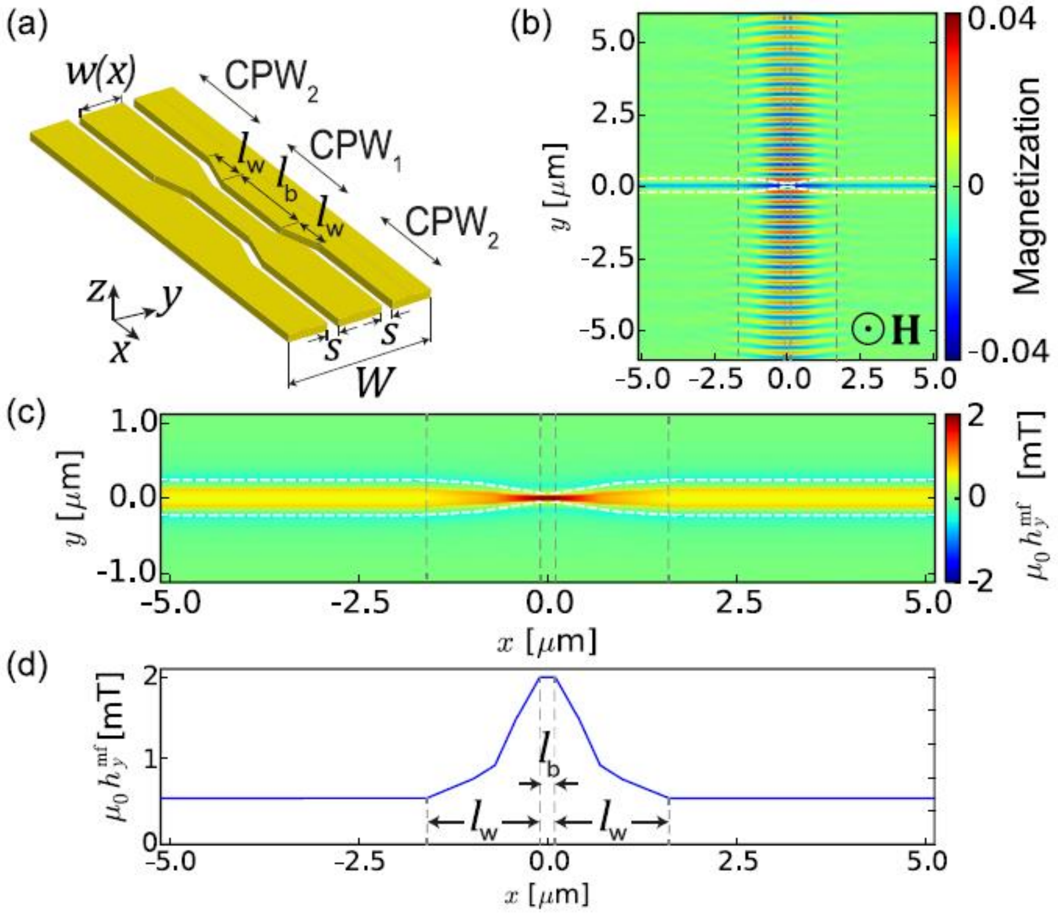
CoFe Nano disk



Dobrovolskiy et al., Nanoscale **12**, 21207 (2020).

Real space imaging of magnons

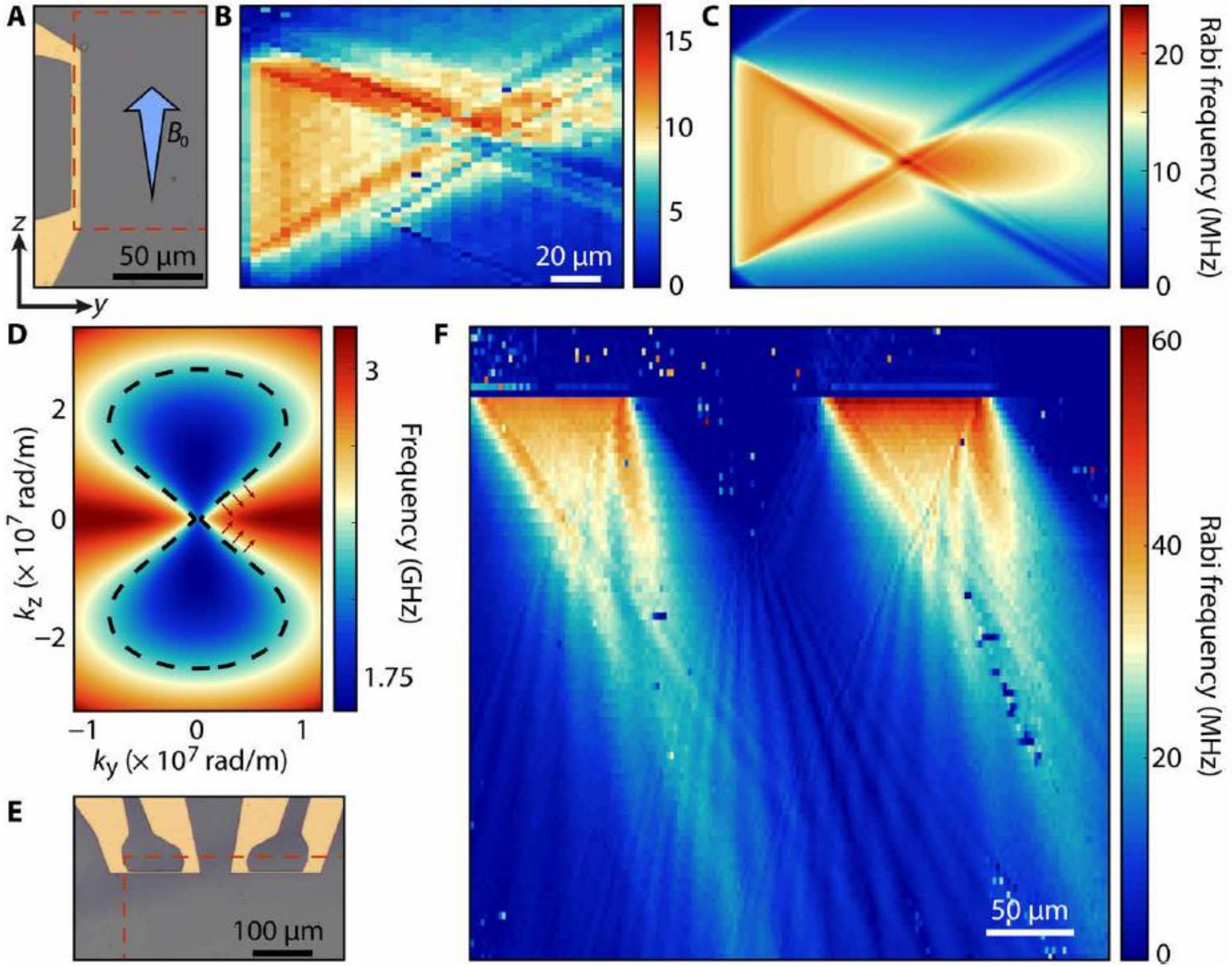
YIG



Gruszecki et al. Sci. Rep. **6**, 22367 (2016)

YIG

NV center ESR detection of magnon fields



Bertelli et al., Sci. Adv. **6**, eabd3556 (2020).

Summary

- Spin wave (classical) in a ferromagnet
- Quantization of spin wave (magnon)
- Magnons in an anti-ferromagnet
- Magnon approximation for weak excitations in ferro- and anti-ferromagnets
- Nambu-Goldstone mode in phase transition
- Experiments on magnons

2022.6.22 Lecture 11

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Review

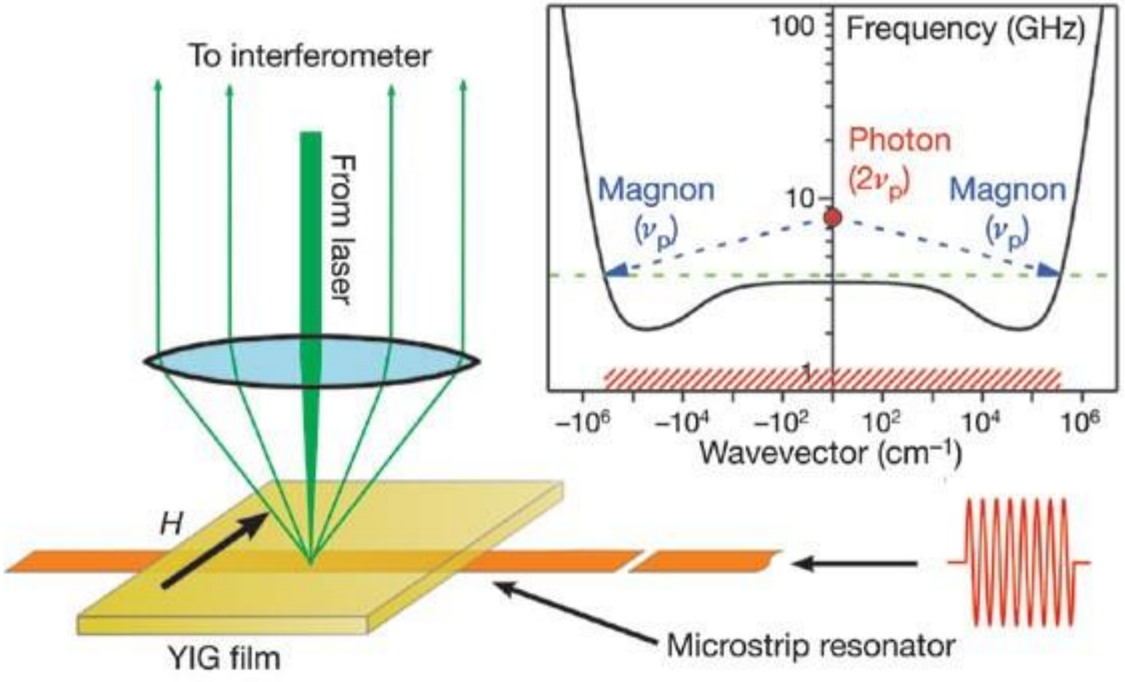
- Spin wave (classical) in a ferromagnet
- Quantization of spin wave (magnon)
- Magnons in an anti-ferromagnet
- Magnon approximation for weak excitations in ferro- and anti-ferromagnets
- Nambu-Goldstone mode in phase transition
- Experiments on magnons

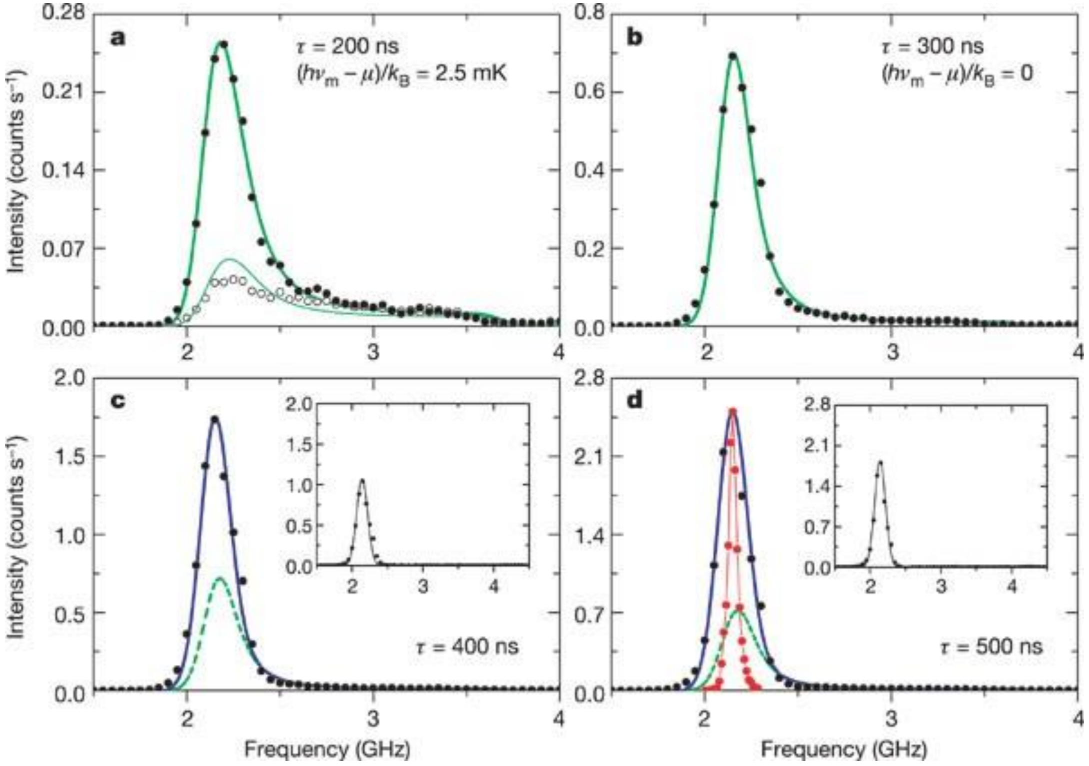
Outline

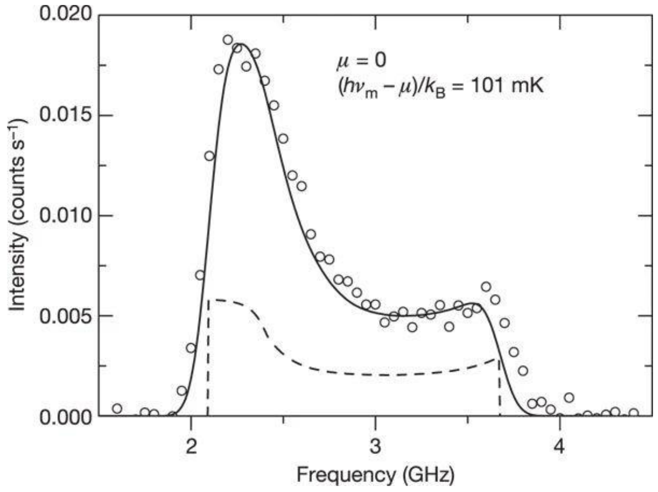
- Ferromagnetic and Antiferromagnetic resonance
- Spin wave resonance
- Experiments on magnons
- Scaling relations
- Renormalization group
- Derivation of scaling ansatz

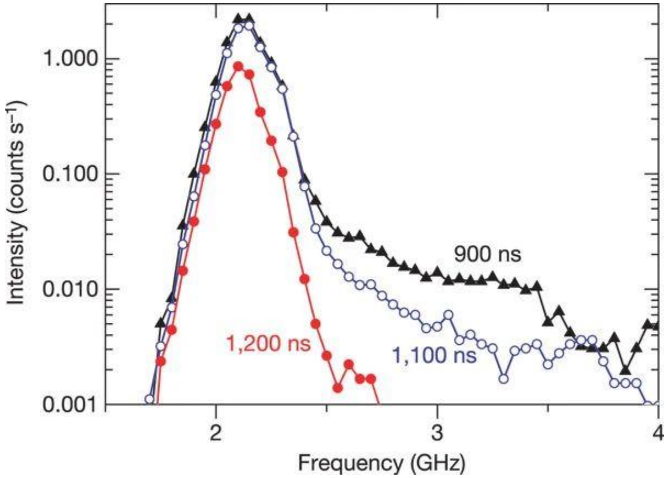
BEC of quasi-equilibrium magnons at room temperature

Demokritov et al., Nature 443, 431 (2006).









Ferromagnetic resonance

Free energy:

$$\mathscr{F} = \sum_{\langle i,j\rangle} \lambda_{ij} \boldsymbol{M}_i \cdot \boldsymbol{M}_j - \sum_{i,j} \boldsymbol{M}_i \mathbf{K}_{i,j} \boldsymbol{M}_j - \sum_i \boldsymbol{M}_i \cdot \left(\boldsymbol{H} - \mathbf{N} \sum_j \boldsymbol{M}_j \right),$$

In case of ferromagnetically ordered state:

$$= -\lambda M^2 + \underbrace{\boldsymbol{M} \cdot \mathbf{K}\boldsymbol{M}}_{\text{Anisotropic field}} - \underbrace{\boldsymbol{M} \cdot (\boldsymbol{H}}_{\text{Zeeman}} - \underbrace{\mathbf{N}\boldsymbol{M}}_{\text{Demagnetizing field}})$$

Effective field other than $\boldsymbol{H}$:

$$\boldsymbol{H}_{\text{eff}} = \lambda \boldsymbol{M} - (\boldsymbol{K} + \boldsymbol{N})\boldsymbol{M}$$

Kinetic equation of macroscopic moment:

$$\frac{1}{\gamma}\frac{d\boldsymbol{M}}{dt} = \boldsymbol{M} \times (\boldsymbol{H} - \mathbf{K}\boldsymbol{M} - \mathbf{N}\boldsymbol{M})$$

γ: gyromagnetic ratio

When the anisotropy is uniaxial, the shape of the sample, the magnetic field are on line:

$$\omega = \gamma\sqrt{(H + (K_x - K_z + N_x - N_z)M)(H + (K_y - K_z + N_y - N_z)M)}$$

Antiferromagnetic resonance

Effective field for two magnetic sublattices (1,2) :

$$\boldsymbol{H}_{\text{eff1}} = -\lambda \boldsymbol{M}_2 + \mathbf{K}_{11}\boldsymbol{M}_1 + \mathbf{K}_{12}\boldsymbol{M}_2 + \mathbf{N}(\boldsymbol{M}_1 + \boldsymbol{M}_2)$$
$$\boldsymbol{H}_{\text{eff2}} = -\lambda \boldsymbol{M}_1 + \mathbf{K}_{21}\boldsymbol{M}_1 + \mathbf{K}_{22}\boldsymbol{M}_2 + \mathbf{N}(\boldsymbol{M}_1 + \boldsymbol{M}_2)$$

In the case of antiferromagnet: $\boldsymbol{M}_1 = -\boldsymbol{M}_2$ No demagnetizing effect!

Anisotropy tensor: $\mathbf{K}_{11} = \mathbf{K}_{22}, \quad \mathbf{K}_{12} = \mathbf{K}_{21}$

Assumption: Anisotropy energy $\mathscr{F}_{\mathrm{A}}$ is uniaxial. $\mathscr{F}_{\mathrm{A}} = -\dfrac{K_1}{2}(\cos^2\theta_1 + \cos^2\theta_2)$ $\quad \theta_1,\ \theta_2\text{: angles to } \boldsymbol{M}_1,\ \boldsymbol{M}_2$

Anisotropy tensor: $K_{zz} = -\dfrac{K_1}{|\boldsymbol{M}_1|}, \quad (\text{others}) = 0$

Resonance frequencies:

$$\frac{\omega_\pm}{\gamma} = \sqrt{2\lambda K_1 + (K_1/|M_1|)^2} \pm H, \qquad H \le H_{\mathrm{c}},$$
$$\frac{\omega_+}{\gamma} = \sqrt{B^2 - 2\lambda K_1} \qquad H > H_{\mathrm{c}}$$

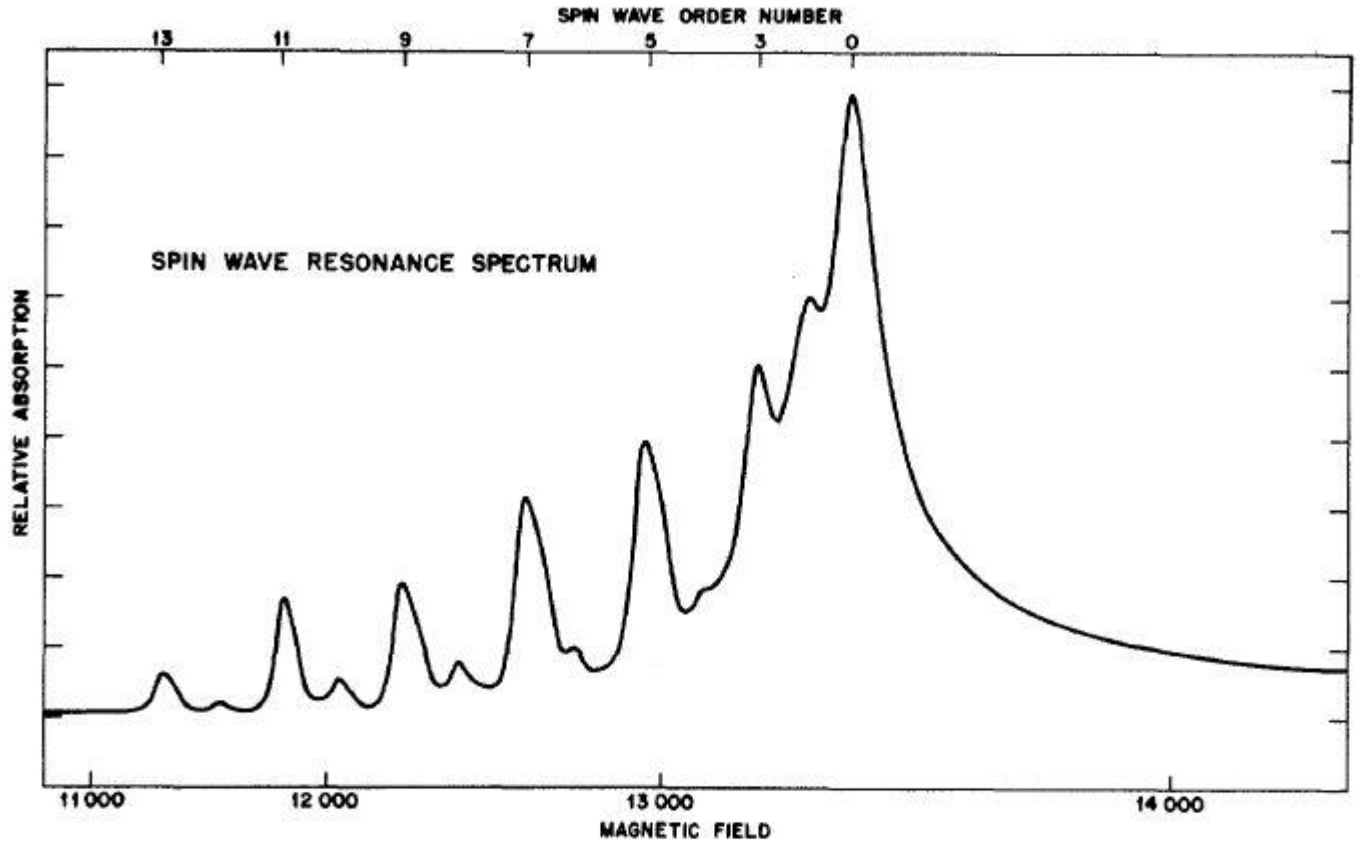
Critical field of spin-flop transition: $H_{\mathrm{c}} = \sqrt{2\lambda K_1}$

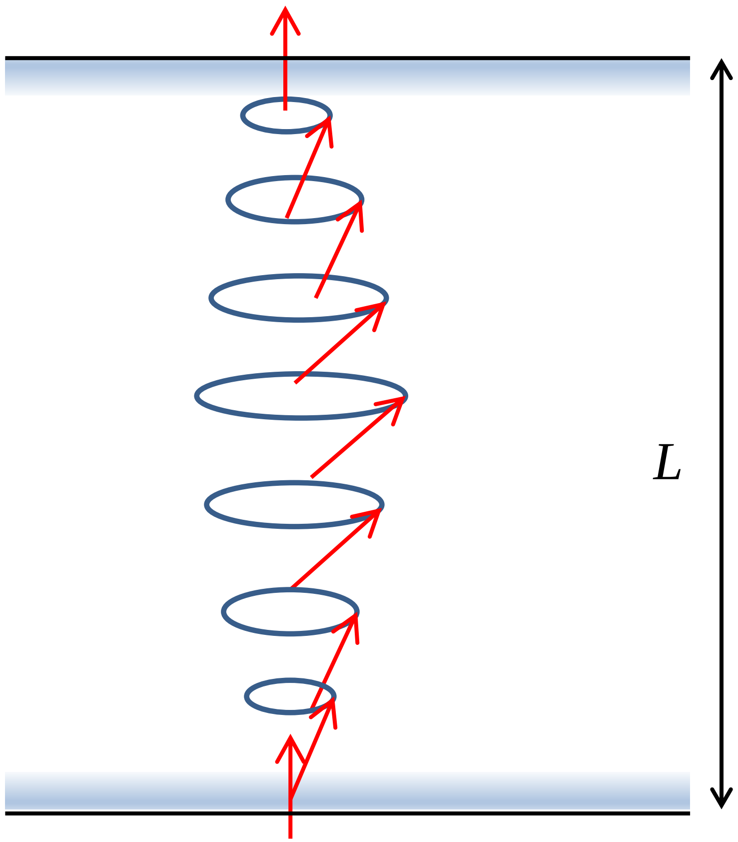
When the anisotropy is small: $\dfrac{\omega_\pm}{\gamma} = \sqrt{2\lambda K_1} \pm H, \quad H \le H_{\mathrm{c}}$

Spin wave (Magnon) resonance

Ferromagnetic spin wave dispersion relation: $\omega_k = \gamma H + \frac{2SJ}{\hbar}(ka)^2$

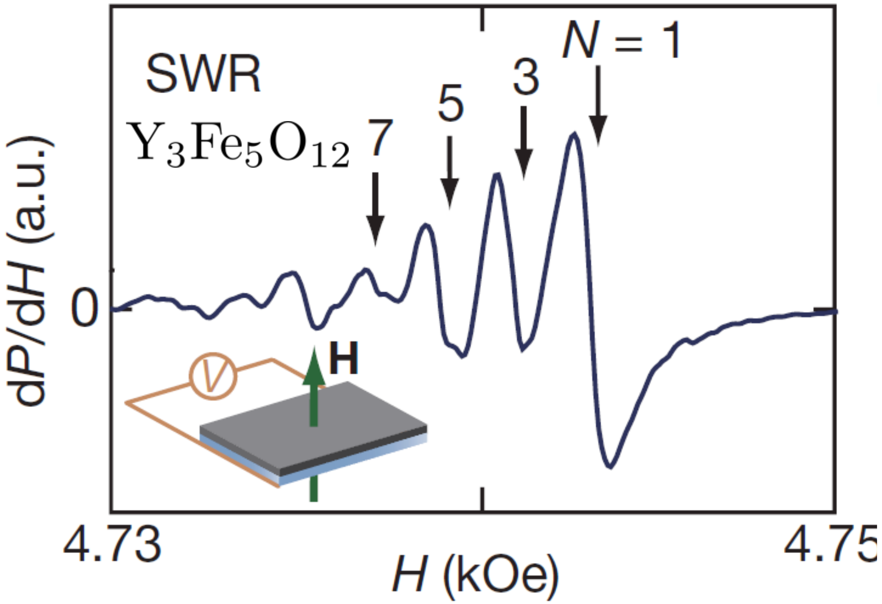
Standing wave condition: $k = \frac{n\pi}{L}, \quad n = 1, 2, \cdots$





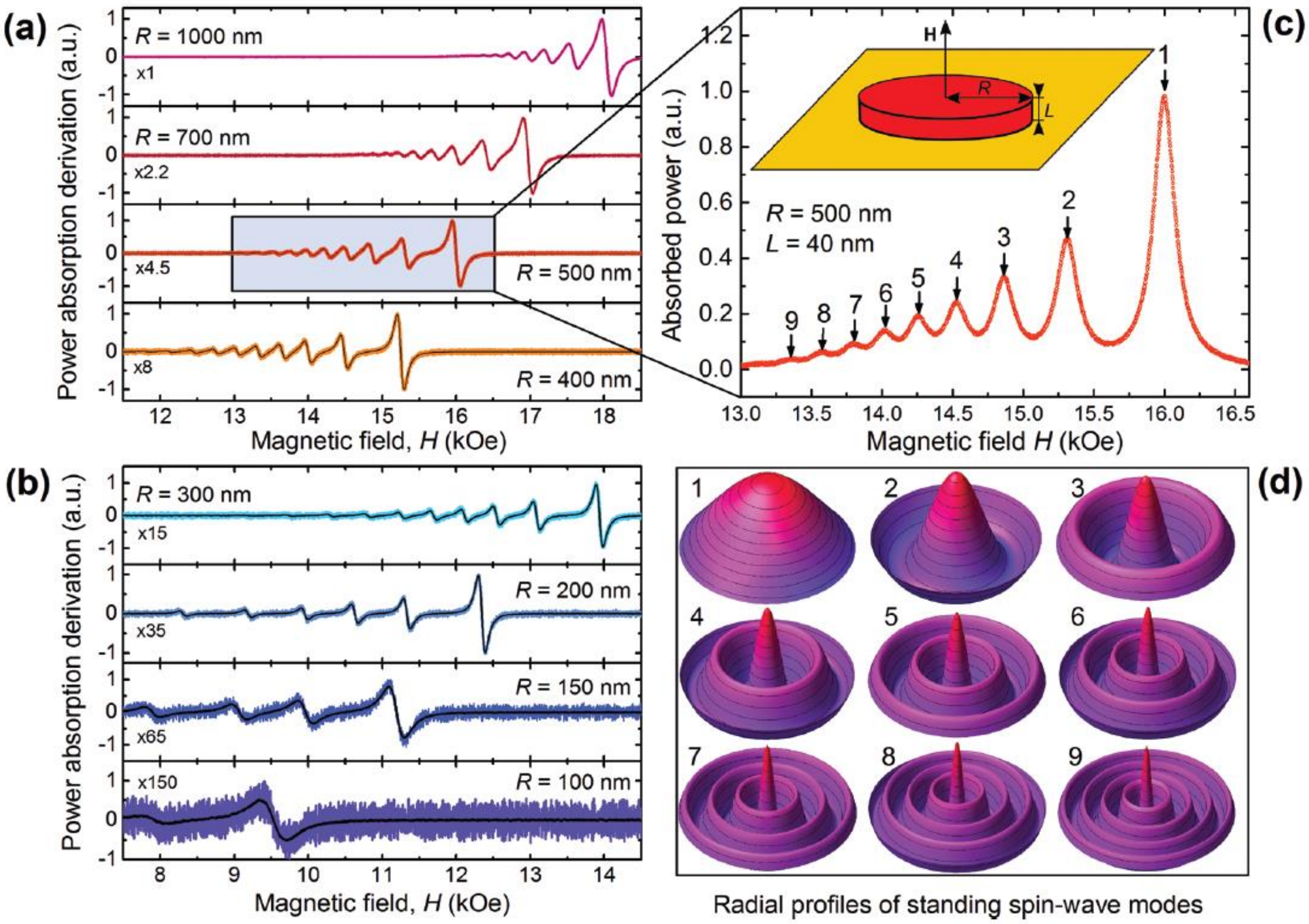
Seavey, Tannenwald, PRL **1**, 168 (1958).

Magnon (spin wave) resonance in thin films



Kajiwara et al., Nature **464**, 262 (2010)

CoFe Nano disk



Spin wave resonance in a thin film

$$\frac{m}{\gamma} = \frac{B}{\mu_0} - 4\pi M_{\rm S} + \frac{2Ak^2}{M_{\rm S}}$$

$$k = \frac{p\pi}{L} \quad p : \text{odd number},$$

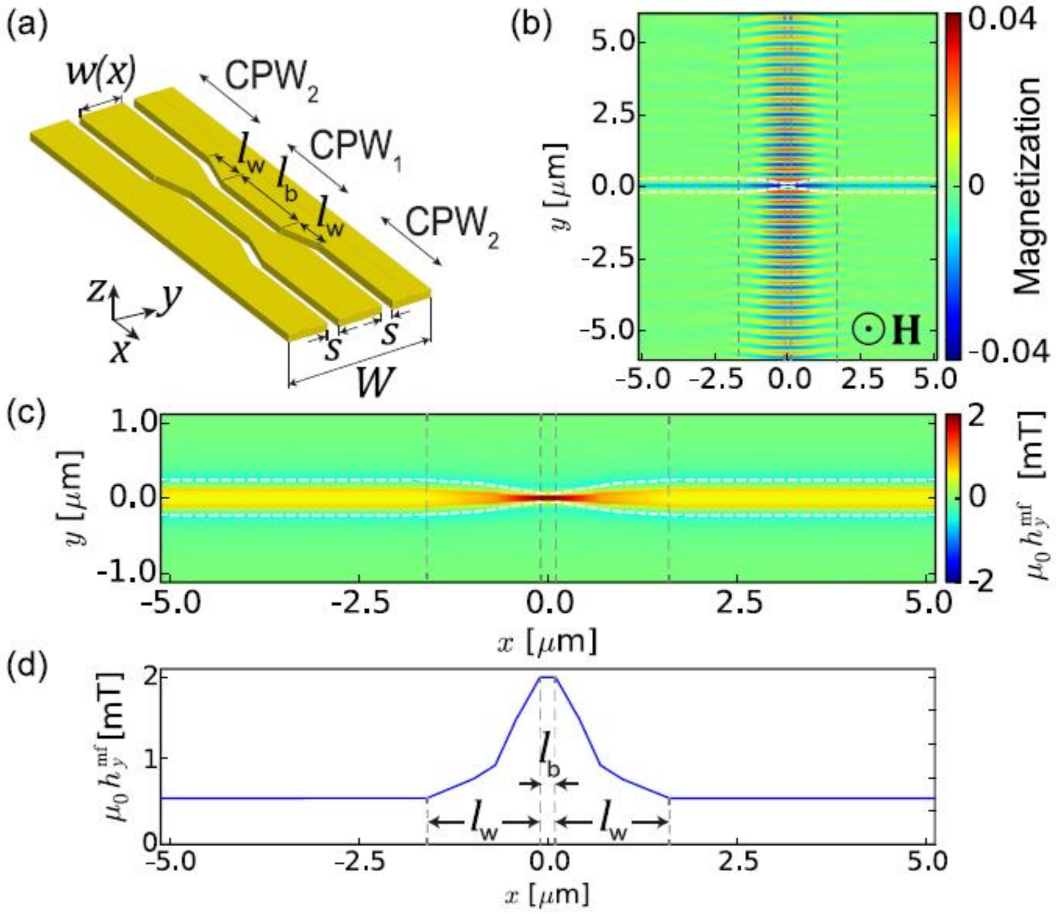
$$L : \text{ film thickness} \qquad A = \frac{\alpha_z S^2 J}{a}$$

Kittel Phys. Rev. **110**, 1295 (1958)

Dobrovolskiy et al., Nanoscale **12**, 21207 (2020).

Real space imaging of magnons

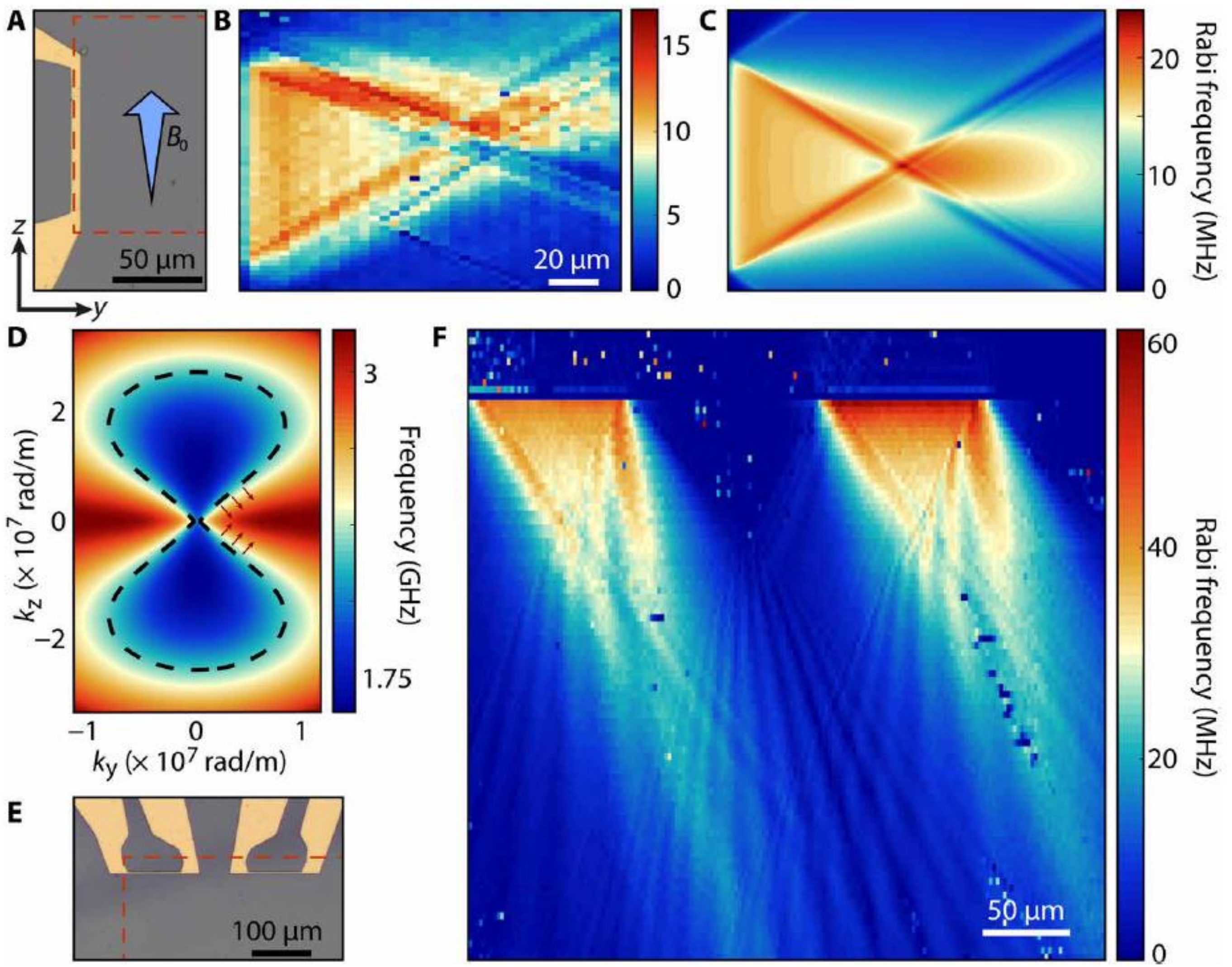
YIG



Gruszecki et al. Sci. Rep. **6**, 22367 (2016)

YIG

NV center ESR detection of magnon fields



Bertelli et al., Sci. Adv. **6**, eabd3556 (2020).

Section 5.10

Renormalization group and scaling theory of phase transition

Kenneth Wilson

1936 - 2013

1982 Nobel prize

Jacques Friedel

1921 - 2014

Jun Kondo

1930 - 2022

Correlation function

Magnetic moment (local) density : $m(\boldsymbol{r})$

Free energy density: $f(m(\boldsymbol{r},\nabla m(\boldsymbol{r}))=f_0+\dfrac{a}{2}m^2+\dfrac{b}{4}m^4+c|\nabla m|^2-hm$

Free energy functional: $\mathscr{F}\{m(\boldsymbol{r})\}=\displaystyle\int_V d\boldsymbol{r}' f(m(\boldsymbol{r}'),\nabla' m(\boldsymbol{r}'))$

Partition function: $Z=\displaystyle\int\mathcal{D}m(\boldsymbol{r})\exp\left[-\frac{\mathscr{F}\{m(\boldsymbol{r})\}}{k_{\mathrm{B}}T}\right]$ $\displaystyle\int\mathcal{D}m(\boldsymbol{r})$: functional integral

Probability density of realization of *m*(**r**) : $p\{m(\boldsymbol{r})\}=\dfrac{1}{Z}\exp\left[-\dfrac{\mathscr{F}\{m(\boldsymbol{r})\}}{k_{\mathrm{B}}T}\right]$

Expectation value of physical quantity *A* $\langle A\rangle=\dfrac{1}{Z}\displaystyle\int\mathcal{D}m(\boldsymbol{r})A\exp\left[-\frac{\mathscr{F}\{m(\boldsymbol{r})\}}{k_{\mathrm{B}}T}\right]$

Temperature dependence assumption: $a=\alpha(T-T_{\mathrm{C}})\quad(\alpha>0),\quad b=\mathrm{const.}\ (>0)$

Correlation function (2)

Correlation function of order parameter fluctuation:

$$g(\boldsymbol{r}) = \langle (m(0) - \langle m(0)\rangle)(m(\boldsymbol{r}) - \langle m(\boldsymbol{r})\rangle)\rangle = \langle m(0)m(\boldsymbol{r})\rangle - \langle m(0)\rangle \langle m(\boldsymbol{r})\rangle$$

The second term = 0 for $T > T_C$

Fourier representation:

$$m(\boldsymbol{r}) = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k}} m_{\boldsymbol{k}} \exp(i\boldsymbol{k}\cdot\boldsymbol{r}) \qquad m_{-\boldsymbol{k}} = m_{\boldsymbol{k}}^*$$

Because $(m_k + m_{-k})(m_k e^{ikr} + m_{-k}e^{-ikr}) = 2|m_k|^2 e^{-ikr} + 2|m_{-k}|^2 e^{ikr}$

And from translational invariance:

$$g(\boldsymbol{r}) = \frac{1}{V}\sum_{\boldsymbol{k}} \langle |m_{\boldsymbol{k}}|^2\rangle \exp(-i\boldsymbol{k}\cdot\boldsymbol{r})$$

Free energy:

$$\mathscr{F} = Vf_0 + \sum_{\boldsymbol{k}} |m_{\boldsymbol{k}}|^2 \left(\frac{a}{2} + ck^2\right) + \frac{b}{4V}\sum_{\boldsymbol{k}_1+\boldsymbol{k}_2+\boldsymbol{k}_3+\boldsymbol{k}_4=\boldsymbol{0}} m_{\boldsymbol{k}_1}m_{\boldsymbol{k}_2}m_{\boldsymbol{k}_3}m_{\boldsymbol{k}_4}$$

Ignore 4th order

Weight function:

$$\frac{1}{Z}\exp\left[-\frac{2}{k_{\rm B}T}\sum_{\boldsymbol{k}}{}' \left(\frac{a}{2} + ck^2\right)\left(m_{\boldsymbol{k}}^{(\rm r)2} + m_{\boldsymbol{k}}^{(\rm i)2}\right)\right]$$

$$p\{m(\boldsymbol{r})\} = \frac{1}{Z}\exp\left[-\frac{\mathscr{F}\{m(\boldsymbol{r})\}}{k_{\rm B}T}\right]$$

Sum over independent $\boldsymbol{k}$

$$\mathrm{Re}[m_{\boldsymbol{k}}] = m_{\boldsymbol{k}}^{(\rm r)}, \quad \mathrm{Im}[m_{\boldsymbol{k}}] = m_{\boldsymbol{k}}^{(\rm i)}$$

Correlation function (3) Scaling relations

Finally $$g(\boldsymbol{r}) = \frac{1}{V}\sum_{\boldsymbol{k}}{}' \frac{k_{\mathrm{B}}T}{a+2ck^2} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} = k_{\mathrm{B}}T \int_0^\infty \frac{e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}}{2ck^2+a} \frac{d^3k}{(2\pi)^3} = \underline{\frac{k_{\mathrm{B}}T}{8\pi d} \frac{\exp(-r/\xi)}{r}}, \qquad \xi = \sqrt{\frac{2c}{a}}$$

Yukawa type function
Exponential decay + (1/r)

Correlation length

$T < T_{\mathrm{C}}$ $\quad \tilde{g}(\boldsymbol{r}) = \langle m(0) m(\boldsymbol{r}) \rangle$ differs from $g(\boldsymbol{r})$ $\quad r \to \infty$

Appearance of long range order

Scaling relations

temperature $t \equiv (T - T_{\mathrm{C}})/T_{\mathrm{C}}$ magnetic field h

Critical exponents:

$$\begin{aligned}
\text{Specific heat}: &\quad C \sim |t|^{-\alpha}, \\
\text{Magnetization (order parameter)}: &\quad m \sim |t|^{\beta} \quad (t<0) \\
&\quad m \sim h^{1/\delta} \quad (t=0), \\
\text{Susceptibility}: &\quad \chi \sim |t|^{-\gamma}, \\
\text{Correlation length}: &\quad \xi \sim |t|^{-\nu}
\end{aligned}$$

Scaling relations

$$g(\boldsymbol{r}) \sim \frac{\exp(-r/\xi)}{r^{d-2+\eta}}$$

d : dimensionality

GL theory gives $\alpha = 0, \ \beta = 1/2, \ \gamma = 1, \ \delta = 3, \ \nu = 1/2, \ \eta = 0$

Scaling relations:
$$\begin{cases} \gamma = (2-\eta)\nu, \\ \alpha + 2\beta + \gamma = 2, \\ \beta + \gamma = \beta\delta. \end{cases}$$

Scaling ansatz: Critical behavior is described by a single relevant parameter. $\frac{h}{|t|^\Delta}$ Δ: Gap exponent

Free energy expression: $f_s \sim |t|^{2-\alpha} f_\pm \left(\frac{h}{|t|^\Delta} \right)$

$$m(h=0) \sim -\frac{\partial f_s}{\partial h} \sim |t|^{2-\alpha-\Delta} f'_\pm(0) \sim |t|^\beta \quad (t<0)$$

$$\chi \sim -\frac{\partial^2 f}{\partial h^2} \sim |t|^{2-\alpha-2\Delta} f''_\pm(0) \sim |t|^{-\gamma}$$

$$\beta = 2 - \alpha - \Delta$$
$$-\gamma = 2 - \alpha - 2\Delta$$
$$\therefore \ \Delta = \beta + \gamma$$

Scaling ansatz and scaling relations

$$f_s \sim |t|^{2-\alpha} f_\pm \left(\frac{h}{|t|^\Delta} \right) \qquad t \to 0 \qquad \frac{h}{|t|^\Delta} \to \infty$$

Then we assume the asymptotic form: $f'_\pm(x) \sim x^{\lambda_\pm} \quad (x \to \infty)$

From the scaling relations: $m \sim |t|^\beta f'_\pm \left(\frac{h}{|t|^\Delta} \right) \sim \frac{h^{\lambda_\pm}}{|t|^{\Delta\lambda_\pm - \beta}}$

For m to be finite at $t \to 0$: $\lambda_\pm = \frac{\beta}{\Delta} = \frac{\beta}{\beta + \gamma}$ Compare with $m \sim h^{1/\delta}$ then $\delta = \frac{\beta + \gamma}{\beta}$

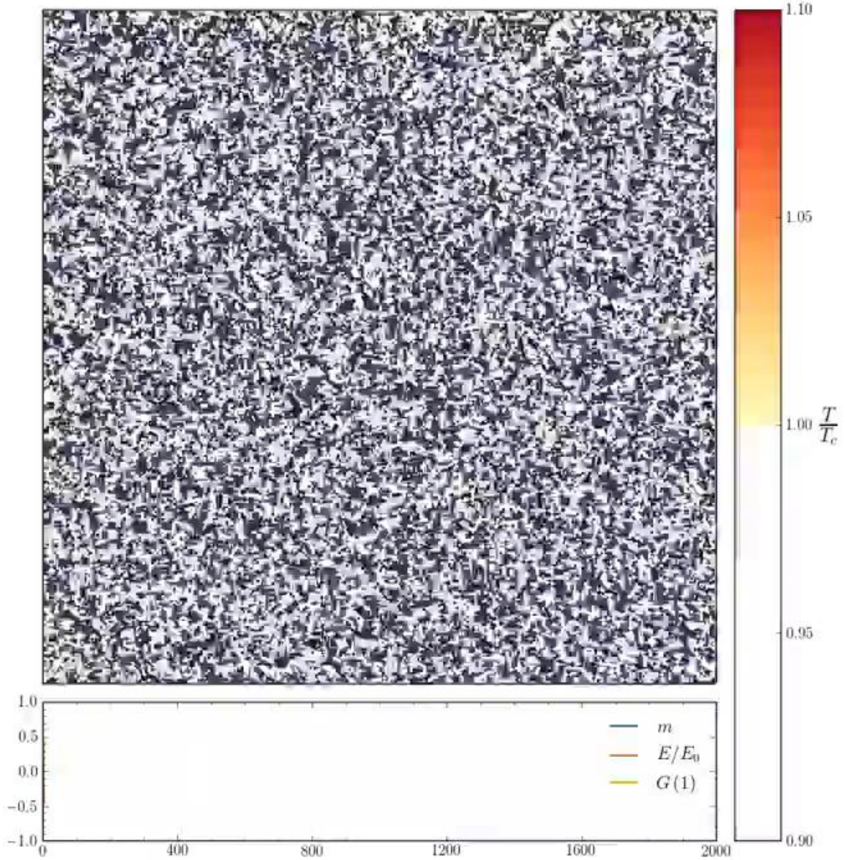
Hyperscaling relation: $2 - \alpha = d\nu$

Ising model

Directions of spins are limited to *z*

$$\mathscr{H} = -J \sum_{\langle i,j \rangle} S_i S_j - h \sum_i S_i$$

Solution: 1d Ising, 2d Onsager

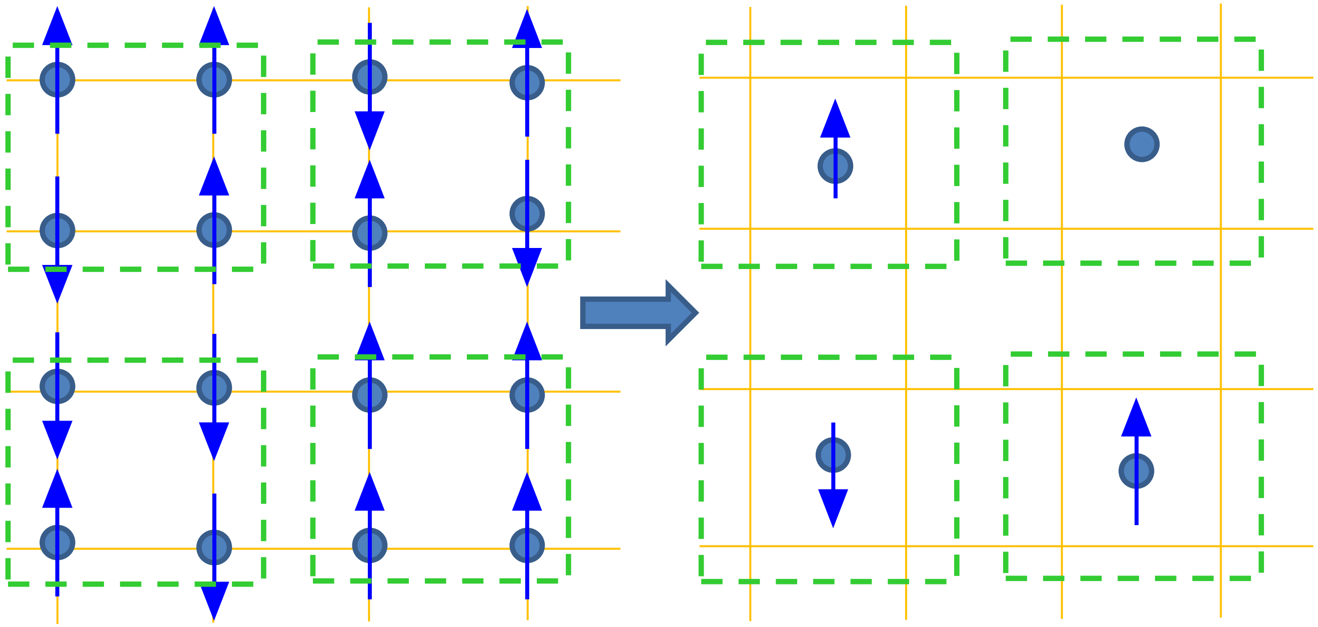


Model (Universality class)	α	β	γ	δ
2D Ising	0	1/8	7/4	15
3D Ising	0.115	0.324	1.239	4.82
3D XY	−0.01	0.34	1.32	4.9
3D Heisenberg	−0.11	0.36	1.39	4.9
Mean field approximation	0	1/2	1	3

https://www.youtube.com/watch?v=kjwKgpQ-l1s

Renormalization group

2D square lattice Ising model



Four spins are averaged and coarse-grained to a single spin.

$$s_q = \frac{1}{4}\sum_i s_{qi} \qquad \sqrt{4} = 2$$

Renormalization group transformation of scaling factor 2.

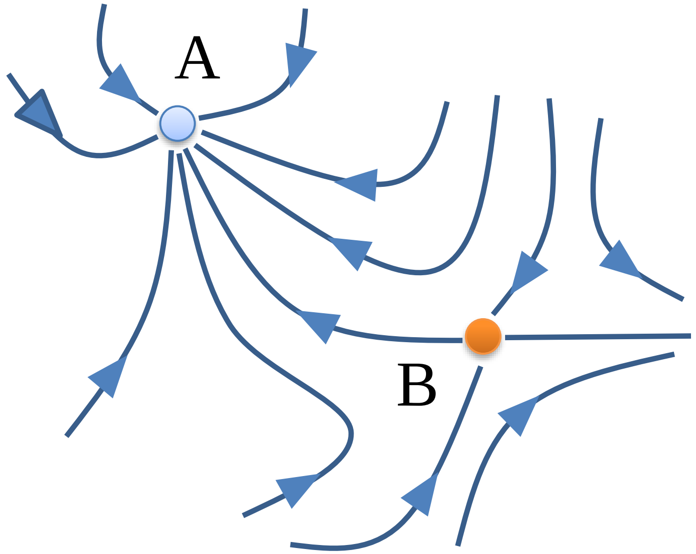
Renormalization group transformation of scaling factor *x* as $\mathcal{R}(x)$

$$\mathscr{H}' = \mathcal{R}(x)\mathscr{H}$$

$$\mathcal{R}(x')\mathcal{R}(x) = \mathcal{R}(x'x)$$

Ordinary no inverse element: Semigroup

Flow diagram



Flow diagram

$\mathcal{R}(x)$ x: continuous variable

Renormalization group transform → changes system parameters

Continuous movement of the system in the parameter space

⇩

Flow diagram

Complete order, complete disorder: the parameters do not change

⇨ Stable fixed points

Just on the critical point: Unstable fixed point

Derivation of scaling ansatz

t: Temperature, h : Magnetic field

Renormalization group transform with scaling factor x
$$\begin{cases} t' = g_1^{(x)}(t,h) \\ h' = g_2^{(x)}(t,h) \end{cases}$$

Expansion around the unstable fixed point $t = h = 0$
$$\begin{cases} t' \simeq \Lambda_{11}(x)t + \Lambda_{21}(x)h, \\ h' \simeq \Lambda_{21}(x)t + \Lambda_{22}(x)h \end{cases}$$

Symmetry difference between t and h. h is reversed by reversing the magnetization but t is not.

Then they cannot have linear relations: $\Lambda_{12}(x) = \Lambda_{21}(x) = 0$

$$(\Lambda_{11}(x))^n = \Lambda_{11}(x^n), \quad (\Lambda_{22}(x))^n = \Lambda_{22}(x^n)$$

This should hold for any x >1, natural number n

Then $\Lambda_{11}(x),\ \Lambda_{22}(x)$ should be power functions of x.

Derivation of scaling ansatz (2)

Hence we write $\Lambda_{11}(x) = x^{\lambda_1}, \quad \Lambda_{22}(x) = x^{\lambda_2}$

Let us consider the case of starting at (*t* , *h*).

n-times operation of RGT with SF *x* System temperature $t_0 = x^{n\lambda_1} t$ is far from the critical point (assume)

Correlation length $\dfrac{\xi(t)}{\xi(t_0)} = x^n = \left(\dfrac{t}{t_0}\right)^{-1/\lambda_1}$

Remember $\xi \sim |t|^{-\nu}$ $\nu = \lambda_1^{-1}$

In a *d*-dimensional system, $f(t,h)$ becomes x^d times of the original.

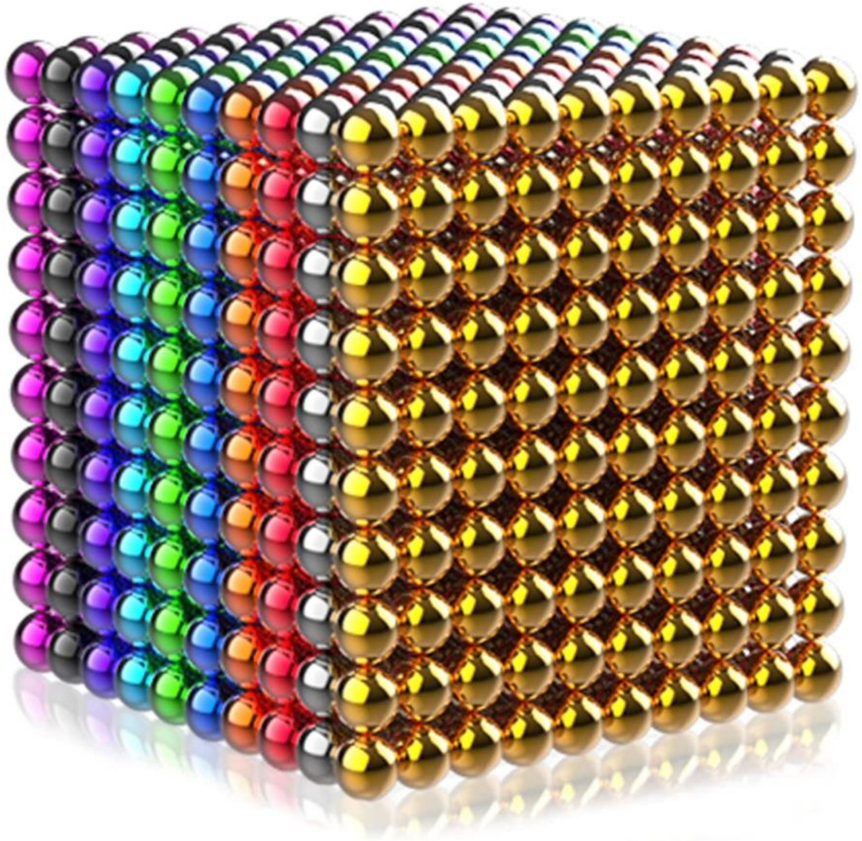
$$x^{nd} f(t,h) = f(x^{n\lambda_1} t, x^{n\lambda_2} h) = f(t_0, (t/t_0)^{-\lambda_2/\lambda_1} h)$$

Hence by some function $f_{\pm}(x)$ we can write

$$f(t,h) = t^{d/\lambda_1} f_{\pm}(t^{-\lambda_2/\lambda_1} h) = t^{d\nu} f_{\pm}\left(\frac{h}{t^{\Delta}}\right) \qquad \Delta = \frac{\lambda_2}{\lambda_1}$$

Chapter 6

Magnetism of Itinerant Electron Systems



Magnetic Puzzle

Summary

- Ferromagnetic and Antiferromagnetic resonance
- Spin wave resonance
- Experiments on magnons
- Scaling relations
- Renormalization group
- Derivation of scaling ansatz

2022.6.29 Lecture 12

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

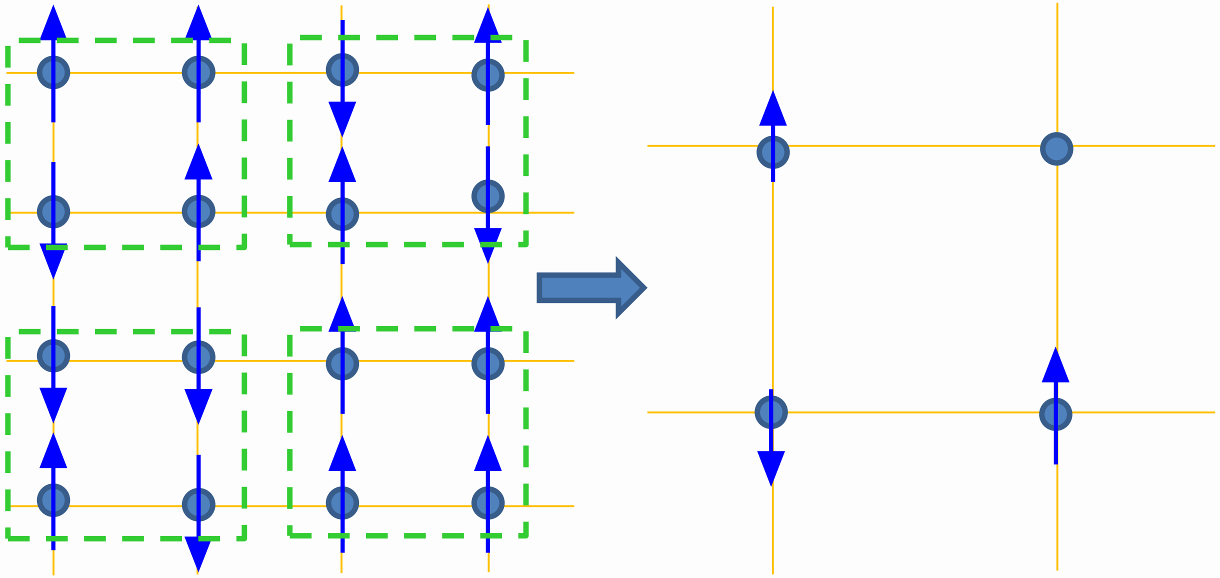
Institute for Solid State Physics, University of Tokyo

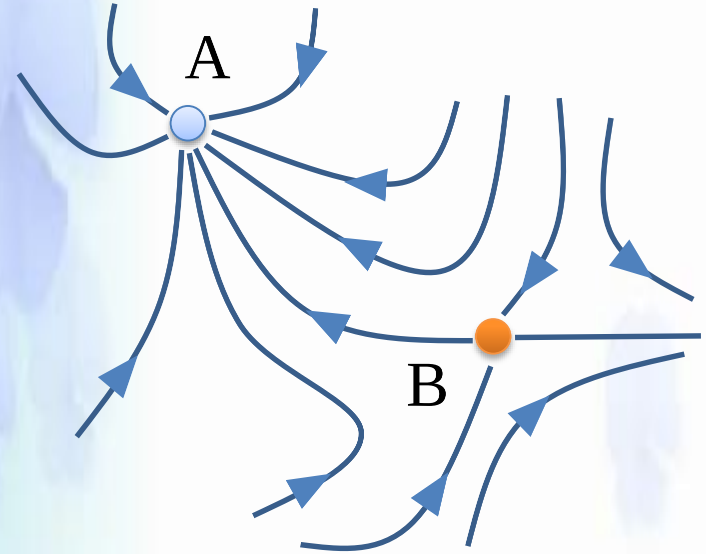
Shingo Katsumoto

Review

- Magnon condensates, Magnonics
- Scaling, Renormalization group

Coarse graining $s_q = \frac{1}{4}\sum_i s_{qi}$





$\mathscr{H}' = \mathcal{R}(x)\mathscr{H}$ System transition in a parameter space

Flow diagram

Stable fixed point: Extreme conditions

Unstable fixed point: critical point

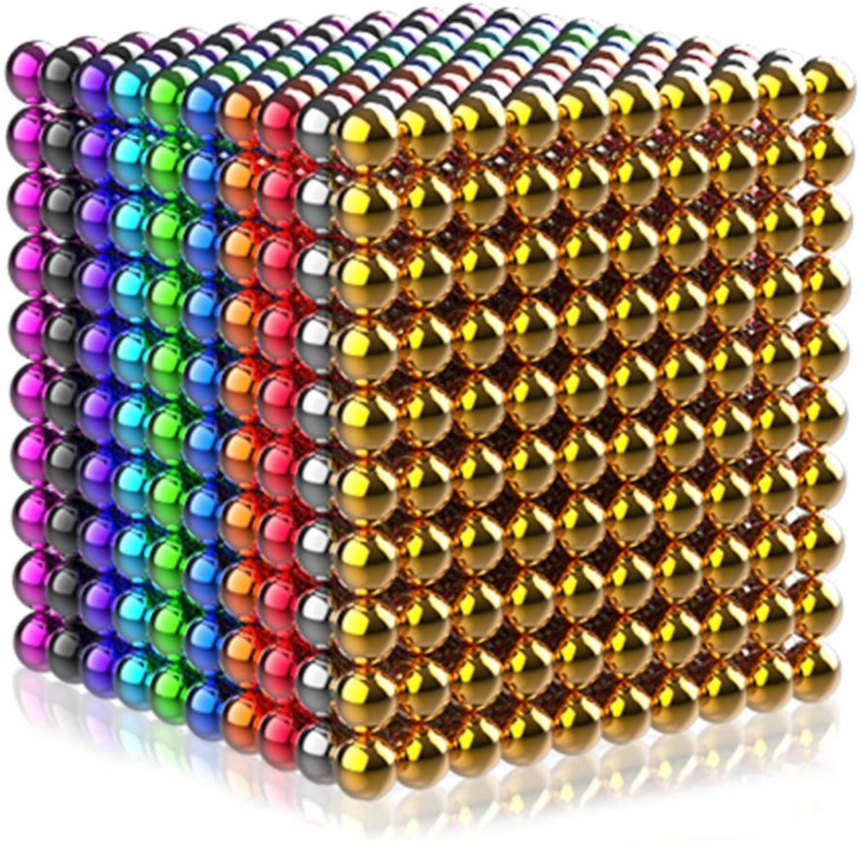
Renormalization group transform with scaling factor *x* $\begin{cases} t' = g_1^{(x)}(t,h) \\ h' = g_2^{(x)}(t,h) \end{cases}$ Renormalization group equation

Chapter 6 Magnetism of Itinerant Electron Systems

- Ferromagnetism in Electron gas
  - Hartree-Fock approximation
  - Diffusion Monte-Carlo calculation
- Hubbard model: mean field theory
  - Hartree-Fock approximation: Stoner criterion
  - Magnetic susceptibility
- Magnetism in 3*d* transition metals
  - Slater-Pauling's curve
  - Density of states by APW method

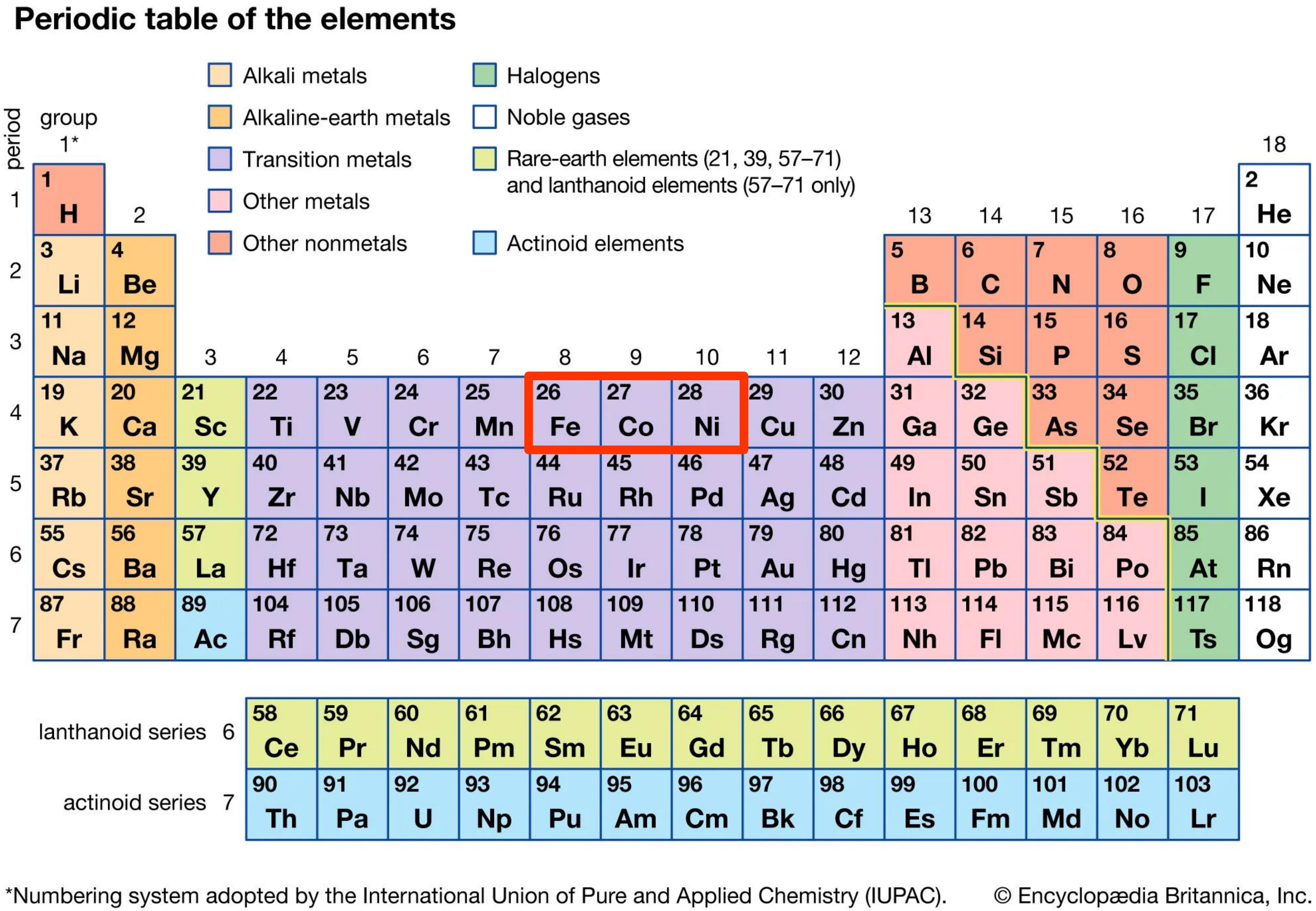
Chapter 6

Magnetism of Itinerant Electron Systems



Magnetic Puzzle

Periodic table of the elements



Hartree-Fock approximation for ferromagnetism in electron gas

Hartree-Fock approximation: A way to treat electron-electron interaction (correlation) in mean field theory.

Let us consider an *N*-particle system Single-particle wavefunctions $\varphi_{k_1}, \varphi_{k_2}, \cdots, \varphi_{k_N}$

Many-particle wavefunction fulfilling particle exchange statistics- Slater determinant:

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{k_1}(x_1) & \cdots & \varphi_{k_N}(x_1) \\ \vdots & \ddots & \vdots \\ \varphi_{k_1}(x_N) & \cdots & \varphi_{k_N}(x_N) \end{vmatrix}$$

x_i: all freedoms of a single particle

Assumption: Hamiltonian = single body + two-body:

$$\mathscr{H} = \sum_{j=1}^{N} h(x_j) + \sum_{\langle i,j \rangle} v(x_i, x_j)$$

Expectation value of the total energy: $\mathcal{W} = (\Phi, \mathscr{H}\Phi)$

Hartree-Fock approximation = minimize $\mathcal{W}$ in variational method on $\{\varphi_{k_j}\}$

Hartree-Fock approximation (2)

Constraint – Orthonormal basis: $\langle k_i | k_j \rangle = \delta_{ij}$

(1) Direct integral
and (2) Exchange integral: $$\mathcal{W} = \sum_{j=1}^{N} \langle k_j | h | k_j \rangle + \sum_{\langle i,j \rangle} [\underbrace{\langle k_i k_j | v | k_i k_j \rangle}_{(1)} - \underbrace{\langle k_i k_j | v | k_j k_i \rangle}_{(2)}]$$

We apply the method of Lagrange multipliers. Consider the quantity: $\mathcal{W} - \sum_{\langle i,j \rangle} \lambda_{ij} \langle k_i | k_j \rangle$

Extremals condition for the variation of $\{\varphi^*_{k_j}\}$ $$h\varphi_{k_j} + \sum_{i=1} [\langle k_i | v | k_i \rangle \varphi_{k_j} - \langle k_i | v | k_j \rangle \varphi_{k_i}] = \sum_{i=1}^{N} \lambda_{ij} \varphi_{k_i}$$

Density matrix (definition): $$\rho(x, x') = \sum_{i=1}^{N} \varphi^*_{k_i}(x) \varphi_{k_i}(x')$$

We further define $$v_{\text{eff}}(x) = \int dx' v(x, x') \rho(x', x), \quad A(x)\varphi(x) = \int dx' v(x, x') \varphi(x') \rho(x', x)$$

Then the extremal condition is $$[h(x) + v_{\text{eff}}(x) - A(x)] \varphi_{k_j}(x) = \sum_{i=1}^{N} \lambda_{ij} \varphi_{k_i}(x)$$

Hartree-Fock approximation (3)

$$\underbrace{[h(x) + v_{\mathrm{eff}}(x) - A(x)]}_{\mathcal{O}}\varphi_{k_j}(x) = \sum_{i=1}^{N} \lambda_{ij}\varphi_{k_i}(x)$$

We take φ_{k_j} for an eigenfunction of operator $\mathcal{O}$ $\quad [h(x) + v_{\mathrm{eff}}(x) - A(x)]\varphi_{k_j}(x) = \epsilon_{k_j}\varphi_{k_j}(x)$

Then taking *N* of eigenstates with the lowest eigen energies, and make the Slater determinant from them.

⇓

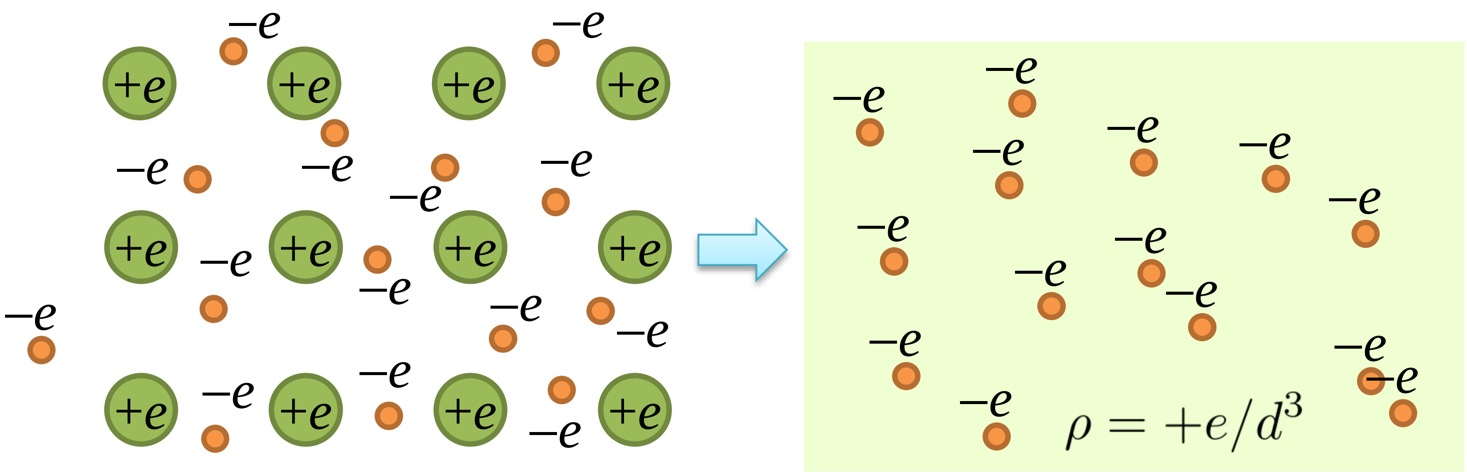
Hartree-Fock ground state

Operator $\mathcal{O}$ depends on $\{\varphi_{k_j}\}$ ⇒ Self-consistent equation

$$\boxed{[h(x) + v_{\mathrm{eff}}(x) - A(x)]\varphi_{k_j}(x) = \epsilon_{k_j}\varphi_{k_j}(x) \qquad \text{Hartree-Fock equation}}$$

Magnetism in jellium model

Electrons in a lattice potential



Jellium model

Electrons in a uniform background

Jellium model ground state of non-interacting electrons

$$|\Psi\rangle = \prod_{E(\boldsymbol{k},\sigma)\le E_{\mathrm{F}}} c^{\dagger}_{\boldsymbol{k}\sigma} |0\rangle$$

Hamiltonian with interaction:

$$\mathscr{H} = \sum_{\boldsymbol{k},\sigma} \epsilon_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \frac{1}{2V} \sum_{\boldsymbol{k},\boldsymbol{k}',\sigma,\sigma',\boldsymbol{q}\neq 0} v_{\boldsymbol{q}} c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q},\sigma} c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q},\sigma'} c_{\boldsymbol{k}'\sigma} c_{\boldsymbol{k}\sigma}$$

$$\epsilon_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m} \qquad v_{\boldsymbol{q}} = \frac{4\pi e^2}{q^2}$$

System parameter: Averaged particle distance measured by Bohr magneton:

$$r_s \equiv \frac{1}{a_{\mathrm{B}}} \left[\frac{3}{4\pi (k_{\mathrm{F}}^3/3\pi^2)} \right]^{1/3}$$

Magnetism in jellium model (2)

In the jellium model, plane waves are already the self-consistent equation. Then the plane wave states that minimize the energy is the solution of HF approximation.

Remember $$\mathcal{W} = \sum_{j=1}^{N} \langle k_j | h | k_j \rangle + \sum_{\langle i,j \rangle} [\langle k_i k_j | v | k_i k_j \rangle - \langle k_i k_j | v | k_j k_i \rangle]$$

Kinetic energy per an electron: $$\epsilon_{\rm ke} = \frac{1}{N}\sum_{\boldsymbol{k}s} \epsilon_{\boldsymbol{k}} n_{\boldsymbol{k}s} = \frac{2V}{N}\int \frac{d^3k}{(2\pi)^3}\frac{\hbar^2 k^2}{2m} n_k = \frac{3}{10}\frac{\hbar^2 k_{\rm F}^2}{m} = \frac{2.21}{r_s^2}{\rm Ry}$$

No direct integral term (Hartree) due to the charge neutral condition in the case of jellium model.

Exchange energy per an electron: $$\epsilon_{\rm ex} = -\frac{1}{2NV}\sum_{\boldsymbol{k},\boldsymbol{q}\neq 0,s} v_{\boldsymbol{q}} \langle \psi | c_{\boldsymbol{k}+\boldsymbol{q},s} c_{\boldsymbol{k}+\boldsymbol{q},s} c^{\dagger}_{\boldsymbol{k}s} c_{\boldsymbol{k}s} | \psi \rangle = \frac{1}{2NV}\sum_{\boldsymbol{k}s} v_{\boldsymbol{q}} n_{\boldsymbol{k}+\boldsymbol{q}} n_{\boldsymbol{k}}$$

Integration gives $$\epsilon_{\rm ex} = -\frac{3e^2}{4}\frac{k_{\rm F}}{\pi} = -\frac{0.92}{r_s}{\rm Ry}$$

Hartree-Fock energy is given by $$\epsilon_{\rm hf} = \left(\frac{2.21}{r_s^2} - \frac{0.92}{r_s}\right){\rm Ry}$$

Magnetism in jellium model (3)

Magnetic polarization: $p \equiv \dfrac{N_\uparrow}{N_\uparrow + N_\downarrow}$

$$E_{\mathrm{ke}}(p) = \frac{\hbar^2}{20\pi^2 m}(k_{\mathrm{F}\uparrow}^5 + k_{\mathrm{F}\downarrow}^5) = \frac{3(6\pi^2)^{2/3}\hbar^2}{10m}(n_\uparrow^{5/3} + n_\downarrow^{5/3}) = \frac{3(6\pi^2)^{2/3}\hbar^2}{10m}[p^{5/3} - (1-p)^{5/3}]n_0^{5/3},$$

$$E_{\mathrm{ex}}(p) = -\frac{3e^2}{4}\left(\frac{6}{\pi}\right)^{1/3}(n_\uparrow^{4/3} + n_\downarrow^{4/3}) = -\frac{3e^2}{4}\left(\frac{6}{\pi}\right)^{1/3}[p^{4/3} - (1-p)^{4/3}]n_0^{4/3}$$

$$\Delta E = [E_{\mathrm{ke}}(1) + E_{\mathrm{ex}}(1)] - [E_{\mathrm{ke}}(0.5) + E_{\mathrm{ex}}(0.5)]$$

$\Delta E < 0$ ⇒ Ferromagnetic state is the ground state

$r_s > 5.4531$

⇓

Overestimation of the stability of ferromagnetism

Table 1.1
FREE ELECTRON DENSITIES OF SELECTED METALLIC ELEMENTS[a]

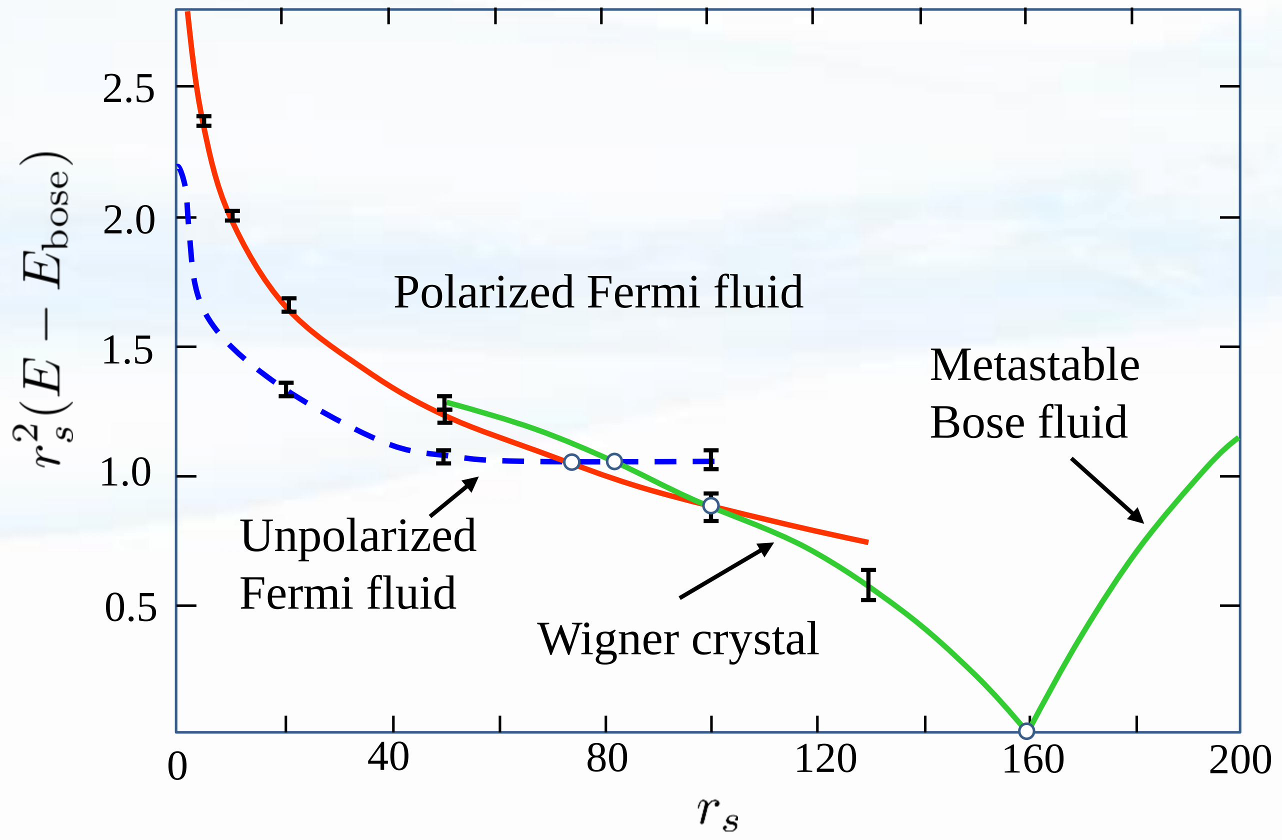
ELEMENT	Z	n (10^{22}/cm^3)	r_s(Å)	r_s/a_0
Li (78 K)	1	4.70	1.72	3.25
Na (5 K)	1	2.65	2.08	3.93
K (5 K)	1	1.40	2.57	4.86
Rb (5 K)	1	1.15	2.75	5.20
Cs (5 K)	1	0.91	2.98	5.62

Taken from Ashcroft-Mermin *Solid State Physics*

Correlation energy

In a realistic electron gas, the electrons keep away from each other lowering the Coulomb energy even between ones with the opposite spin directions.

Difference from the HF interaction energy: Correlation energy



Phase diagram by diffusion Monte-Carlo method

$70 < r_s < 90$

Huge deviation from 3*d* metals

Ceperly, Adler, PRL **45**, 566 (1980).

Hubbard model

24	25	26	27	28	29
Cr	Mn	Fe	Co	Ni	Cu
$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$

3*d* transition metals: 3*d*4*s* open shell

(1) 3*d*: Tendency to localize

(2) 4*s*: Delocalize, light mass → screen long range Coulomb interaction

Two-site Hubbard Hamiltonian

$$\mathscr{H} = t \sum_{\sigma=\uparrow\downarrow} (a^\dagger_{1\sigma} a_{2\sigma} + a^\dagger_{2\sigma} a_{1\sigma}) + U(n_{1\uparrow}n_{1\downarrow} + n_{2\uparrow}n_{2\downarrow})$$

General Hubbard Hamiltonian

$$\mathscr{H} = \underline{\sum_{i,j,s} t_{ij} c^\dagger_{is} c_{js}} + U \underline{\sum_{i}^{N} \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}}$$

(1) → Hopping On-site Coulomb ← (2)

Fermion commutation relation: $\{c^\dagger_{is}, c_{is'}\} = \delta_{ij}\delta_{ss'}$

In the present case, this Hamiltonian only acts on *d*-electrons explicitly.

Hubbard model (2)

Hubbard Hamiltonian $$\mathscr{H} = \sum_{i,j,s} t_{ij} c_{is}^{\dagger} c_{js} + U \sum_{i}^{N} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

Fourier expansion $$c_{is} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} e^{i\boldsymbol{R}_i \cdot \boldsymbol{k}} a_{\boldsymbol{k}s}, \quad t_{ij} = \frac{1}{N} \sum_{\boldsymbol{k}} \epsilon_{\boldsymbol{k}} e^{i\boldsymbol{k} \cdot (\boldsymbol{R}_i - \boldsymbol{R}_j)}$$

$$\underline{\sum_{\langle i,j \rangle, s} t_{ij} c_{is}^{\dagger} c_{js}} = \sum_{i,j,s} \frac{2}{N^2} \sum_{\boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_3} \epsilon_{\boldsymbol{k}_1} e^{i\boldsymbol{k}_1 \cdot (\boldsymbol{R}_i - \boldsymbol{R}_j)} e^{-i\boldsymbol{k}_2 \cdot \boldsymbol{R}_i} a_{\boldsymbol{k}_2 s}^{\dagger} e^{i\boldsymbol{k}_3 \cdot \boldsymbol{R}_j} a_{\boldsymbol{k}_3 s} = \underline{\sum_{\boldsymbol{k}, s} \epsilon_{\boldsymbol{k}} a_{\boldsymbol{k}s}^{\dagger} a_{\boldsymbol{k}s}}$$

Tendency to localize but still itinerant

Itinerant electron system

$$\mathscr{H} = \sum_{\boldsymbol{k}, s} \epsilon_{\boldsymbol{k}} a_{\boldsymbol{k}s}^{\dagger} a_{\boldsymbol{k}s} + U \sum_{i}^{N} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

HF approximation in Hubbard model

Local magnetic moment, electron number (per site)

$$m = \langle n_\uparrow \rangle - \langle n_\downarrow \rangle \,, \quad n = \langle n_\uparrow \rangle + \langle n_\downarrow \rangle$$

$$U \sum_i \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} = U \sum_i [\langle \hat{n}_\uparrow \rangle \hat{n}_{i\downarrow} + \langle \hat{n}_\downarrow \rangle \hat{n}_{i\uparrow} - \langle \hat{n}_\uparrow \rangle \langle \hat{n}_\downarrow \rangle + \underline{(\hat{n}_{i\uparrow} - \langle n_\uparrow \rangle)(\hat{n}_{i\downarrow} - \langle n_\downarrow \rangle)}]$$

$$\simeq U \sum_i (\underline{\langle \hat{n}_\uparrow \rangle \hat{n}_{i\downarrow} + \langle \hat{n}_\downarrow \rangle \hat{n}_{i\uparrow}}) - NU \langle n_\uparrow \rangle \langle n_\downarrow \rangle$$

$$\text{Take average } \rightarrow = \frac{NU}{4}(n^2 - m^2)$$

Fluctuation term: dropped in HF approximation

Moving in the averaged field of opposite spin

$$\mathscr{H}_{\mathrm{HF}} = \sum_{\boldsymbol{k},s} (\epsilon_{\boldsymbol{k}} + U \langle n_{-s} \rangle) n_{\boldsymbol{k}s} - NU \langle n_\uparrow \rangle \langle n_\downarrow \rangle$$

$$\uparrow, \downarrow \rightarrow s = \pm 1 \qquad \langle n_s \rangle = \frac{1}{2}(n + sm)$$

HF approximation in Hubbard model (2)

$$\uparrow, \downarrow \to s = \pm 1 \qquad \langle n_s \rangle = \frac{1}{2}(n + sm) \qquad \sum_{\boldsymbol{k},s} \hat{n}_{\boldsymbol{k}s} \to N(\langle n_\uparrow \rangle + \langle n_\downarrow \rangle)$$ averaging

$$\mathscr{H}_{\mathrm{HF}} = \sum_{\boldsymbol{k},s} (\epsilon_{\boldsymbol{k}} + U \langle n_{-s} \rangle) n_{\boldsymbol{k}s} - NU \langle n_\uparrow \rangle \langle n_\downarrow \rangle$$

$$\mathscr{H}_{\mathrm{HF}} = \sum_{\boldsymbol{k},s} \left(\epsilon_{\boldsymbol{k}} - \frac{sUm}{2} \right) \hat{n}_{\boldsymbol{k}s} + \frac{NU}{4}(n^2 + m^2)$$

$$\equiv \sum_{\boldsymbol{k},s} \tilde{\epsilon}_{\boldsymbol{k}s} \hat{n}_{\boldsymbol{k}s} + \frac{NU}{4}(n^2 + m^2)$$

Single electron energy shift: $\Delta\mu = (-s)Um/2$

Total energy: $$E = \sum_{\tilde{\epsilon}_{\boldsymbol{k}s} \le \mu} \left(\epsilon_{\boldsymbol{k}} - \frac{sUm}{2} \right) + \frac{NU}{4}(n^2 + m^2)$$

$$= \sum_{\tilde{\epsilon}_{\boldsymbol{k}s} \le \mu} \epsilon_{\boldsymbol{k}} + \frac{NU}{4}(n^2 \underline{- m^2})$$

Energy shift by magnetization

Spin-dependence of $\Delta\mu$ $\Rightarrow$ Difference in the numbers of ↑ electrons and ↓ electrons should be consistent with *m*

HF approximation in Hubbard model (3)

Self-consistent equation $m = 2\underline{\mathscr{D}(E_\mathrm{F})}\Delta\mu = \mathscr{D}(E_\mathrm{F})Um$ $\quad U\mathscr{D}(E_\mathrm{F}) = 1$ for non-zero *m*

Density of states

Increase in the kinetic energy by spontaneous magnetization $\mathscr{D}(E_\mathrm{F})(\Delta\mu)^2 = \dfrac{m^2}{4\mathscr{D}(E_\mathrm{F})}$

Decrease in interaction energy by spontaneous magnetization $-NUm^2/4$

$$\Delta E = \frac{N}{4}\left[\frac{m^2}{\mathscr{D}(E_\mathrm{F})} - Um^2\right]$$

$\Delta E < 0$

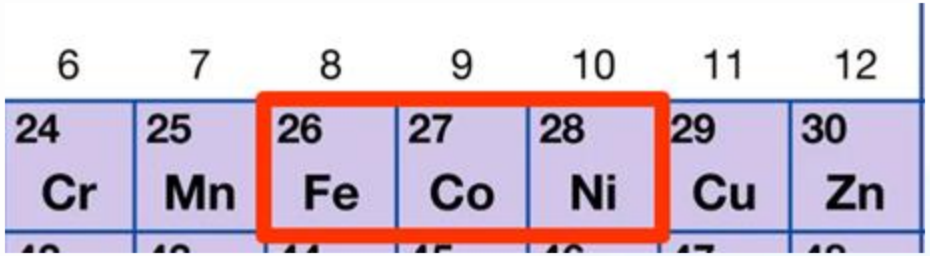
$$\boxed{U\mathscr{D}(E_\mathrm{F}) \geq 1 \qquad \text{Stoner condition}}$$

For ferromagnetism to take place, the Coulomb energy should be larger than the band width.

(Still has a problem of overestimating the Coulomb effect in the case of anti-parallel spins.)

Magnetism in 3d transition metals

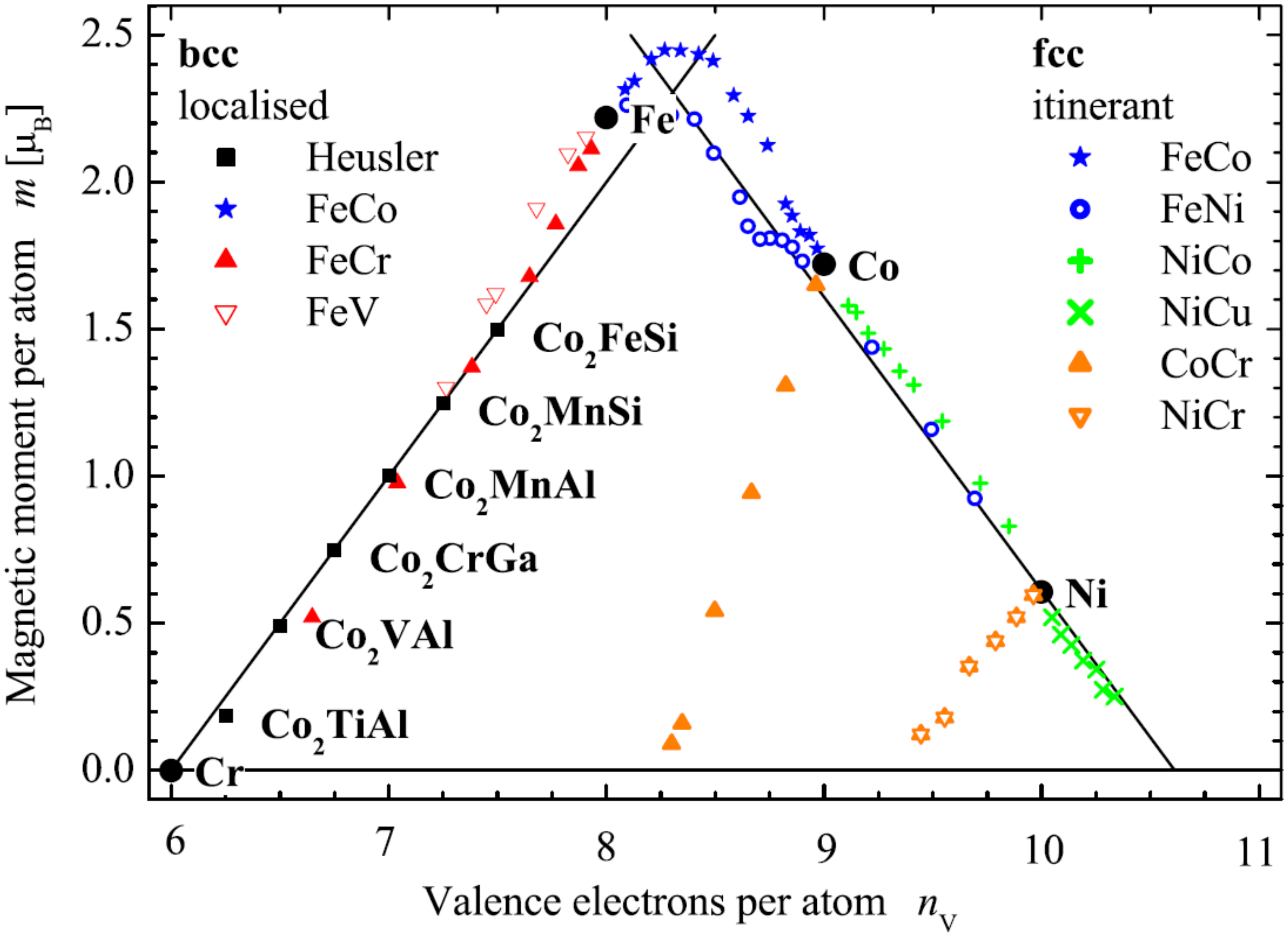
Elementary ferromagnetic metals



	structure /density (kgm^{-3})	lattice parameters (pm)	T_C (K)	M_S (MAm^{-1})	K_1 (kJm^{-3})	λ_S (10^{-6})	α	P (%)
Fe	bcc 7874	287	1044	1.71	48	-7	1.6	45
Co	hcp 8836	251 407 (fcc)	1388	1.45	530	-62	8.0	42
Ni	fcc 8902	352	628	0.49	-5	-34		44

From D. Coey in *Materials for Spin Electronics*, Springer 2008

Magnetism of 3*d* transition metals: Slater-Pauling's curve



Balke et al., Sci. Technol. Adv. Mater. **9**, 014102 (2008).

24	25	26	27	28	29
Cr	Mn	Fe	Co	Ni	Cu
$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$

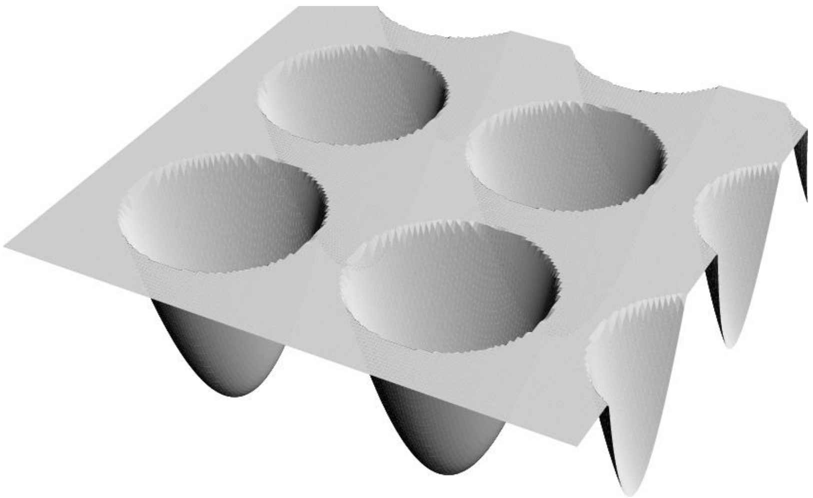
Slater-Pauling's curve

Experimental data are in line.

The gradient is ± 1 !

Abrupt change around Fe

APW method to calculate DOS



$$\mathscr{H}\phi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\phi(\boldsymbol{r}) = E\phi(\boldsymbol{r})$$

Muffin-tin potential: $$V(\boldsymbol{r}) = \begin{cases} V_{\mathrm{a}}(r) \ \ \text{(spherical)} & (r < r_{\mathrm{c}}) \\ V_{\mathrm{o}} \ (= V_{\mathrm{a}}(r_{\mathrm{c}}):\ \text{const.}) & (r \geq r_{\mathrm{c}}) \end{cases}$$

Hartree: $$V_{\mathrm{d}}(\boldsymbol{r}) = \sum_i \langle \phi_i(\boldsymbol{r}')| \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}'|} |\phi_i(\boldsymbol{r}')\rangle$$

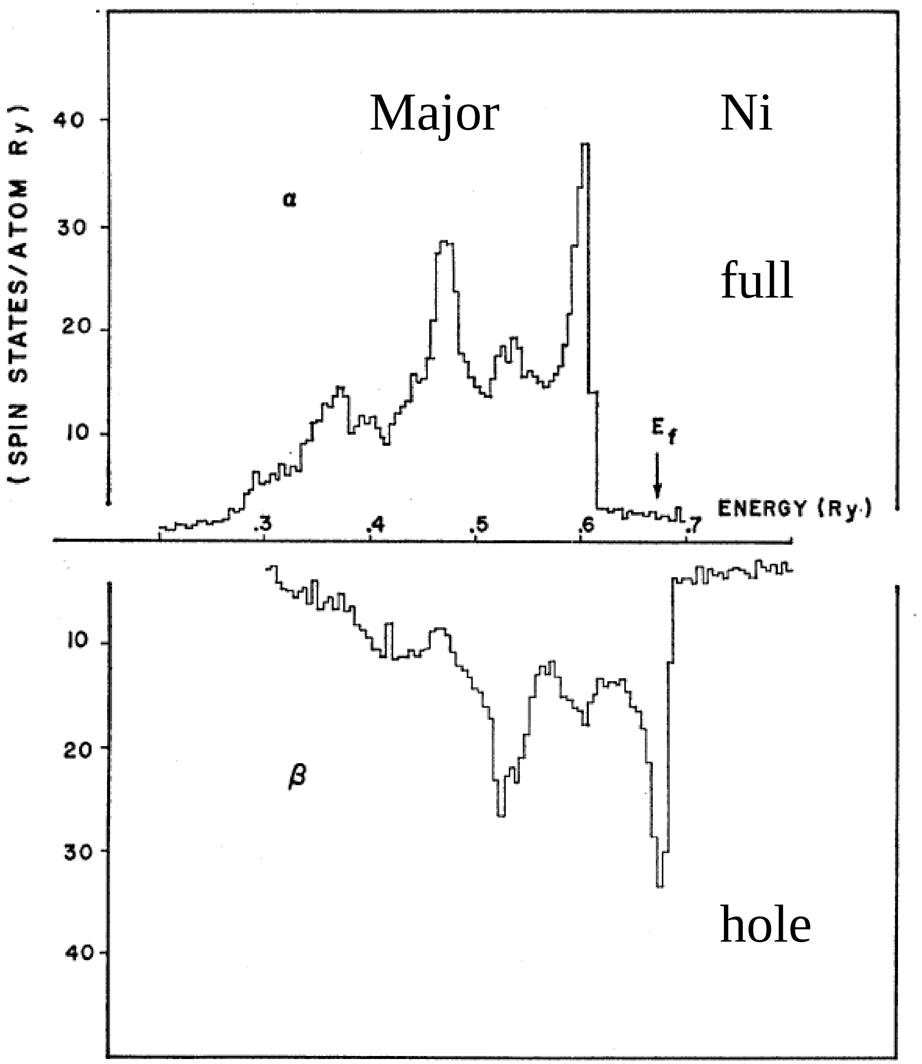
Exchange: $$V_{\mathrm{ex}\uparrow} = -3e^2\left(\frac{3}{4\pi}\right)^{1/3} \rho_\uparrow(\boldsymbol{r})^{1/3}$$

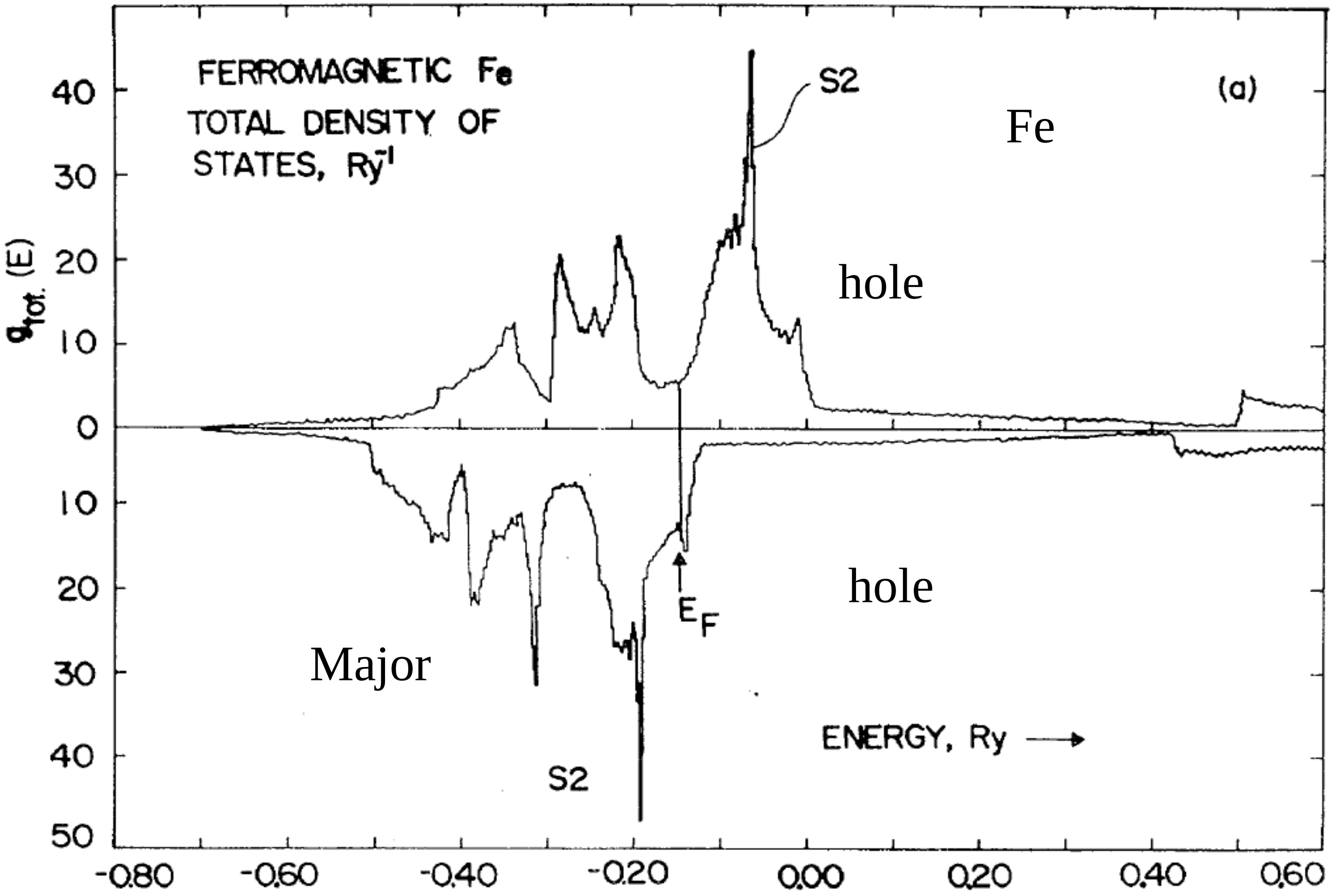
Variational wavefunction: $$\Phi_{\mathrm{vr}}(\boldsymbol{r}) = \begin{cases} \sum_{l,m} A_{lm} R_l(r) Y_l^m(\theta, \varphi) & r < r_{\mathrm{c}}, \\ \sum_{n=0}^{N} B_n \exp[i(\boldsymbol{k} + \boldsymbol{K}_n)\cdot \boldsymbol{r}] & r > r_{\mathrm{c}} \end{cases}$$

$$\Downarrow$$

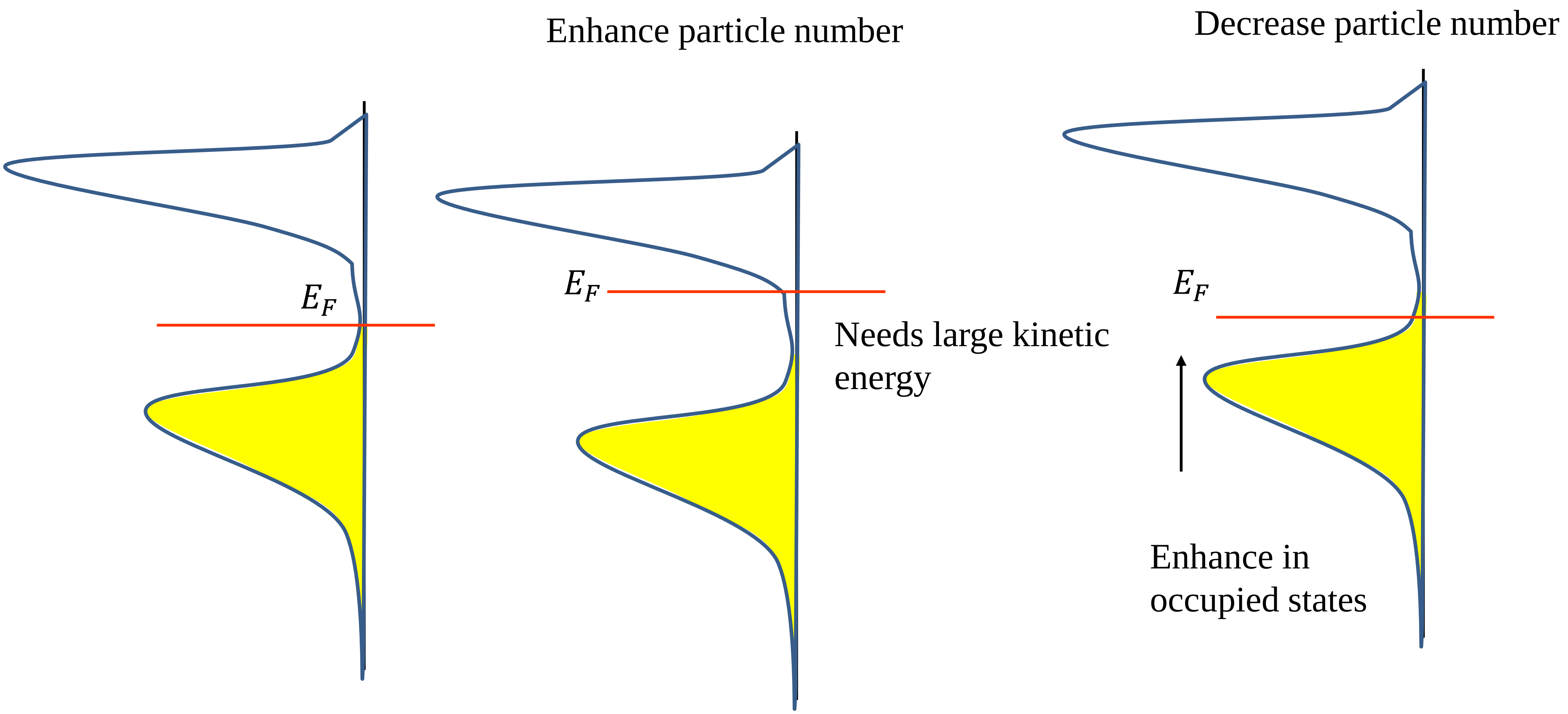
Iteration for convergence for each ***k***

Density of states in Ni and Fe





Fermi energy "locking" around a valley in density of states



Summary

Chapter 6 Magnetism of Itinerant Electron Systems

- Ferromagnetism in Electron gas
  - Hartree-Fock approximation
  - Diffusion Monte-Carlo calculation
- Hubbard model: mean field theory
- Magnetism in 3*d* transition metals
  - Slater-Pauling's curve
  - Density of states by APW method

2022.7.6 Lecture 13

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

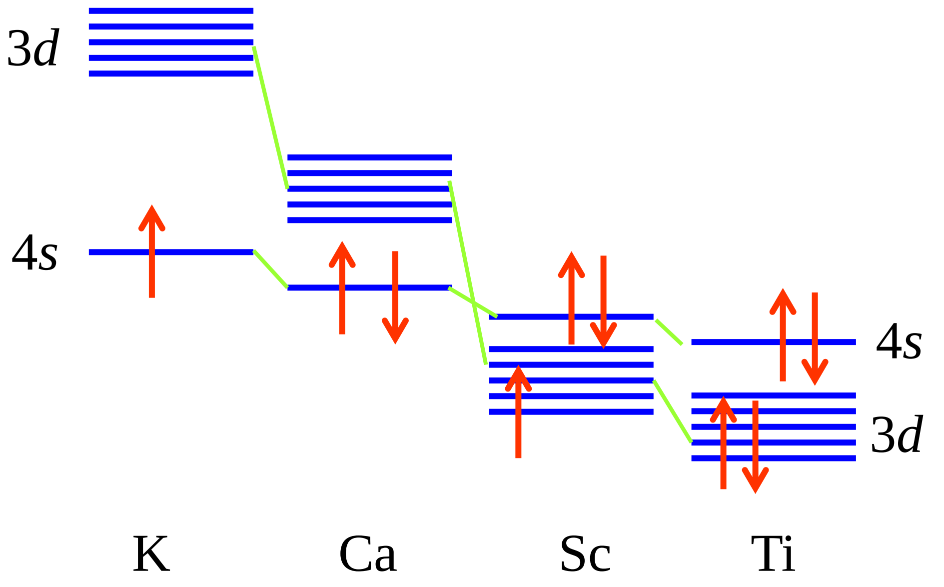
Chapter 6 Magnetism of Itinerant Electron Systems

- Ferromagnetism in Electron gas
  - Hartree-Fock approximation
  - Diffusion Monte-Carlo calculation
- Hubbard model: mean field theory
  - Hartree-Fock approximation: Stoner criterion
  - Magnetic susceptibility
- Magnetism in 3*d* transition metals
  - Slater-Pauling's curve
  - Density of states by APW method

Outline

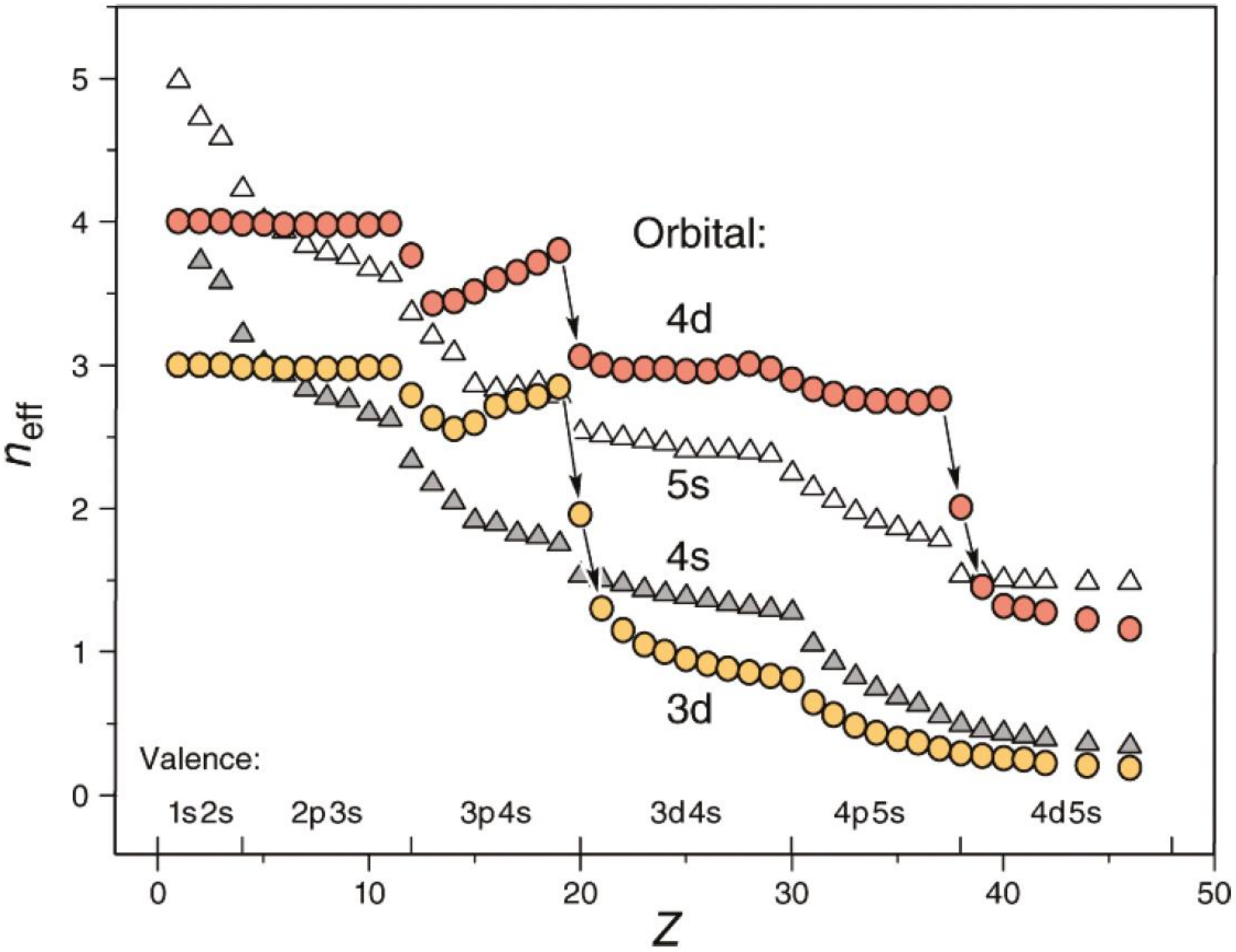
- Magnetism in 3*d* transition metals
  - Slater-Pauling's curve
  - Density of states by APW method
- Kubo formula (linear response)
- Fluctuation dissipation theorem
- Random phase approximation (RPA)

3*d* and 4*s* electrons in isolated transition metal atoms

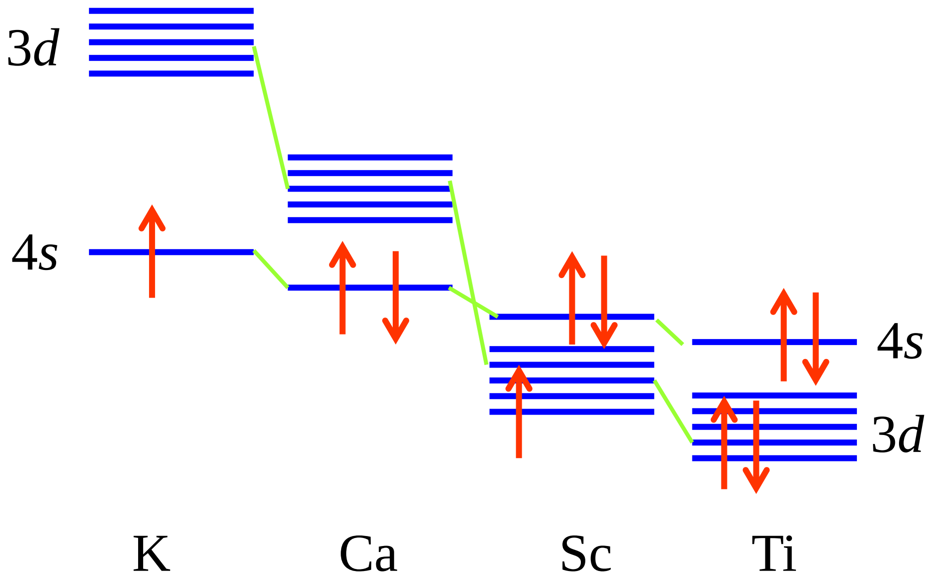


Radial wavefunction

$$
\begin{cases}
|4s\rangle \propto R_{40}(r) \propto \exp\left(-\frac{r}{4a_B}\right) \\
|3d\rangle \propto R_{32}(r) \propto \left(\frac{r}{r_B}\right)^2 \exp\left(-\frac{r}{3a_B}\right)
\end{cases}
$$

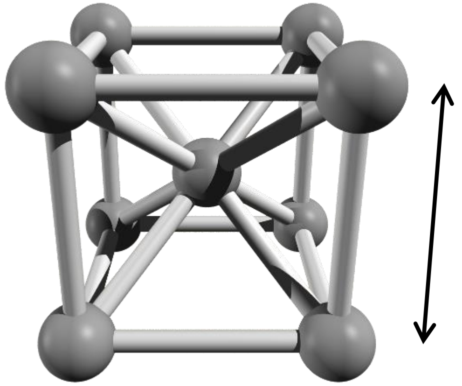


$3d$ and $4s$ electrons in isolated transition metal atoms



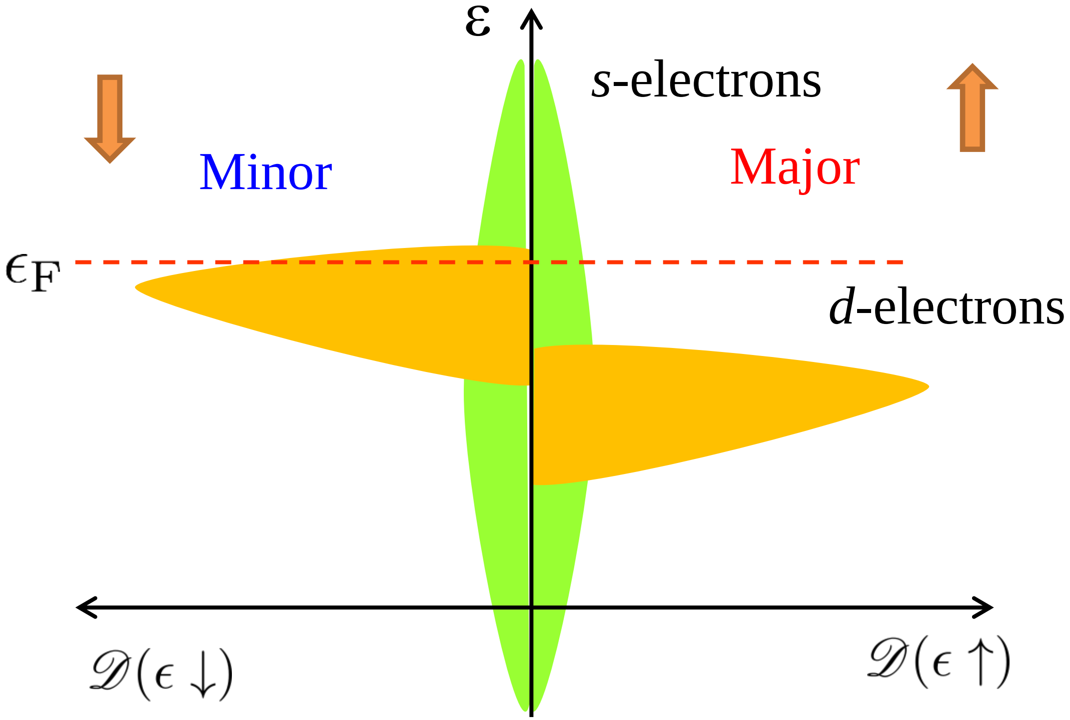
Radial wavefunction

$$\begin{cases} |4s\rangle \propto R_{40}(r) \propto \exp\left(-\dfrac{r}{4a_{\mathrm{B}}}\right) \\ |3d\rangle \propto R_{32}(r) \propto \left(\dfrac{r}{r_{\mathrm{B}}}\right)^2 \exp\left(-\dfrac{r}{3a_{\mathrm{B}}}\right) \end{cases}$$

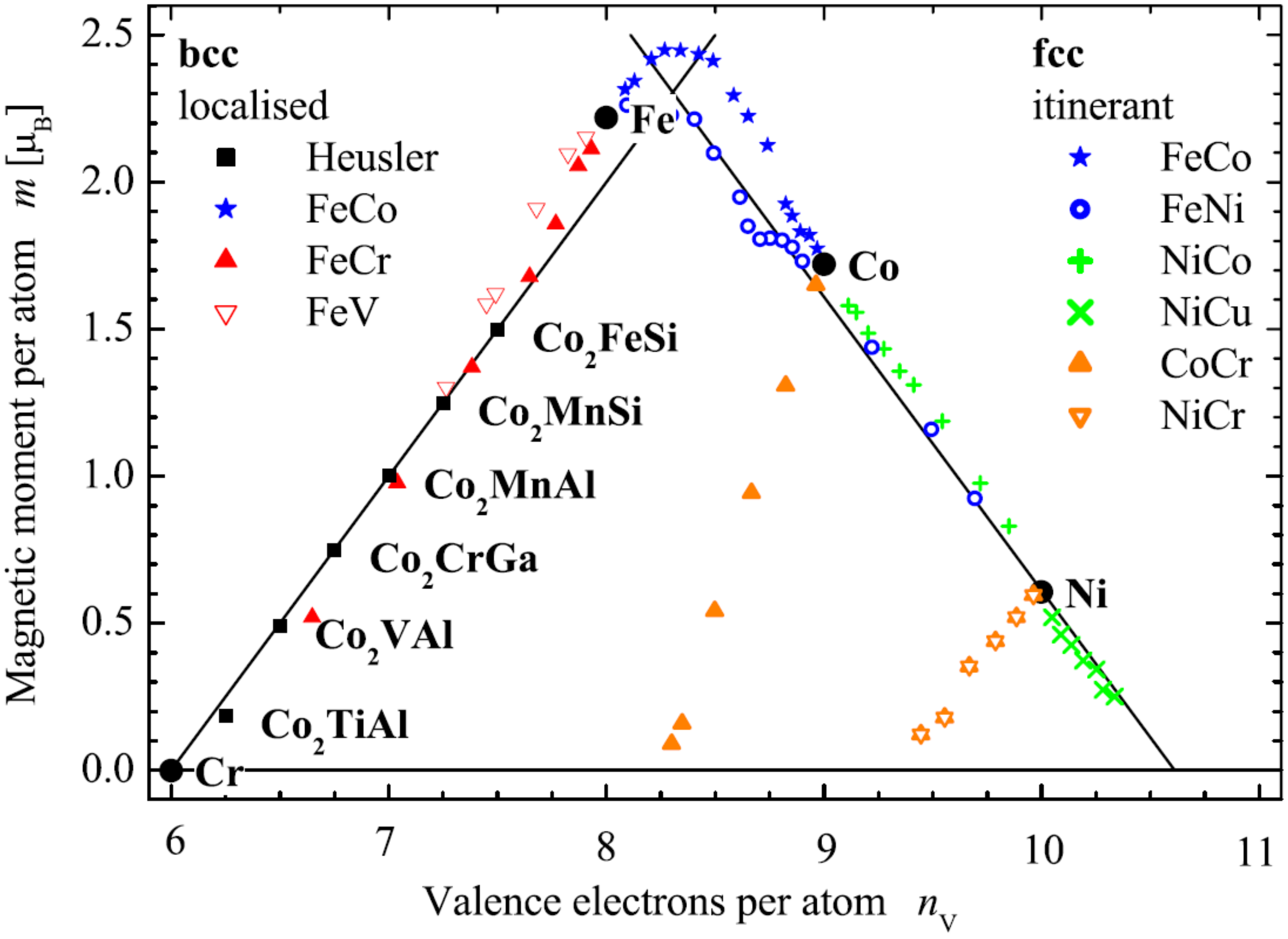


bcc α-Fe

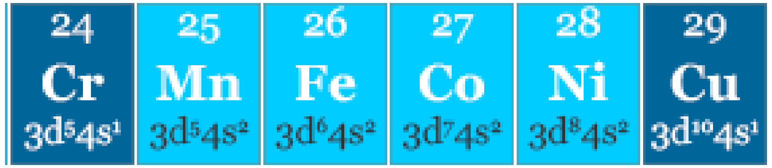
$2.86 \times 10^{-10}\mathrm{m} = 5.4a_{\mathrm{B}}$



Magnetism of 3*d* transition metals: Slater-Pauling's curve



Balke et al., Sci. Technol. Adv. Mater. **9**, 014102 (2008).



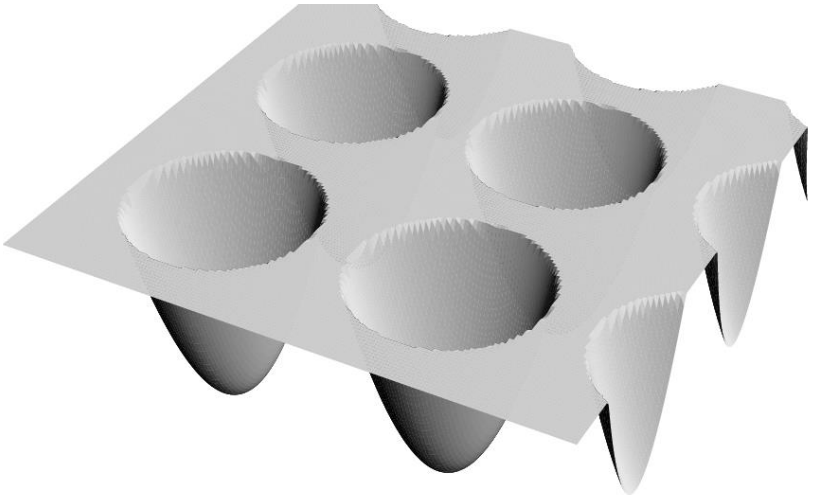
Slater-Pauling's curve

Experimental data are in line.

The gradient is ± 1 !

Abrupt change around Fe

APW method to calculate DOS



Muffin-tin potential

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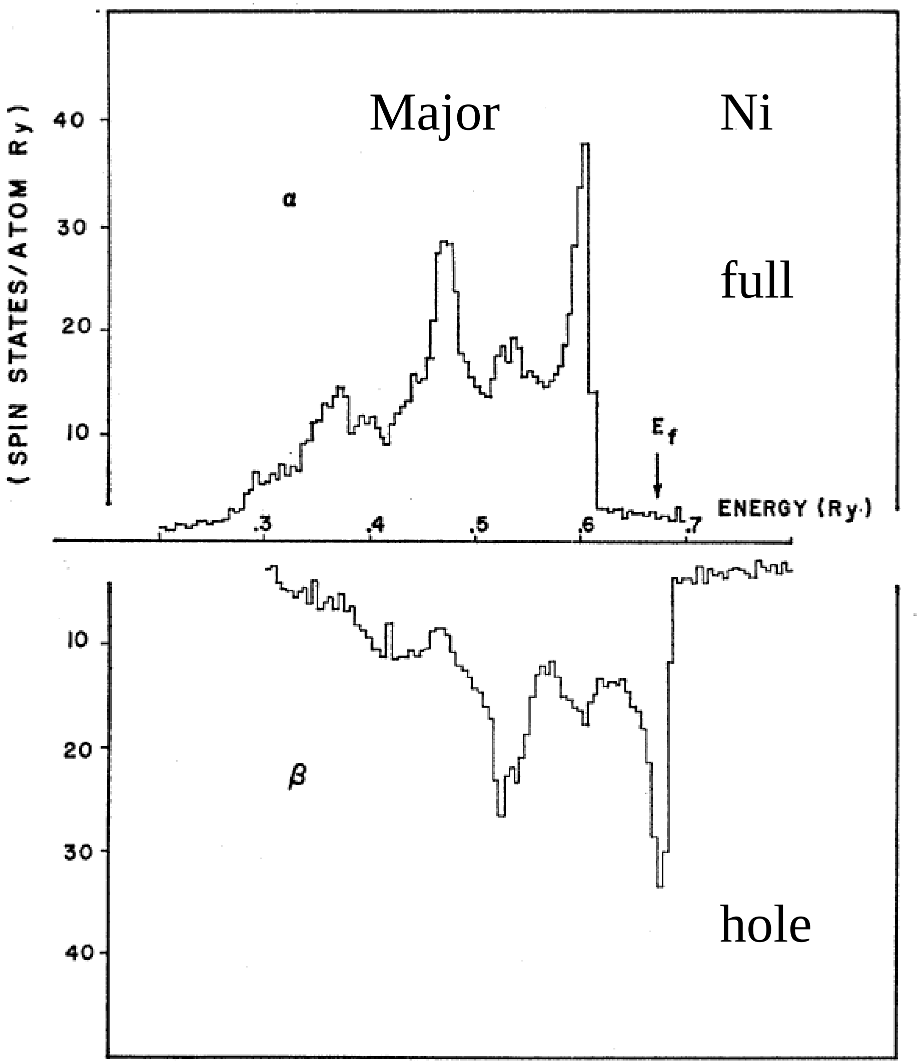
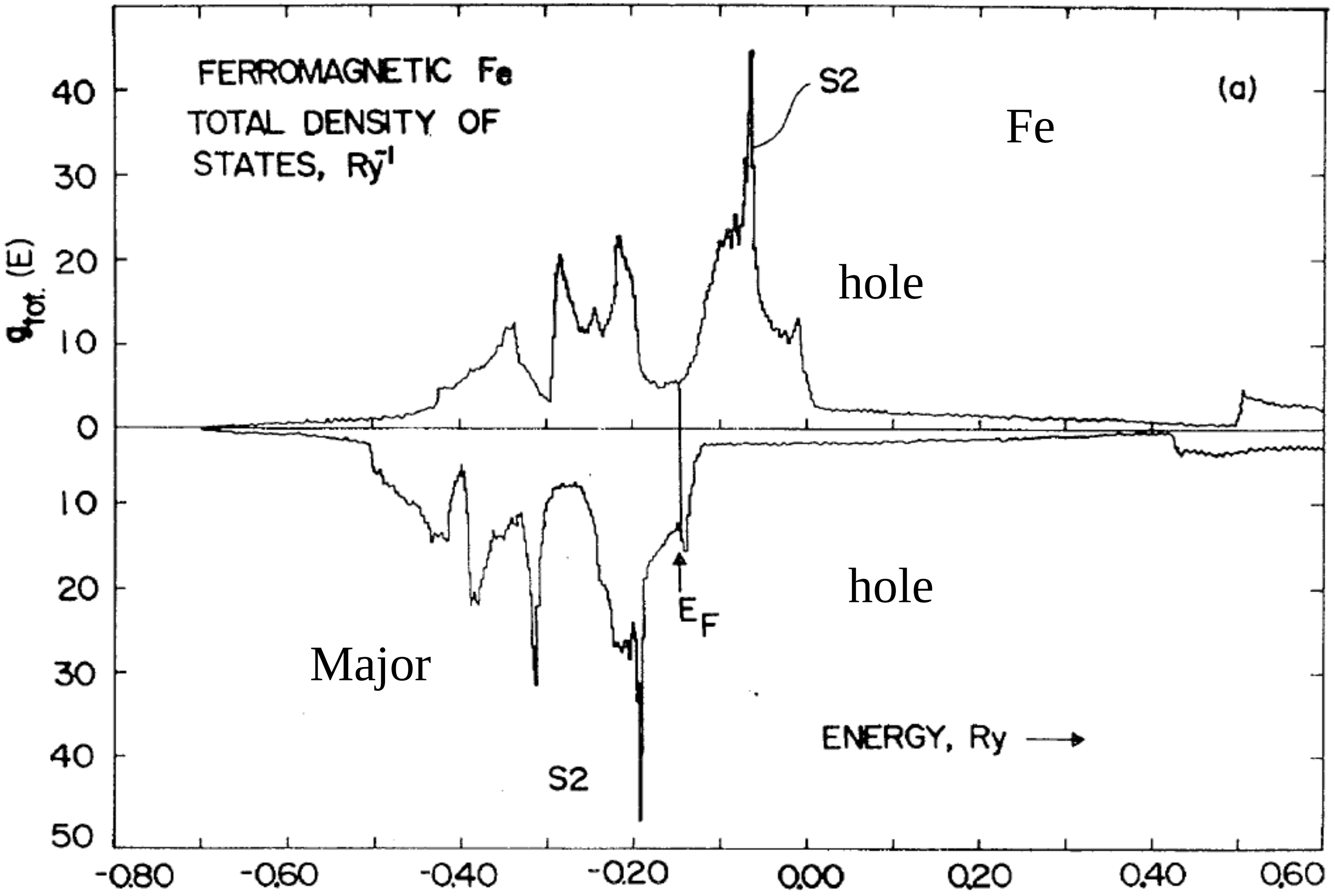
$\Downarrow$

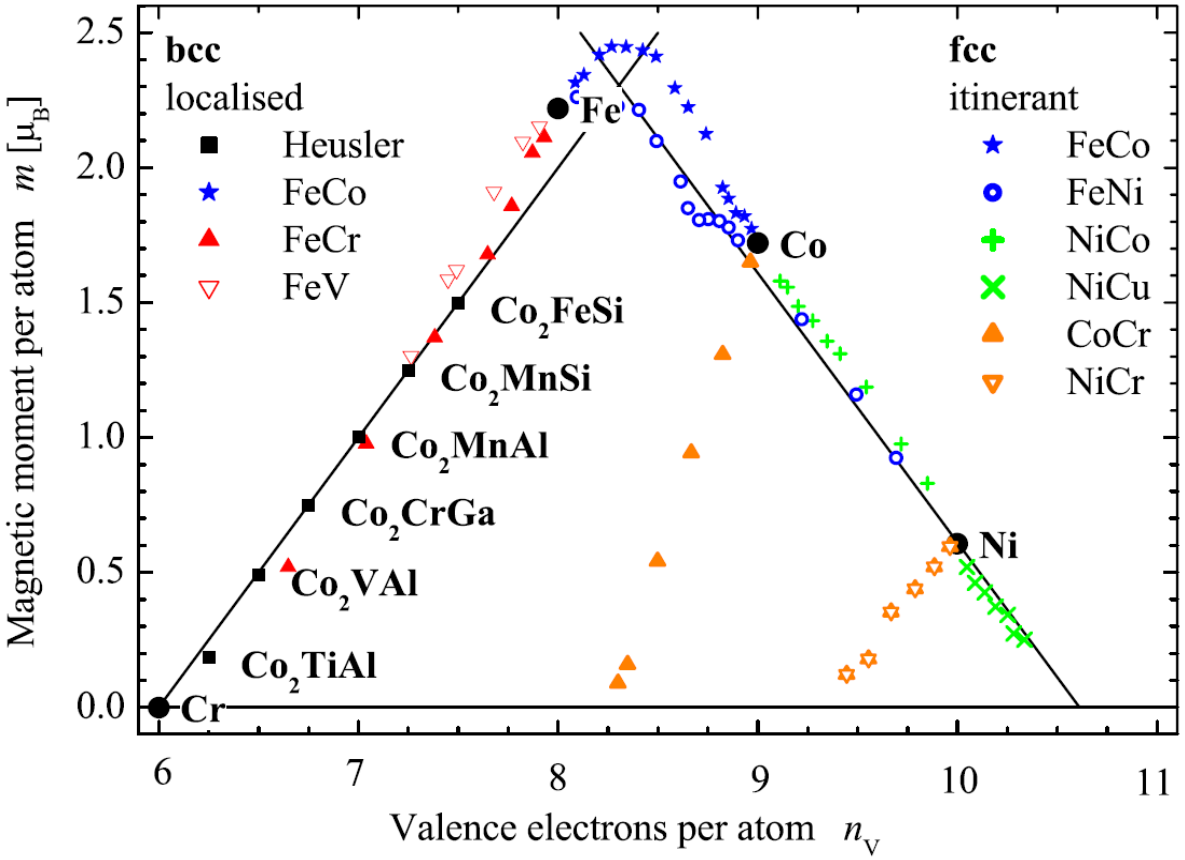
Iteration for convergence for each $\boldsymbol{k}$

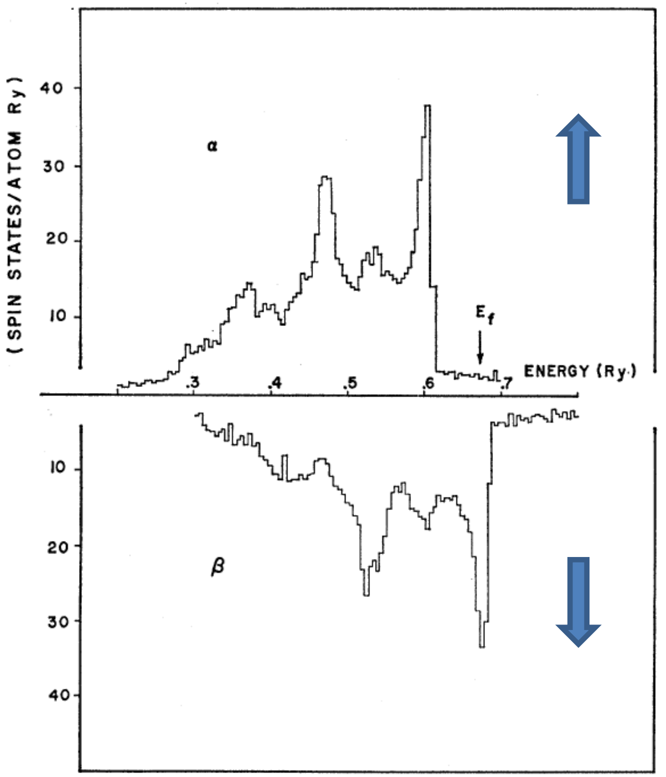
Density of states in Ni and Fe





Explanation of Slater-Pauling's curve (1)





Case of Ni

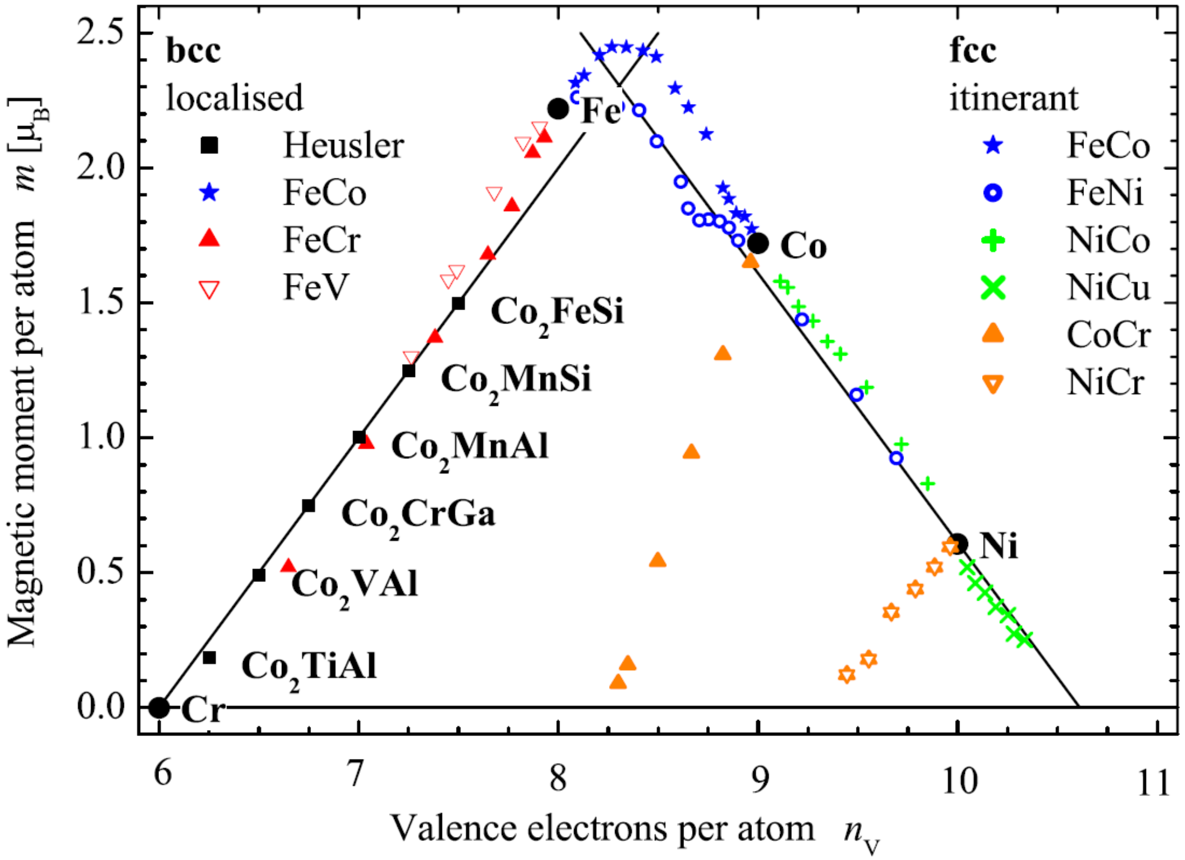
$3d\uparrow$: full 5 electrons

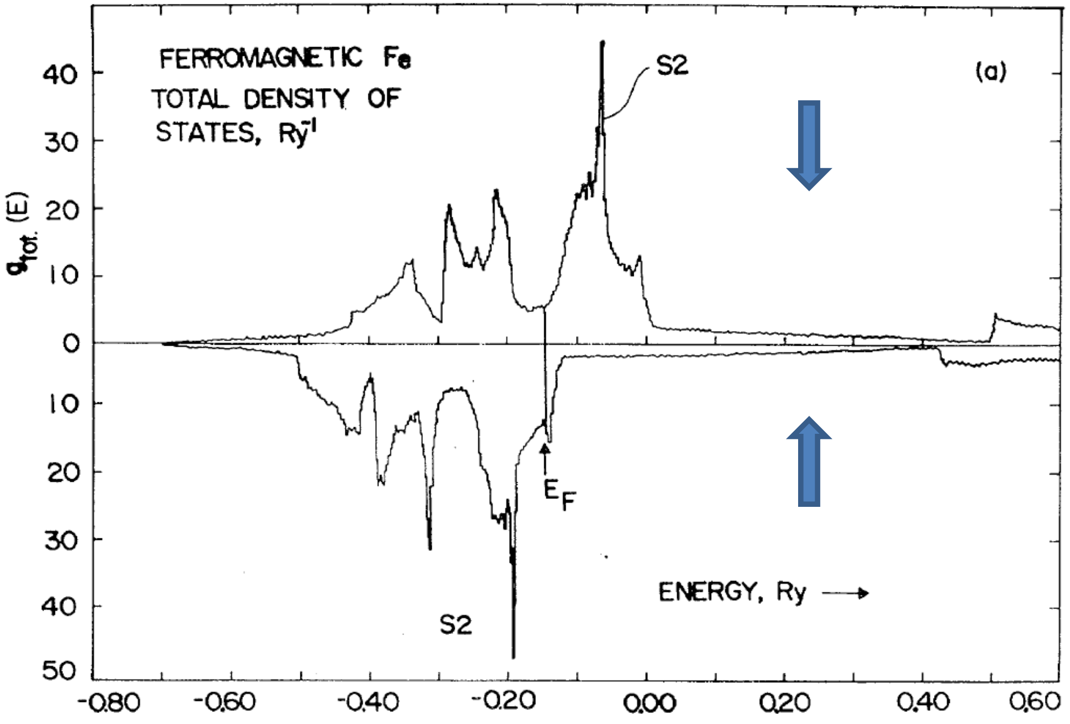
$3d\downarrow$: 4.4 electrons

Increase of electrons → filling up the holes and the magnetic moment decreases

Decrease of electrons → opening holes in $3d\downarrow$ and the magnetic moment increases

Explanation of Slater-Pauling's curve (2)





Case of Fe $3d\downarrow$: 2.5 electrons

$3d\uparrow$: 4.7 electrons (not full, hole exists)

Increase of electrons → filling up the holes in ↑ and the magnetic moment increases

After complete filling up of ↑ → filling up the holes in ↓ and the magnetic moment decreases

Magnetic susceptibility in HF approximation

Magnetic moment: $$M = \frac{g\mu_B}{2}\sum_i [\langle n_{i\uparrow}\rangle - \langle n_{i\downarrow}\rangle] = \frac{g\mu_B}{2}\sum_i n_{i-}$$

Magnetic susceptibility per atom: $$\chi = \frac{M}{NB} = \frac{g\mu_B}{2}\frac{n_-}{B}$$

Electron energy in magnetic field: $$E_B = E(0) + E_2 n_-^2 - N\frac{g\mu_B}{2}Bn_-$$

where $$E_2 = \frac{1}{2}\frac{d^2(\Delta E)}{dn_-^2}$$ with $$\Delta E = \frac{N}{4}\left[\frac{m^2}{\mathscr{D}(E_F)} - Um^2\right]$$

This should be positive for the appearance of ferromagnetism. (remember GL theory).

Then minimization of E_B should give n_- as $$\chi = \frac{(g\mu_B)^2 N}{4E_2}$$

We finally obtain $$\chi = \left(\frac{g\mu_B}{2}\right)^2 \frac{\mathscr{D}(E_F)}{1 - U\mathscr{D}(E_F)} = \frac{\chi_{\text{Pauli(a)}}}{\underline{1 - U\mathscr{D}(E_F)}}$$

Stoner factor

Temperature dependence of susceptibility in HF approximation

By using the identity for degenerated Fermi gas:

$$\mu = \mu_0 \left[1 - \frac{\pi^2}{6} \frac{d \log \mathscr{D}(\mu_0)}{d \log \mu_0} \left(\frac{k_B T}{\mu_0} \right)^2 + \cdots \right]$$

we write

$$\delta\mu = -\frac{\pi^2 \mathcal{D}'_F}{6\mathcal{D}_F}(k_B T)^2 \qquad d\mathscr{D}(E)/dE|_{E=E_F} \to \mathcal{D}'_F$$

By defining

$$A = \frac{\pi^2}{6}\left(\frac{(\mathcal{D}'_F)^2}{\mathcal{D}_F} - \mathcal{D}''_F \right)$$

Susceptibility with temperature correction:

$$\chi = \left(\frac{g\mu_B}{2} \right)^2 \frac{\mathscr{D}(E_F)}{1 - U\mathscr{D}(E_F) + UA(k_B T)^2}$$

$$\Rightarrow \quad \chi = \frac{C}{T^2 - T_C^2}$$

This is not Curie-Weiss observed in experiments.

Kubo formula

Dynamical response to magnetic field $\mathscr{H}_0 + \underline{\mathscr{H}_{\text{ext}}(t)}$ Time-dependent perturbation

Heisenberg equation of motion $i\hbar\dfrac{\partial\rho}{\partial t} = [\mathscr{H}_0 + \mathscr{H}_{\text{ext}}(t), \rho(t)]$

Single body density matrix: $\rho(x, x') = \sum_{i=1}^{N} \varphi^*_{k_i}(x)\varphi_{k_i}(x')$

Initial condition: $t = -\infty$ $\rho(-\infty) = \rho_{\text{eq}} = \dfrac{1}{Z_0}\exp\left(-\dfrac{\mathscr{H}_0}{k_{\text{B}}T}\right)$

Unperturbed system partition function: $Z_0 = \text{Tr}[\exp(-\mathscr{H}_0/k_{\text{B}}T)]$

Then the density matrix should satisfy (see lecture note for the calculation)

$$\rho(t) = \rho_{\text{eq}} + \frac{1}{i\hbar}\int_{-\infty}^{t} dt'[U_0(t-t')\mathscr{H}_{\text{ext}}(t')U_0^{-1}(t-t'), U_0(t-t')\rho(t')U_0^{-1}(t-t')]$$

$$= \rho_{\text{eq}} + \frac{1}{i\hbar}\int_{-\infty}^{t} dt' U_0(t-t')[\mathscr{H}_{\text{ext}}(t'), \rho(t')]U_0^{-1}(t-t')$$

where

$$U_0(t) \equiv \exp\left(\frac{\mathscr{H}_0}{i\hbar}t\right)$$

Kubo formula (2)

For linear response we can replace $\rho(t') \to \rho_{\mathrm{eq}}$ made of eigenstates of unperturbed Hamiltonian

Then we can write $$\rho(t) \simeq \rho_{\mathrm{eq}} + \frac{1}{i\hbar}\int_{-\infty}^{t} dt' [U_0(t-t')\mathscr{H}_{\mathrm{ext}}(t')U_0^{-1}(t-t'), \rho_{\mathrm{eq}}]$$

External field $\mathscr{H}_{\mathrm{ext}}(t) = -PF(t)$

Expectation value of general physical quantity Q $$\langle Q(t)\rangle = \mathrm{Tr}\{\rho(t)Q\} = \langle Q_{\mathrm{eq}}\rangle + \frac{1}{i\hbar}\int_{-\infty}^{t} dt' \langle [P, Q(t-t')]\rangle F(t')$$

where $\langle Q_{\mathrm{eq}}\rangle = \mathrm{Tr}\{\rho_{\mathrm{eq}}Q\}, \quad Q(t) = U_0(t)^{-1}QU_0(t)$

$\langle [P, Q(t-t')]\rangle$ is a pure imaginary.

Field with frequency ω $F(t) = F_0\cos(\omega t) = \mathrm{Re}[F_0 e^{-i\omega t}]$

Definition of susceptibility $\chi(\omega)$ $\mathit{\Delta} Q(t) = \langle Q(t)\rangle - \langle Q_{\mathrm{eq}}\rangle = \mathrm{Re}[\chi(\omega)F_0 e^{-i\omega t}]$

We can equalize this with $$\mathit{\Delta} Q(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} dt' \langle [P, Q(t-t')]\rangle \mathrm{Re}[F_0 e^{-i\omega t'}]$$

Kubo formula (3)

Definition of susceptibility $\chi(\omega)$ $\quad \Delta Q(t) = \langle Q(t) \rangle - \langle Q_{\text{eq}} \rangle = \text{Re}[\chi(\omega) F_0 e^{-i\omega t}]$

We can equalize this with $\quad \Delta Q(t) = \dfrac{1}{i\hbar} \displaystyle\int_{-\infty}^{t} dt' \, \langle [P, Q(t-t')] \rangle \, \text{Re}[F_0 e^{-i\omega t'}]$

The first equation → $\quad \text{Re}[\chi(\omega) F_0 e^{-i\omega t}] = \dfrac{F_0}{2} [\chi^*(\omega) e^{i\omega t} + \chi(\omega) e^{-i\omega t}]$

The second equation → $\quad \dfrac{F_0}{2i\hbar} \left\{ \left[\displaystyle\int_0^{\infty} d\tau \, \langle [P, Q(\tau)] \rangle \, e^{-i\omega\tau} \right] e^{i\omega t} + \left[\displaystyle\int_0^{\infty} d\tau \, \langle [P, Q(\tau)] \rangle \, e^{i\omega\tau} \right] e^{-i\omega t} \right\}$

$\tau = t - t'$

Kubo formula $\quad \chi_{QP}(\omega) = \dfrac{i}{\hbar} \displaystyle\int_0^{\infty} \langle [Q(\tau), P] \rangle \, e^{i\omega\tau} d\tau$

Fluctuation-dissipation theorem

Green's function $G^{\pm}_{QP}(t) = \mp \frac{i}{\hbar}\theta(\pm t)\langle[Q(t), P]\rangle$ (+: retarded, –: advanced)

$$\theta(t) = \begin{cases} 1 & (t \geq 0) \\ 0 & (t < 0) \end{cases}$$ Heaviside function

Kubo formula is re-written as: $\chi_{QP}(\omega) = -\mathcal{G}^{+}_{QP}(\omega) = -\underline{\mathscr{F}_\omega}\{G^{+}_{QP}(t)\}$

Fourier transform to ω-space

$$\mathcal{S}_{QP}(\omega) = \int_{-\infty}^{\infty} dt\, \underline{\langle Q(t), P\rangle}\, e^{i\omega t}$$

Correlation function

Fluctuation-dissipation theorem:

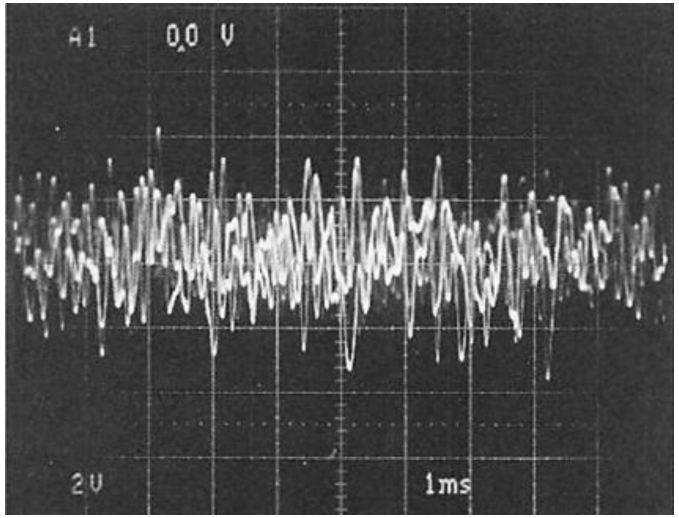
$$\mathcal{S}_{QP}(\omega) = \frac{i}{1 - e{-}\beta\hbar\omega}[\mathcal{G}^{+}_{QP}(\omega) - \mathcal{G}^{-}_{QP}(\omega)]$$

See the lecture note for the calculation

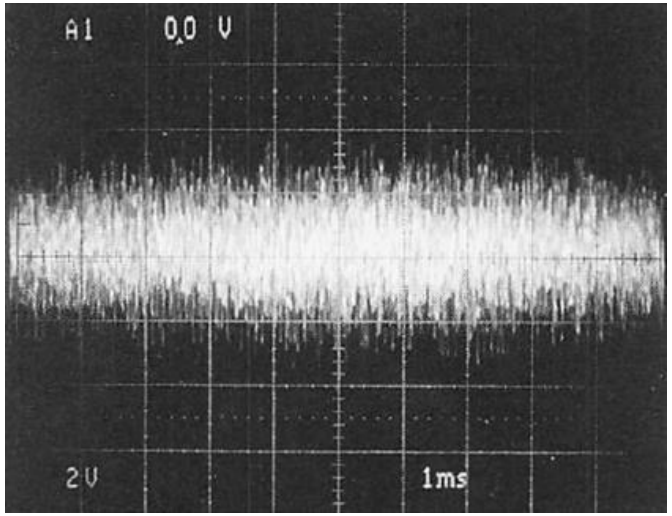
Example of fluctuation-dissipation theorem

$$G_{\mathrm{v}}(\omega) = 4k_{\mathrm{B}}T\mathrm{Re}[Z(i\omega)]$$
$$= 4k_{\mathrm{B}}TR$$

Johnson-Nyquist noise
Thermal noise



Low pass 5 kHz



100 kHz

Random phase approximation (RPA)

External magnetic field: $\boldsymbol{B}(\boldsymbol{r},t) = \boldsymbol{B}(\boldsymbol{q},\omega)e^{i(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)}$

Hubbard model: $\mathscr{H} = \sum_{i,j,s} t_{ij} c^\dagger_{is} c_{js} + U \sum_i^N \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$

Local magnetization (in unit $-g\mu_{\mathrm{B}}$): $\boldsymbol{S}(\boldsymbol{r}) = \frac{1}{2}\sum_i \sum_{\alpha,\beta} \delta(\boldsymbol{r}-\boldsymbol{r}_i) c^\dagger_{i\alpha} \boldsymbol{\sigma}_{\alpha\beta} c_{i\beta}$ $\qquad \boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$

Perturbation Hamiltonian: $\mathscr{H}_{\mathrm{ext}}(t) = g\mu_{\mathrm{B}} \int \boldsymbol{B}(\boldsymbol{r},t)\cdot \boldsymbol{S}(\boldsymbol{r}) d^3\boldsymbol{r} = g\mu_{\mathrm{B}} \boldsymbol{S}_{-\boldsymbol{q}} \cdot \boldsymbol{B}(\boldsymbol{q},\omega) e^{-i\omega t}$

Magnetization in q-space

$$\left.\begin{aligned} S_{\boldsymbol{q}+} &= S_{\boldsymbol{q}x} + iS_{\boldsymbol{q}y} = \sum_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}\uparrow} a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, \\ S_{\boldsymbol{q}-} &= S_{\boldsymbol{q}x} - iS_{\boldsymbol{q}y} = \sum_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}\downarrow} a_{\boldsymbol{k}+\boldsymbol{q}\uparrow}, \\ S_{\boldsymbol{q}z} &= (1/2)\sum_{\boldsymbol{k}} (a^\dagger_{\boldsymbol{k}\uparrow} a_{\boldsymbol{k}+\boldsymbol{q}\uparrow} - a^\dagger_{\boldsymbol{k}\downarrow} a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}). \end{aligned}\right\}$$

RPA: susceptibility

Kubo formula $$\chi_{QP}(\omega) = \frac{i}{\hbar}\int_0^\infty \langle [Q(\tau), P]\rangle\, e^{i\omega\tau} d\tau$$

Correspondence $$P \to g\mu_{\mathrm{B}}\boldsymbol{S}_{-\boldsymbol{q}} \qquad Q \to g\mu_{\mathrm{B}}\boldsymbol{S}_{\boldsymbol{q}}$$

Susceptibility $$\chi_{zz}(\boldsymbol{q},\omega) = (g\mu_{\mathrm{B}})^2 \frac{i}{\hbar}\int_0^\infty dt\, \langle [S_{\boldsymbol{q}z}(t), S_{-\boldsymbol{q}z}]\rangle\, e^{i\omega t}$$

$$\chi_{+-}(\boldsymbol{q},\omega) = (g\mu_{\mathrm{B}})^2 \frac{i}{\hbar}\int_0^\infty dt\, \langle [S_{\boldsymbol{q}+}, S_{-\boldsymbol{q}-}]\rangle\, e^{i\omega t}$$

To calculate above, let us consider a Green's function $$G^{+}_{\boldsymbol{kq}}(t) = -i\theta(t)\,\langle [a^\dagger_{\boldsymbol{k}\uparrow}(t) a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}(t), S_{-\boldsymbol{q}-}]\rangle$$

$$i\hbar\frac{\partial G_{\boldsymbol{kq}}}{\partial t} = -i\theta(t)\,\langle [e^{i\mathscr{H}t/\hbar}[a^\dagger_{\boldsymbol{k}\uparrow} a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, \mathscr{H}]e^{-i\mathscr{H}t/\hbar}, S_{-\boldsymbol{q}-}]\rangle + \delta(t)\hbar\,\langle [a^\dagger_{\boldsymbol{k}\uparrow}(t) a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}(t), S_{-\boldsymbol{q}-}]\rangle$$

RPA: susceptibility (2)

Hubbard Hamiltonian $\mathscr{H} = \mathscr{H}_{\mathrm{k}} + \mathscr{H}_{\mathrm{int}}$

$$
\begin{aligned}
[a^\dagger_{\boldsymbol{k}\uparrow}a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, S_{-\boldsymbol{q}-}] &= \sum_{\boldsymbol{k}'}[a^\dagger_{\boldsymbol{k}\uparrow}a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, a^\dagger_{\boldsymbol{k}'+\boldsymbol{q}\downarrow}a_{\boldsymbol{k}'\uparrow}] \\
&= a^\dagger_{\boldsymbol{k}\uparrow}a_{\boldsymbol{k}\uparrow} - a^\dagger_{\boldsymbol{k}+\boldsymbol{q}\downarrow}a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, \\
[a^\dagger_{\boldsymbol{k}\uparrow}a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, \mathscr{H}_{\mathrm{k}}] &= (\epsilon_{\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{\boldsymbol{k}})a^\dagger_{\boldsymbol{k}\uparrow}a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, \\
[a^\dagger_{\boldsymbol{k}\uparrow}a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, \mathscr{H}_{\mathrm{int}}] &= (U/N)\sum_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{p}}[a^\dagger_{\boldsymbol{k}\uparrow}a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, a^\dagger_{\boldsymbol{k}_1+\boldsymbol{p}\uparrow}a^\dagger_{\boldsymbol{k}_2-\boldsymbol{p}\downarrow}a_{\boldsymbol{k}_2\downarrow}a_{\boldsymbol{k}_1\uparrow}] \\
&= -(U/N)\left[\sum_{\boldsymbol{k}_1,\boldsymbol{p}} a^\dagger_{\boldsymbol{k}\uparrow}a^\dagger_{\boldsymbol{k}_1+\boldsymbol{p}\uparrow}a_{\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{p}\downarrow}a_{\boldsymbol{k}_1\uparrow} + \sum_{\boldsymbol{k}_2,\boldsymbol{p}} a^\dagger_{\boldsymbol{k}+\boldsymbol{p}\uparrow}a^\dagger_{\boldsymbol{k}_2-\boldsymbol{q}\downarrow}a_{\boldsymbol{k}_2\downarrow}a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}\right].
\end{aligned}
$$

Mean field approximation

$$
-\sum_{\boldsymbol{p}} a^\dagger_{\boldsymbol{k}+\boldsymbol{p}\uparrow}a_{\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{p}\downarrow}\langle a^\dagger_{\boldsymbol{k}\uparrow}a_{\boldsymbol{k}\uparrow}\rangle + \sum_{\boldsymbol{k}_1} a^\dagger_{\boldsymbol{k}\uparrow}a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}\langle a^\dagger_{\boldsymbol{k}_1\uparrow}a_{\boldsymbol{k}_1\uparrow}\rangle
$$

Random phase approximation (RPA)

$$
-\sum_{\boldsymbol{k}_2} a^\dagger_{\boldsymbol{k}\uparrow}a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}\langle a^\dagger_{\boldsymbol{k}_2\downarrow}a_{\boldsymbol{k}_2\downarrow}\rangle + \sum_{\boldsymbol{p}} a^\dagger_{\boldsymbol{k}+\boldsymbol{p}\uparrow}a_{\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{p}\downarrow}\langle a^\dagger_{\boldsymbol{k}+\boldsymbol{q}\downarrow}a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}\rangle
$$

RPA: susceptibility (3)

In paramagnetic state:

$$i\hbar\frac{\partial G_{\boldsymbol{kq}}}{\partial t} = (\epsilon_{\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{\boldsymbol{k}})G_{\boldsymbol{kq}}(t)$$
$$- (U/N)(\langle a^\dagger_{\boldsymbol{k}\uparrow} a_{\boldsymbol{k}\uparrow}\rangle - \langle a^\dagger_{\boldsymbol{k}+\boldsymbol{q}\downarrow} a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}\rangle)\sum_{\boldsymbol{p}} G_{(\boldsymbol{k}+\boldsymbol{p})\boldsymbol{q}}(t)$$
$$+ (\langle a^\dagger_{\boldsymbol{k}\uparrow} a_{\boldsymbol{k}\uparrow}\rangle - \langle a^\dagger_{\boldsymbol{k}+\boldsymbol{q}\downarrow} a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}\rangle)\delta(t)$$

Fourier transformation:

$$\mathcal{G}_{\boldsymbol{kq}}(\omega) = \frac{f_{\boldsymbol{k}\uparrow} - f_{\boldsymbol{k}+\boldsymbol{q}\downarrow}}{\hbar\omega + \epsilon_{\boldsymbol{k}} - \epsilon_{\boldsymbol{k}+\boldsymbol{q}}}\left[1 - \frac{U}{N}\sum_{\boldsymbol{p}} \mathcal{G}_{\boldsymbol{pq}}(\omega)\right]$$

$$f_{\boldsymbol{k}s} = \langle a^\dagger_{\boldsymbol{k}s} a_{\boldsymbol{k}s}\rangle$$

Fermi distribution function

Summation on ***k***

$$\chi_{+-}(\boldsymbol{q},\omega) = N(g\mu_{\mathrm{B}})^2\frac{2\chi^{(0)}(\boldsymbol{q},\omega)}{1 - 2U\chi^{(0)}(\boldsymbol{q},\omega)}$$

Susceptibility of non-interacting system:

$$\chi^{(0)}(\boldsymbol{q},\omega) = \frac{1}{2N}\sum_{\boldsymbol{k}}\frac{f_{\boldsymbol{k}+\boldsymbol{q}\downarrow} - f_{\boldsymbol{k}\uparrow}}{\hbar\omega + \epsilon_{\boldsymbol{k}} - \epsilon_{\boldsymbol{k}+\boldsymbol{q}}}$$

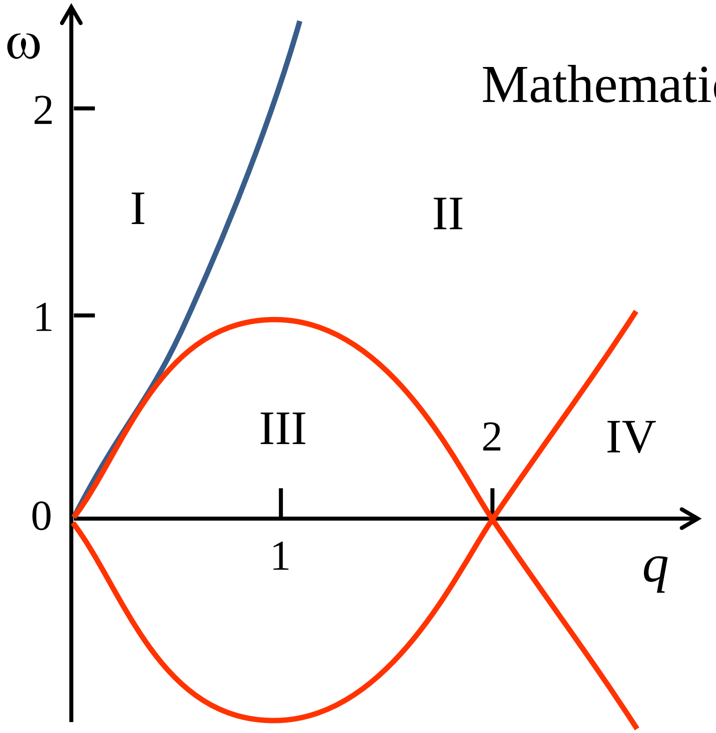
unit $(g\mu_{\mathrm{B}})^2$

Susceptibility of non-interacting system

$\hbar \to 1$ Wavenumber unit: k_F Energy unit: E_F

$$\frac{1}{2N}\sum_{\boldsymbol{k}} \frac{f_{\boldsymbol{k}}}{\omega + \epsilon_{\boldsymbol{k}-\boldsymbol{q}} - \epsilon_{\boldsymbol{k}}} = \frac{1}{2}\rho(\epsilon_{\mathrm{F}}) \int_0^1 k^2 dk \int_{-1}^{1} \frac{d(\cos\theta)}{\omega + q^2 - 2kq\cos\theta}$$

$$= \frac{1}{2}\rho(\epsilon_{\mathrm{F}}) \int_0^1 k^2 dk \frac{1}{2kq} \log \frac{\omega + q^2 + 2kq}{\omega + q^2 - 2kq}$$



Mathematical identity: $\displaystyle \int x \log(ax+b)dx = \frac{1}{2}\left[x^2 - \left(\frac{b}{a}\right)^2\right] \log(ax+b) - \frac{x^2}{4} + \frac{b}{2a}x$

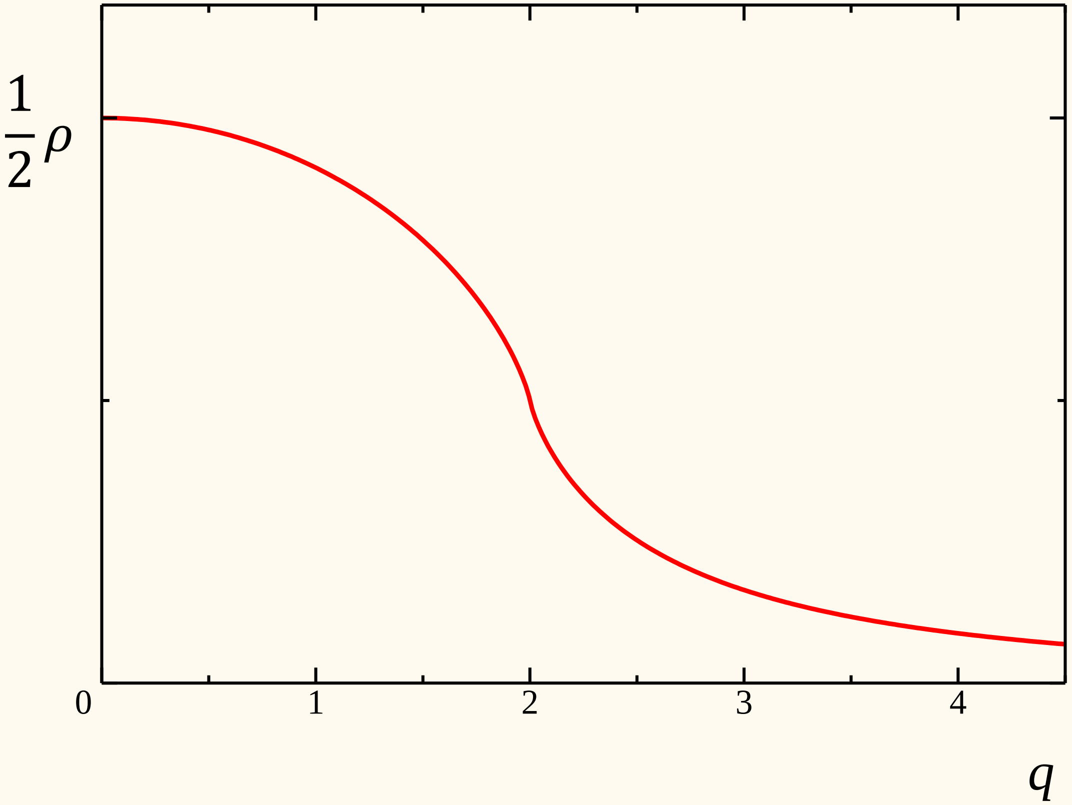
$$\chi^{(0)}(q,\omega) = \frac{\rho(\epsilon_{\mathrm{F}})}{2}\frac{1}{2q}\left\{\frac{1}{2}\left[1 - \left(\frac{\omega+q^2}{2q}\right)^2\right]\log\frac{\omega+q^2+2q}{\omega+q^2-2q} + \frac{\omega+q^2}{2q}\right.$$

$$\left. -\frac{1}{2}\left[1 - \left(\frac{-\omega+q^2}{2q}\right)^2\right]\log\frac{-\omega+q^2-2q}{\omega+q^2+2q} + \frac{-\omega+q^2}{2q}\right\}$$

Boundary of Kohn anomaly: $\omega = \pm(q^2 \pm 2q)$

Kohn anomaly, Stoner condition, SDW

$\mathrm{Re}[\chi^{(0)}(q,0)]$



In region III

$$\mathrm{Im}[\chi^{(0)}(q,\omega)] = \frac{\rho(\epsilon_F)}{2}\frac{\pi}{4}\frac{\omega}{q}$$

$$\mathrm{Re}[\chi^{(0)}(q,0)] = \frac{\rho(\epsilon_F)}{2}\frac{1}{2q}\left\{\left(1-\frac{q^2}{4}\right)\log\left|\frac{2+q}{2-q}\right| + q\right\}$$

$$\to \frac{\rho(\epsilon_F)}{2} \qquad (q \to 0)$$

$$\chi_{+-}(\boldsymbol{q},\omega) = N(g\mu_B)^2 \frac{2\chi^{(0)}(\boldsymbol{q},\omega)}{1-2U\chi^{(0)}(\boldsymbol{q},\omega)}$$

$$U\chi^{(0)}(\boldsymbol{q}_{\max},0) \geq \frac{1}{2}$$ Magnetic order

$\boldsymbol{q}_{\max} = 0$ Stoner condition

$\boldsymbol{q}_{\max} \neq 0$ Spin density wave (SDW)

Summary

- Magnetism in $3d$ transition metals
  - Slater-Pauling's curve
  - Density of states by APW method
- Kubo formula (linear response)
- Fluctuation dissipation theorem
- Random phase approximation (RPA)

2022.7.13 Lecture 14

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

Institute for Solid State Physics, University of Tokyo

Shingo Katsumoto

Notification

Deadline for exercise 0629 is now 21st July.

Problems for the final report will be uploaded in the evening of 14 July.
The deadline for the submission of report is 2nd August.

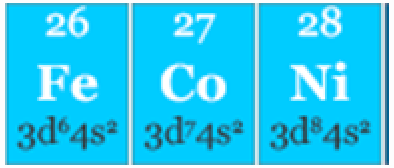
Review

- Magnetism in 3*d* transition metals
  - Slater-Pauling’s curve
  - Density of states by APW method
- Kubo formula (linear response)
- Fluctuation dissipation theorem
- Random phase approximation (RPA)

- Paramagnon theory
- Self-consistent renormalization spin-fluctuation theory

Why and how we consider magnons in marginally paramagnetic metals?

Itinerant electron magnetism



- Hartree-Fock approximation for jellium model
  - ➢ overestimation of stability of ferromagnetism
- HFA for Hubbard Hamiltonian
  - ➢ Some successes: Explanation of Slater-Pauling curve
  - ➢ Still has the overestimation problem
- Dynamic mean field approximation by random phase approximation
  - ➢ Curie-Weiss law cannot be reproduced
  - ➢ Finding of spin-density-wave (SDW) i.e. existence of spin fluctuation (magnon)

Hypothesis to improve the approximation: Spin fluctuations exist in thermal equilibrium and lower the energy of marginally paramagnetic states

Agenda: Hellmann-Feynman theorem to treat the effect of fluctuation, fluctuation-dissipation theorem

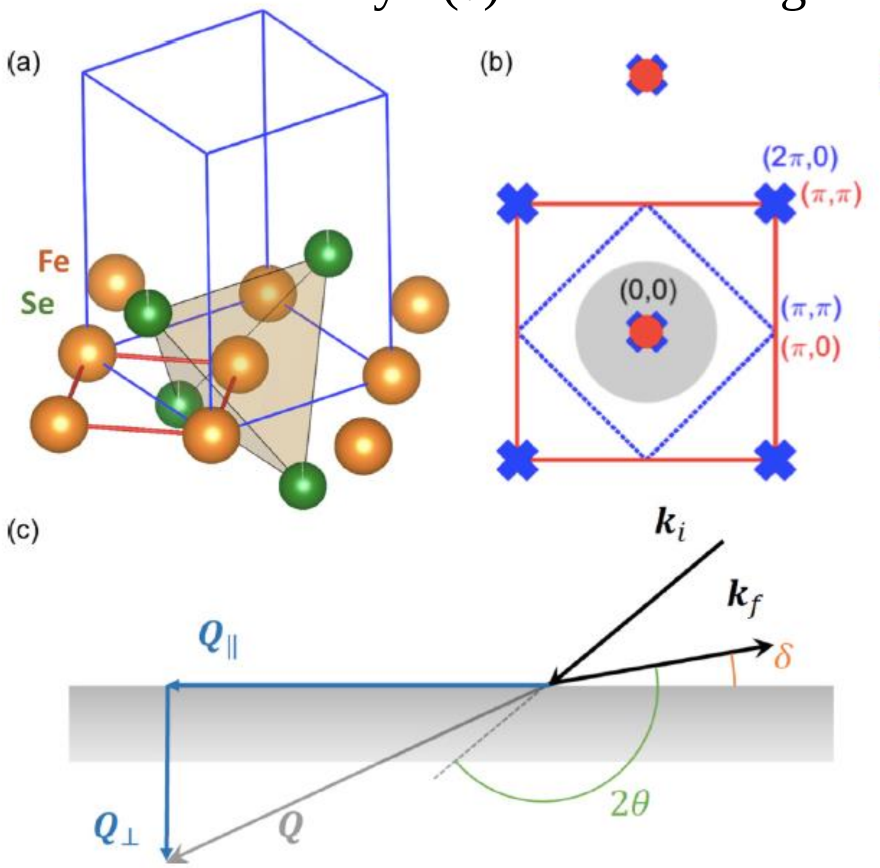
Paramagnons in “nearly ferromagnetic” materials

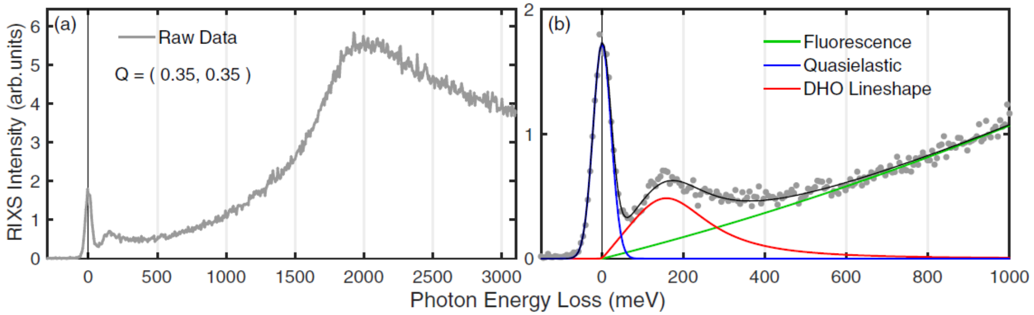
β-FeSe iron-based superconductor

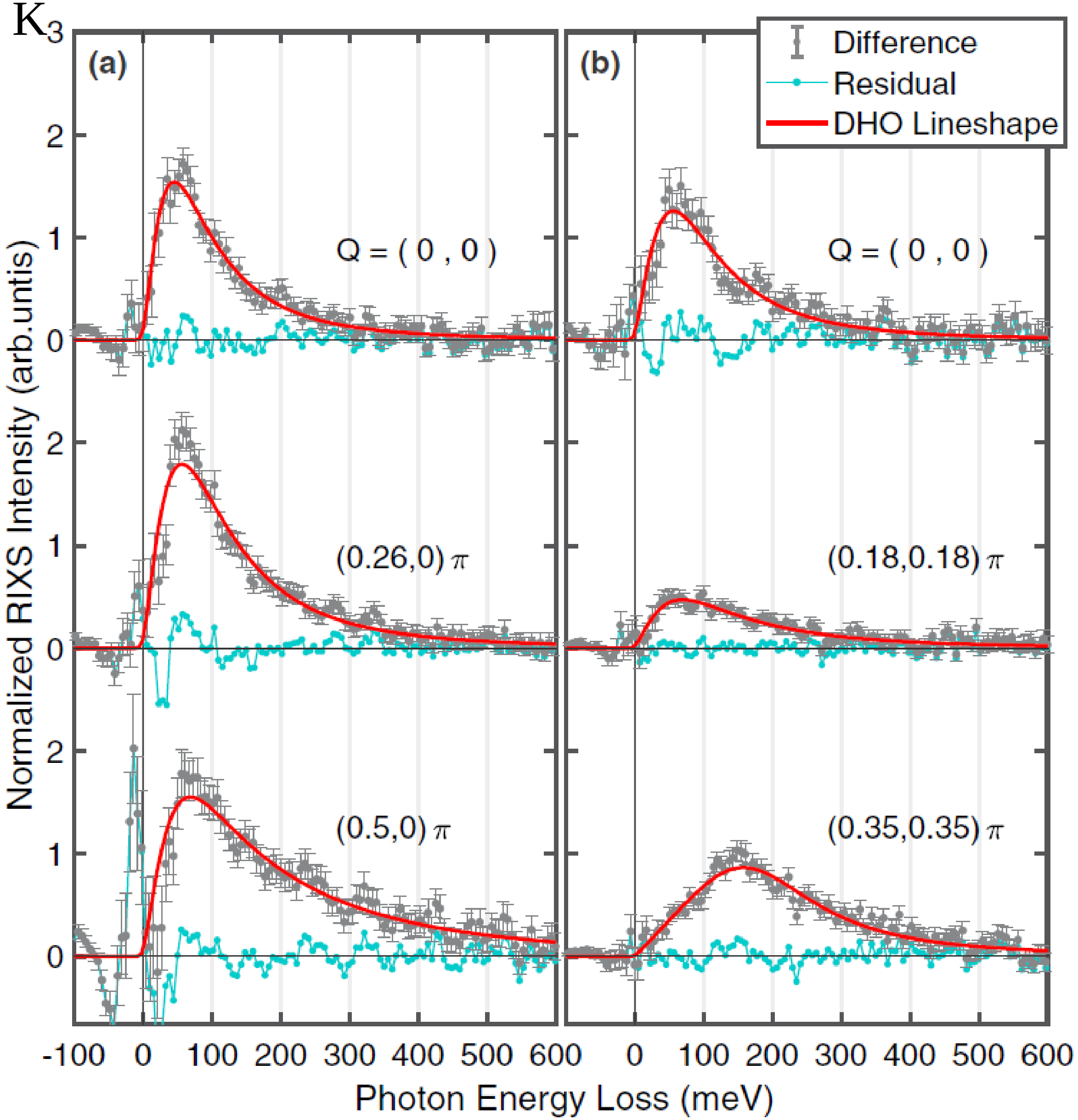
T_C 100 K in monolayer(?) anti-ferromagnetic order at 90 K

Resonant inelastic x-ray scattering

Rhan et at., PRB **99**, 014505 (2019).







Hellmann-Feynman theorem

Hamiltonian with parameter p $\quad \mathscr{H}(p) = \mathscr{H}_0 + \mathscr{H}_1(p)$

Normalized eigenstates $\quad |p, n\rangle$ with eigenenergy $E_n(p)$

Variation in an eigenstate $|p, n\rangle$ caused by a small variation δp in p is expressed as a linear combination of $\{|p, m\rangle\}$

$$|p + \delta p, n\rangle = |p, n\rangle + \sum_m C_m |p, m\rangle$$

Linear approximation $\quad C_m = c_m \delta p$

Then taking the inner product $\quad \langle p + \delta p, n | p + \delta p, n\rangle = |1 + c_n \delta p|^2 \langle p, n | p, n\rangle + \sum_{m \neq n} |c_m|^2 |\delta p|^2 \langle p, m | p, m\rangle$

Therefore $c_n = 0$ from the normalization condition. Hence $C_n = 0$ within the linear approximation in δp.

Within linear in δp $\quad \langle p + \delta p | \mathscr{H}(p) | p + \delta p\rangle = \langle p | \mathscr{H}(p) | p\rangle = E_n(p)$

(Other contribution should be in the second order of δp.)

Hellmann-Feynman theorem (2)

Then the shift in the eigenenergy is given by

$$\begin{aligned} E_n(p+\delta p) &= \langle p+\delta p, n|\mathscr{H}(p+\delta p)|p+\delta p, n\rangle \\ &= \left\langle p+\delta p, n \left| \mathscr{H}(p) + \delta p \frac{\partial \mathscr{H}(p)}{\partial p} \right| p+\delta p, n \right\rangle \\ &= E_n(p) + \delta p \left\langle p, n \left| \frac{\partial \mathscr{H}(p)}{\partial p} \right| p, n \right\rangle \end{aligned}$$

Hellmann-Feynman theorem $\dfrac{dE_n(p)}{dp} = \left\langle p, n \left| \dfrac{\partial \mathscr{H}_1(p)}{\partial p} \right| p, n \right\rangle$

Free energy of the system under consideration: $F(p)$

$$\frac{\partial F(p)}{\partial p} = \frac{1}{Z} \sum_n \exp\left[\frac{-E_n(p)}{k_{\mathrm{B}}T}\right] \frac{\partial E_n(p)}{\partial p}$$

Paramagnon theory

Hamiltonian $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_I$ Interaction Hamiltonian with interaction parameter I

Introduction of interaction I': $0 \rightarrow I$

$$F(I) = F(0) + \int_0^I \left\langle \frac{\partial \mathscr{H}_{I'}}{\partial I'} \right\rangle dI'$$

We consider paramagnon (spin-fluctuation) contribution to specific heat

Hubbard Hamiltonian

$$\mathscr{H} = \sum_{\boldsymbol{k},s} \epsilon_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}s} a_{\boldsymbol{k}s} + U \sum_i^N \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} = \mathscr{H}_0 + \mathscr{H}_I$$

Fourier expansion

$$c_{is} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} e^{i\boldsymbol{R}_i \cdot \boldsymbol{k}} a_{\boldsymbol{k}s}$$

$$\mathscr{H}_I = \frac{U}{N} \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}} a^\dagger_{\boldsymbol{k}+\boldsymbol{q}\uparrow} a_{\boldsymbol{k}\uparrow} a^\dagger_{\boldsymbol{k}'-\boldsymbol{q}\downarrow} a_{\boldsymbol{k}'\downarrow} \qquad I = U/N$$

Interaction parameter

Up/down operators

$$\left.\begin{aligned} S_+(\boldsymbol{q}) &= \sum_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}\uparrow} a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, \\ S_-(\boldsymbol{q}) &= \sum_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}\downarrow} a_{\boldsymbol{k}+\boldsymbol{q}\uparrow} \end{aligned}\right\}$$

Paramagnon theory (2)

The interaction Hamiltonian can be developed as

$$\mathscr{H}_I = I \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}} a^\dagger_{\boldsymbol{k}+\boldsymbol{q}\uparrow} a_{\boldsymbol{k}\uparrow} (\delta_{\boldsymbol{k}',\boldsymbol{k}'-\boldsymbol{q}} - a_{\boldsymbol{k}'\downarrow} a^\dagger_{\boldsymbol{k}'-\boldsymbol{q}\downarrow})$$

Fermion commutation relation

$$= I \left[\sum_{\boldsymbol{k},\boldsymbol{k}'} a^\dagger_{\boldsymbol{k}\uparrow} a_{\boldsymbol{k}\uparrow} - \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}} a^\dagger_{\boldsymbol{k}+\boldsymbol{q}\uparrow} a_{\boldsymbol{k}'\downarrow} a^\dagger_{\boldsymbol{k}-\boldsymbol{q}\downarrow} a_{\boldsymbol{k}\uparrow} \right]$$

Change of summation representation

$$\boldsymbol{q} \to -\boldsymbol{q} + \boldsymbol{k}' - \boldsymbol{k}$$

$$\left.\begin{aligned} &\boldsymbol{k} + \boldsymbol{q} \to \boldsymbol{k} - \boldsymbol{q} + \boldsymbol{k}' - \boldsymbol{k} = \boldsymbol{k}' - \boldsymbol{q} \\ &\boldsymbol{k}' - \boldsymbol{q} \to \boldsymbol{k} + \boldsymbol{q} \end{aligned}\right\}$$

$$\mathscr{H}_I = I \left[\sum_{\boldsymbol{k},\boldsymbol{k}'} a^\dagger_{\boldsymbol{k}\uparrow} a_{\boldsymbol{k}\uparrow} - \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}} a^\dagger_{\boldsymbol{k}'-\boldsymbol{q}\uparrow} a_{\boldsymbol{k}'\downarrow} a^\dagger_{\boldsymbol{k}+\boldsymbol{q}\downarrow} a_{\boldsymbol{k}\uparrow} \right]$$

$$\left.\begin{aligned} S_+(\boldsymbol{q}) &= \sum_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}\uparrow} a_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, \\ S_-(\boldsymbol{q}) &= \sum_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}\downarrow} a_{\boldsymbol{k}+\boldsymbol{q}\uparrow} \end{aligned}\right\}$$

$$= I \left[\sum_{\boldsymbol{k},\boldsymbol{k}'} a^\dagger_{\boldsymbol{k}\uparrow} a_{\boldsymbol{k}\uparrow} - \sum_{\boldsymbol{q}} S_+(-\boldsymbol{q}) S_-(\boldsymbol{q}) \right] = I \left[\sum_{\boldsymbol{k},\boldsymbol{k}'} a^\dagger_{\boldsymbol{k}\uparrow} a_{\boldsymbol{k}\uparrow} - \sum_{\boldsymbol{q}} S_+(\boldsymbol{q}) S_-(-\boldsymbol{q}) \right]$$

Paramagnon theory (3)

$$\mathscr{H}_I = I\left[\sum_{\boldsymbol{k},\boldsymbol{k}'} a^\dagger_{\boldsymbol{k}\uparrow}a_{\boldsymbol{k}\uparrow} - \sum_{\boldsymbol{q}} S_+(\boldsymbol{q})S_-(-\boldsymbol{q})\right]$$

does not change by spin inversion in paramagnetic state

Then can be written in a form $\mathscr{H}_I = \dfrac{N_e U}{2} - \dfrac{I}{2}\sum_{\boldsymbol{q}}\{S_+(\boldsymbol{q}), S_-(-\boldsymbol{q})\}_+$

$\{A, B\}_+ = AB + BA$

anti-commutation relation

Variation of free energy $\Delta F = \dfrac{N_e U}{2} - \dfrac{1}{2}\sum_{\boldsymbol{q}}\int_0^I dI' \langle\{S_+(\boldsymbol{q}), S_-(-\boldsymbol{q})\}_+\rangle$

Remember retarded Green's function $\mathcal{G}^+_{QP}(\omega) = \sum_{n,m}\langle n|Q|m\rangle\langle m|P|n\rangle \dfrac{e^{-\beta E_n} - e^{-\beta E_m}}{E_n - E_m + \hbar\omega + i\eta}$

By writing a parallel expression for an advanced Green's function, we can obtain $\mathcal{G}^+_{QP}(\omega) - \mathcal{G}^-_{QP}(\omega) = -2i\mathrm{Im}[\chi_{QP}(\omega)]$

Paramagnon theory (4)

Fluctuation-dissipation $$\mathcal{S}_{QP}(\omega) = \frac{2}{1-e^{-\beta\hbar\omega}}\mathrm{Im}[\chi_{QP}(\omega)]$$

Linear response $$\chi_{+-}(\boldsymbol{q},\omega) = -(g\mu_{\mathrm{B}})^2\frac{i}{\hbar}\int_0^\infty dt\,\langle[S_-(-\boldsymbol{q}),S_+(\boldsymbol{q},t)]\rangle\,e^{i\omega t}$$

Let $|n\rangle$ be a many-body eigenstate with eigenenergy E_n

$$\mathrm{Im}[\chi_{+-}(\boldsymbol{q},\omega)] = \frac{\pi(g\mu_{\mathrm{B}})^2}{\hbar}\sum_{m,n}(\rho_m-\rho_n)\delta(\omega-\Delta E_{mn}/\hbar)\,\langle n|S_-(-\boldsymbol{q})|m\rangle\,\langle m|S_+(\boldsymbol{q})|n\rangle$$

Boltzmann factor $$\rho_n = \frac{1}{Z}\exp\left[-\frac{E_n}{k_{\mathrm{B}}T}\right], \quad \Delta E_{mn} = E_m - E_n$$

See Appendix 14A for the derivation of the above equation

Multiply both sides with $\coth(\beta\omega\hbar/2)$ and integrate with ω

Paramagnon theory (5)

$$\int_{-\infty}^{\infty} d\omega \mathrm{Im}\chi_{+-}(\boldsymbol{q},\omega)\coth\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)$$
$$=\frac{\pi(g\mu_{\mathrm{B}})^2}{\hbar}\sum_{m,n}(\rho_m-\rho_n)\coth\left(\frac{\Delta E_{nm}}{k_{\mathrm{B}}T}\right)\langle n|S_-(-\boldsymbol{q})|m\rangle\langle m|S_+(\boldsymbol{q})|n\rangle$$
$$=\frac{\pi(g\mu_{\mathrm{B}})^2}{\hbar}\langle\{S_-(-\boldsymbol{q}),S_+(\boldsymbol{q})\}_+\rangle$$

Then from $\Delta F=\frac{N_eU}{2}-\frac{1}{2}\sum_{\boldsymbol{q}}\int_0^I dI'\langle\{S_+(\boldsymbol{q}),S_-(-\boldsymbol{q})\}_+\rangle$

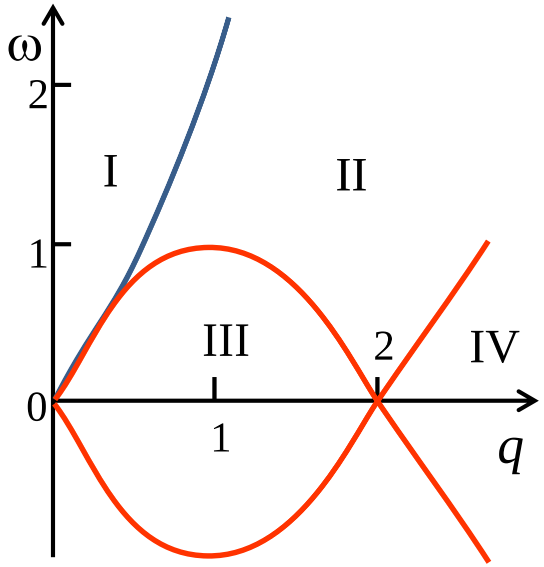
$$\boxed{\Delta F=\frac{N_eU}{2}-\sum_{\boldsymbol{q}}\int_0^I dI'\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\coth\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)\mathrm{Im}[\chi_{+-}(\boldsymbol{q},\omega)]}$$

RPA expression $\chi_{+-}(\boldsymbol{q},\omega)=N(g\mu_{\mathrm{B}})^2\frac{2\chi^{(0)}(\boldsymbol{q},\omega)}{1-2U\chi^{(0)}(\boldsymbol{q},\omega)}$

$$\Delta F=\frac{N_eU}{2}+\sum_{\boldsymbol{q}}\frac{1}{\pi}\int_0^{\infty}d\omega\coth\left(\frac{\hbar\omega}{k_{\mathrm{B}}T}\right)\mathrm{Im}\{\log[1-2U\chi^{(0)}(\boldsymbol{q},\omega)]\}$$

Paramagnon theory (6)

In order for calculation of specific heat we pick up temperature-dependent part from the free energy variation.



$$\coth\frac{\hbar\omega}{k_{\mathrm{B}}T}=\underline{1}+\frac{2}{e^{\hbar\omega/k_{\mathrm{B}}T}-1}$$

Paramagnon zero-point motion and ignored

Contribution from region-III is the largest, where we can expand

$$\chi^{(0)}(q,\omega)=\frac{1}{2}\rho(\epsilon_{\mathrm{F}})\left[1-A_0\left(\frac{q}{k_{\mathrm{F}}}\right)^2+iC_0\frac{\hbar\omega}{\epsilon_{\mathrm{F}}}\frac{k_{\mathrm{F}}}{q}\right]\qquad A_0=\frac{1}{12},\quad C_0=\frac{\pi}{4}$$

$$\alpha\equiv U\rho(\epsilon_{\mathrm{F}})$$

$$\begin{aligned}\Delta F(T)&=\frac{N}{2}\rho(\epsilon_{\mathrm{F}})\epsilon_{\mathrm{F}}^2\int_0^{q_c}q^2dq\int_0^{\infty}d\omega\frac{2}{e^{\beta\omega}-1}\mathrm{Im}\left[\log\left(1-\alpha+\alpha A_0q^2-i\alpha C_0\frac{\omega}{q}\right)\right]\\&=-\frac{N}{2}\rho(\epsilon_{\mathrm{F}})\epsilon_{\mathrm{F}}^2\int_0^{q_c}q^2dq\int_0^{\infty}d\omega\frac{2}{e^{\beta\omega}-1}\arctan\left[\frac{\omega}{q}\frac{C_0}{K_0^2+A_0q^2}\right]\end{aligned}$$

$\hbar\to 1$ Wavenumber unit: k_F Energy unit: E_F

Cutoff $q_c\sim 1$ $$K_0^2=\frac{1-\alpha}{\alpha}$$

Paramagnon theory (7)

Low temperature approximation $\omega \ll 1 \qquad \arctan x \sim x$

$$\frac{\Delta F(T)}{N} = -\frac{2\pi^2}{3}\rho(\epsilon_{\mathrm{F}})(k_{\mathrm{B}}T)^2 \frac{C_0}{2\pi A_0} \log \frac{K_0^2 + A_0 q_{\mathrm{c}}^2}{K_0^2}$$

Because the free energy is proportional to T^2 we can write

$$C = \gamma T, \quad \gamma_0 \equiv \frac{2\pi^2}{3} k_{\mathrm{B}}^2 \rho(\epsilon_{\mathrm{F}})$$ Free electron expression

$$\gamma = \gamma_0 \left(1 + \frac{C_0}{\pi A_0} \log \frac{K_0^2 + A_0 q_{\mathrm{c}}^2}{K_0^2}\right)$$

Logarithmic divergence for the Stoner condition $\alpha \to 1, \quad K_0 \to 0$

Self-consistent renormalization spin fluctuation theory

In paramagnon theory, we take the effect of spin-fluctuation (magnon) into account.
However, the effect of magnons should be reflected back to magnons and they should be self-consistent.
Otherwise, we cannot treat ferromagnetic cases, in which spontaneous magnetization appears.

Free energy in the presence of magnetization

$$F(M,T) = \underbrace{F_0(M,T)}_{\text{Non-interacting}} + \frac{N_e U}{2} \underbrace{- bM}_{\text{Zeeman}} - \sum_{\boldsymbol{q}} \int_0^I dI' \frac{1}{2\pi} \int d\omega \coth \frac{\hbar\omega}{2k_{\mathrm{B}}T} \mathrm{Im}[\chi_{+-}\underline{(M,I'}; \boldsymbol{q}, \omega)]$$

Magnetic equation of state $\dfrac{\partial F(M,T)}{\partial M} = 0$ → determines spontaneous magnetization

HF approximation is expressed in these terms

$$\Delta F_{\mathrm{HF}} = \frac{N_e U}{2} - I \sum_{\boldsymbol{q}} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right) \mathrm{Im}[\chi_{+-}(M,0;\boldsymbol{q},\omega)]$$

SCR-SF theory (2)

Non-interacting starting point derivative:

$$\left\langle \frac{\partial \mathscr{H}}{\partial I} \right\rangle_{I=0} = N \sum_i^N \langle n_{i\uparrow} n_{i\downarrow} \rangle_{I=0} = N \sum_i^N \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle$$

$$= \frac{N^2}{4}(n_+^2 - n_-^2) = \frac{N^2}{4}[n^2 - (2m)^2] = \frac{N_e^2}{4} - M^2$$

where $\quad n_+ = n_\uparrow + n_\downarrow, \quad n_- = n_\uparrow - n_\downarrow, \quad m = \frac{n_-}{2}$

$$F(M,T) = F_0(M,T) + I\left(\frac{N_e^2}{4} - M^2\right) - bM \quad : \text{HF Approximation}$$

$$- \sum_{\boldsymbol{q}} \int_0^I dI' \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth \frac{\hbar\omega}{k_\mathrm{B}T} \mathrm{Im}[\chi_{+-}(M, I'; \boldsymbol{q}, \omega) - \chi_{+-}(M, 0; \boldsymbol{q}, \omega)] \quad : \text{Correction}$$

We apply RPA to $\chi_{\pm-}$

$$F(M,T) = F_0(M,T) + I\left(\frac{N_e^2}{4} - M^2\right) - bM$$

$$- \sum_{\boldsymbol{q}} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth \frac{\hbar\omega}{k_\mathrm{B}T} \mathrm{Im}[\log\{1 - 2U\chi^{(0)}(M; \boldsymbol{q}, \omega)\} + 2U\chi^{(0)}(M; \boldsymbol{q}, \omega)].$$

$$\chi^{(0)}(M; \boldsymbol{q}, \omega) = \frac{1}{2N}\chi_{+-}(M, 0; \boldsymbol{q}, \omega)$$

SCR-SF theory (3)

To obtain magnetic equation of state, we take differentiation by $m = M/N$

$$\frac{\partial F_0}{N\partial m} - 2Um - b - \frac{1}{N}\sum_{\boldsymbol{q}}\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \coth\frac{\hbar\omega}{2k_{\rm B}T}\,{\rm Im}\left[\frac{2U\chi^{(0)}(M;\boldsymbol{q},\omega)}{1-2U\chi^{(0)}(M;\boldsymbol{q},\omega)}2U\frac{\partial\chi^{(0)}(M;\boldsymbol{q},\omega)}{\partial m}\right] = 0$$

$$\chi = \frac{\partial m}{\partial b}, \qquad \frac{1}{\chi} = \frac{\partial b}{\partial m}$$

Magnetic equation of state for non-interacting system $\frac{\partial F_0}{N\partial m} - b = 0$ then $\frac{\partial^2 F_0}{N\partial m^2} = \frac{1}{\chi_0}$

In paramagnetic case

$$\begin{aligned}\frac{1}{\chi} = \frac{1}{\chi_0} - 2U \\ - \frac{1}{N}\sum_{\boldsymbol{q}}\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \coth\frac{\hbar\omega}{2k_{\rm B}T}(2U)^2 \\ \times\,{\rm Im}\left[\chi(\boldsymbol{q},\omega)\left.\frac{\partial^2\chi^{(0)}(\boldsymbol{q},\omega)}{\partial m^2}\right|_{m=0} + \chi^2(\boldsymbol{q},\omega)\left\{\frac{1}{\chi^{(0)}}(\boldsymbol{q},\omega)\left.\frac{\partial\chi^{(0)}(\boldsymbol{q},\omega)}{\partial m}\right|_{m=0}\right\}^2\right]\end{aligned}$$

Square of spin-fluctuation
Ignored

SCR-SF theory (4)

Coupling constant $$g = -(2U)^2 \chi_0 \left. \frac{\partial^2 \chi^{(0)}(\boldsymbol{q}, \omega)}{\partial m^2} \right|_{m=0, q=0, \omega=0}$$

$$\frac{\chi_0}{\chi} = 1 - 2U\chi_0 + \frac{g}{N} \sum_{\boldsymbol{q}} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth \frac{\hbar\omega}{2k_B T} \mathrm{Im}[\chi(\boldsymbol{q}, \omega)]$$

Application of RPA → Breakdown of self-consistency

$T = 0$ $$\frac{\chi_0}{\chi(T=0)} = 1 - 2U\chi_0 + \underline{\frac{g}{N} \sum_{\boldsymbol{q}} \frac{1}{\pi} \int_0^{\infty} d\omega \mathrm{Im}[\chi(\boldsymbol{q}, \omega)]_{T=0}}$$

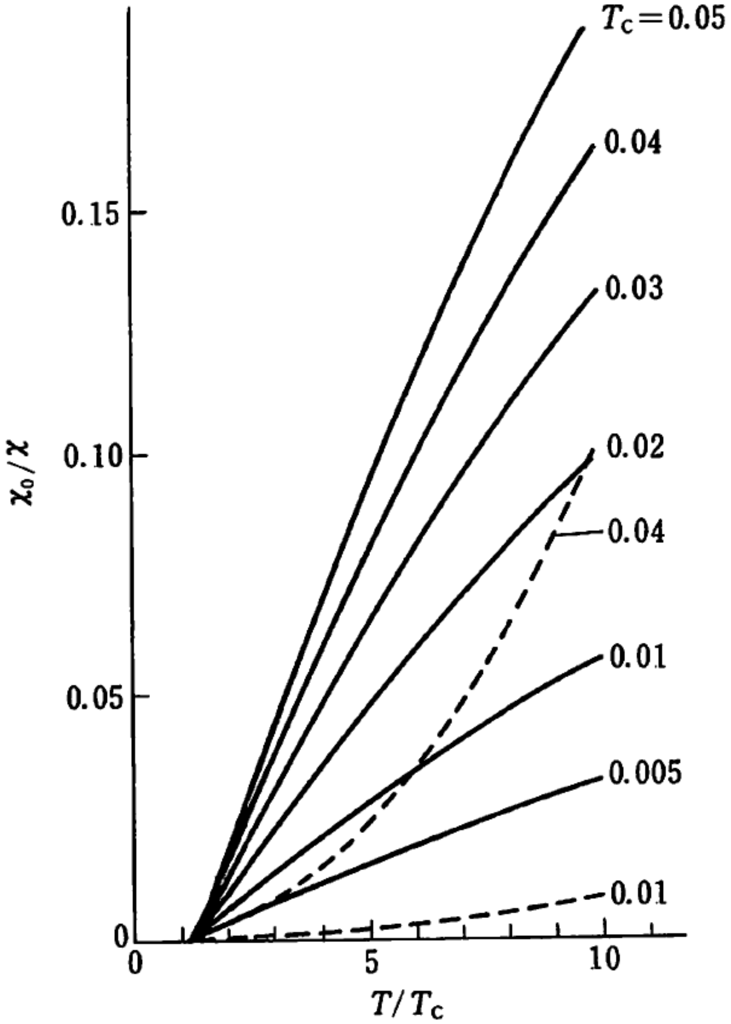
Correction of overestimation of stability in ferromagnetic state

Ignore magnon zero-point motion $$\frac{\chi_0}{\chi} = \frac{\chi_0}{\chi(T=0)} + \frac{g}{N} \sum_{\boldsymbol{q}} \frac{1}{\pi} \int_0^{\infty} d\omega \frac{2}{e^{\hbar\omega\beta} - 1} \mathrm{Im}[\chi(\boldsymbol{q}, \omega)]$$

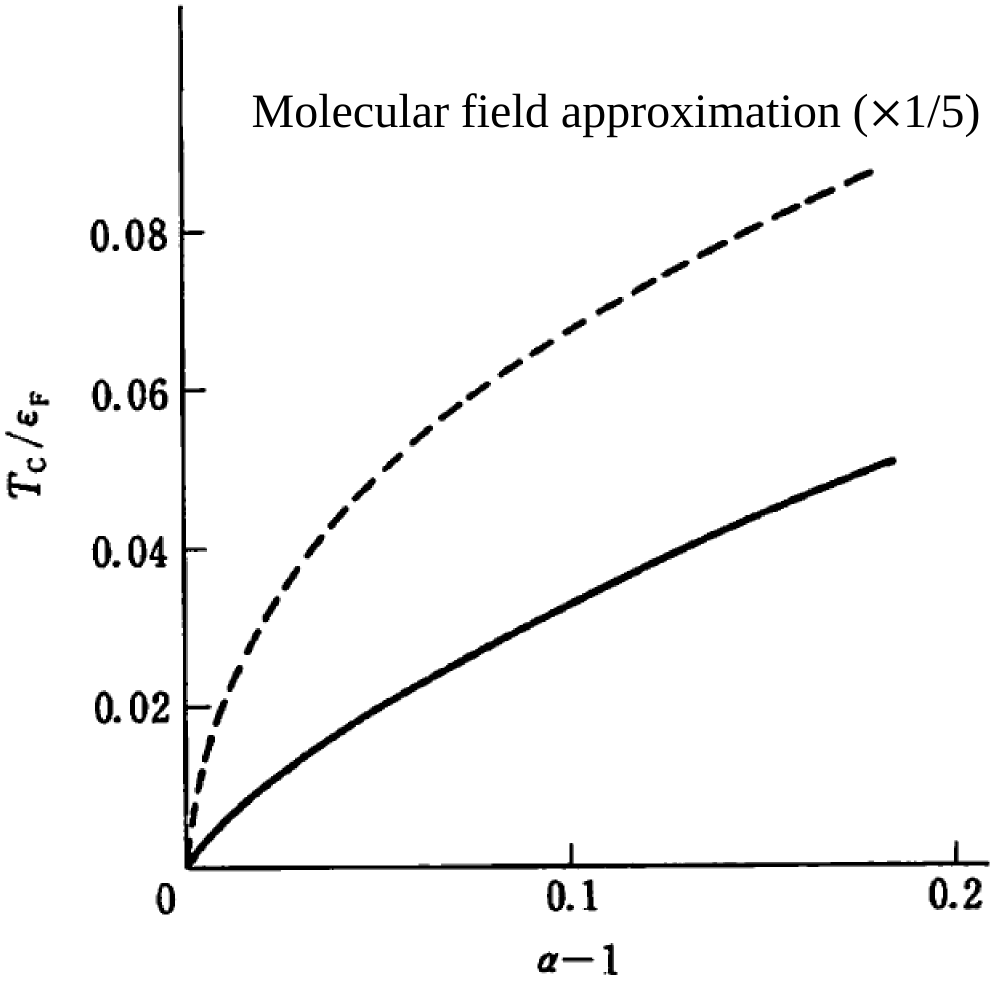
Expansion around (0,0) $$\frac{\chi_0}{\chi(\boldsymbol{q}, \omega)} = \frac{\chi_0}{\chi(+0, +0)} + A\left(\frac{q}{k_F}\right)^2 - iC\frac{\omega}{\epsilon_F}\frac{k_F}{q}$$

Self-consistent determination of χ

Improvements by SCR-SF theory

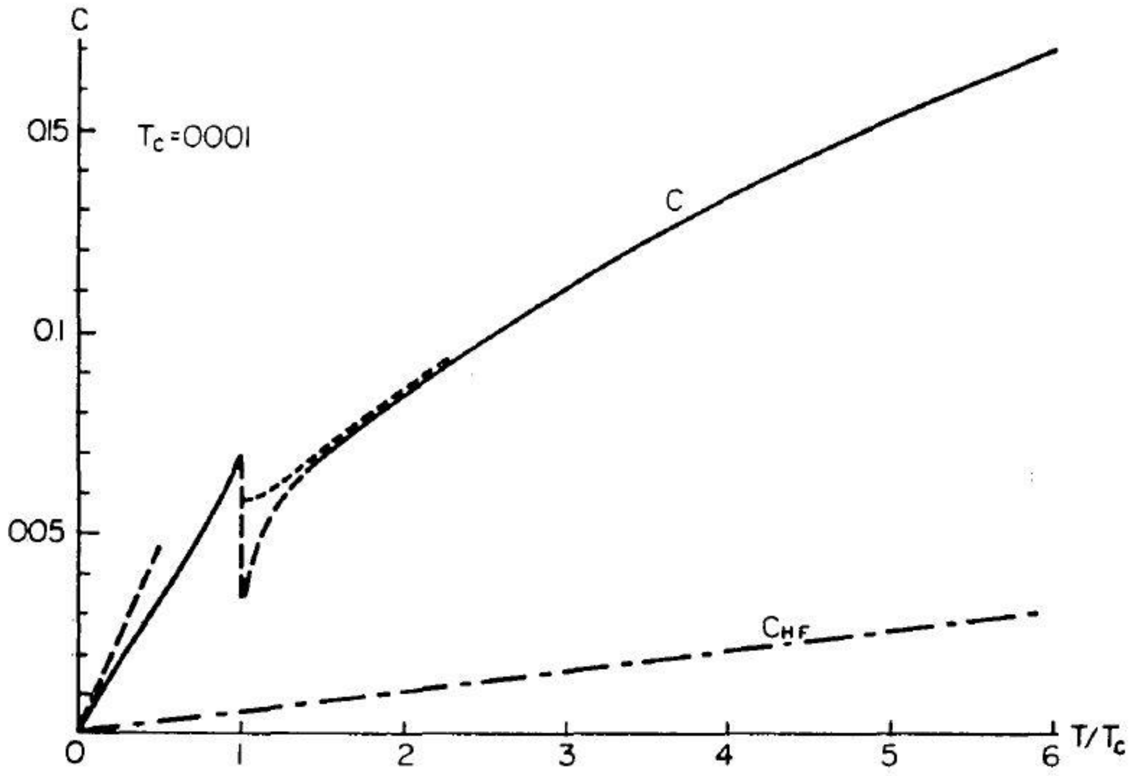


Temperature dependence of susceptibility

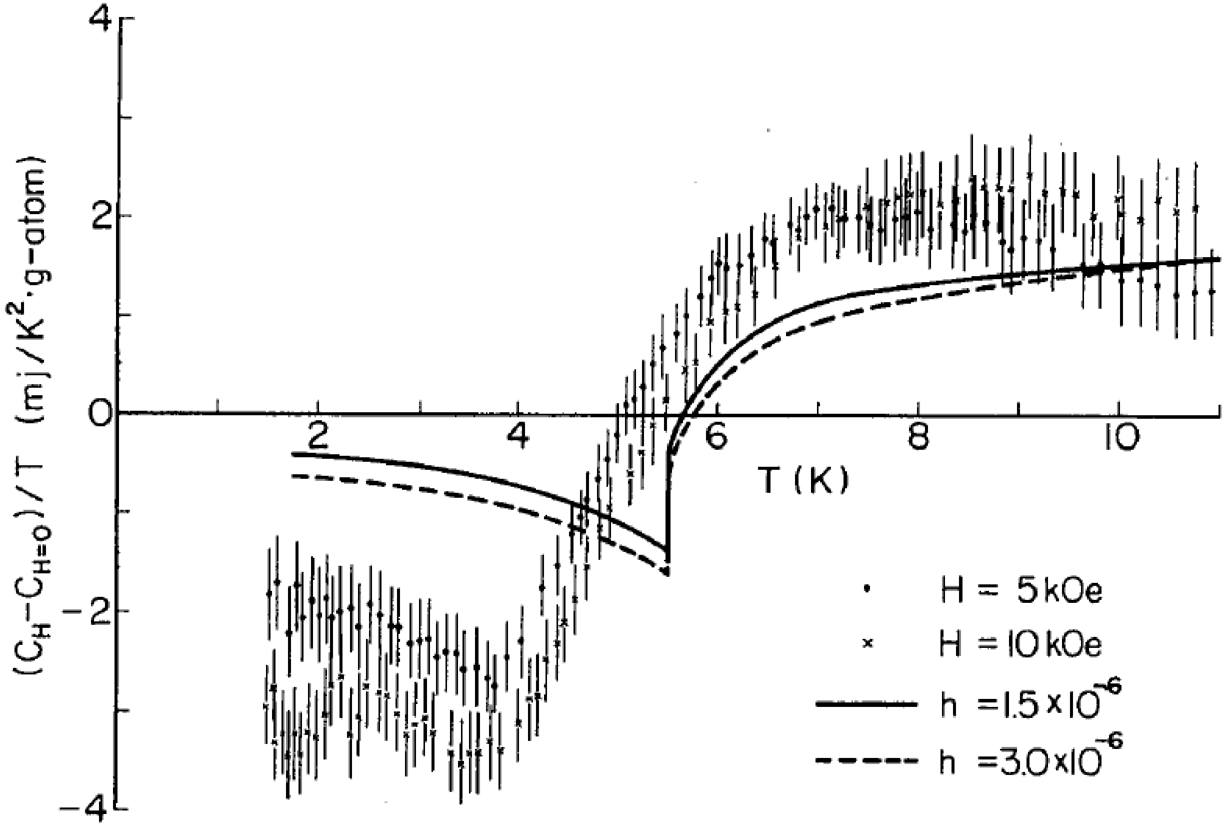


Critical temperature vs interaction parameter

Problems in SCR-SF theory

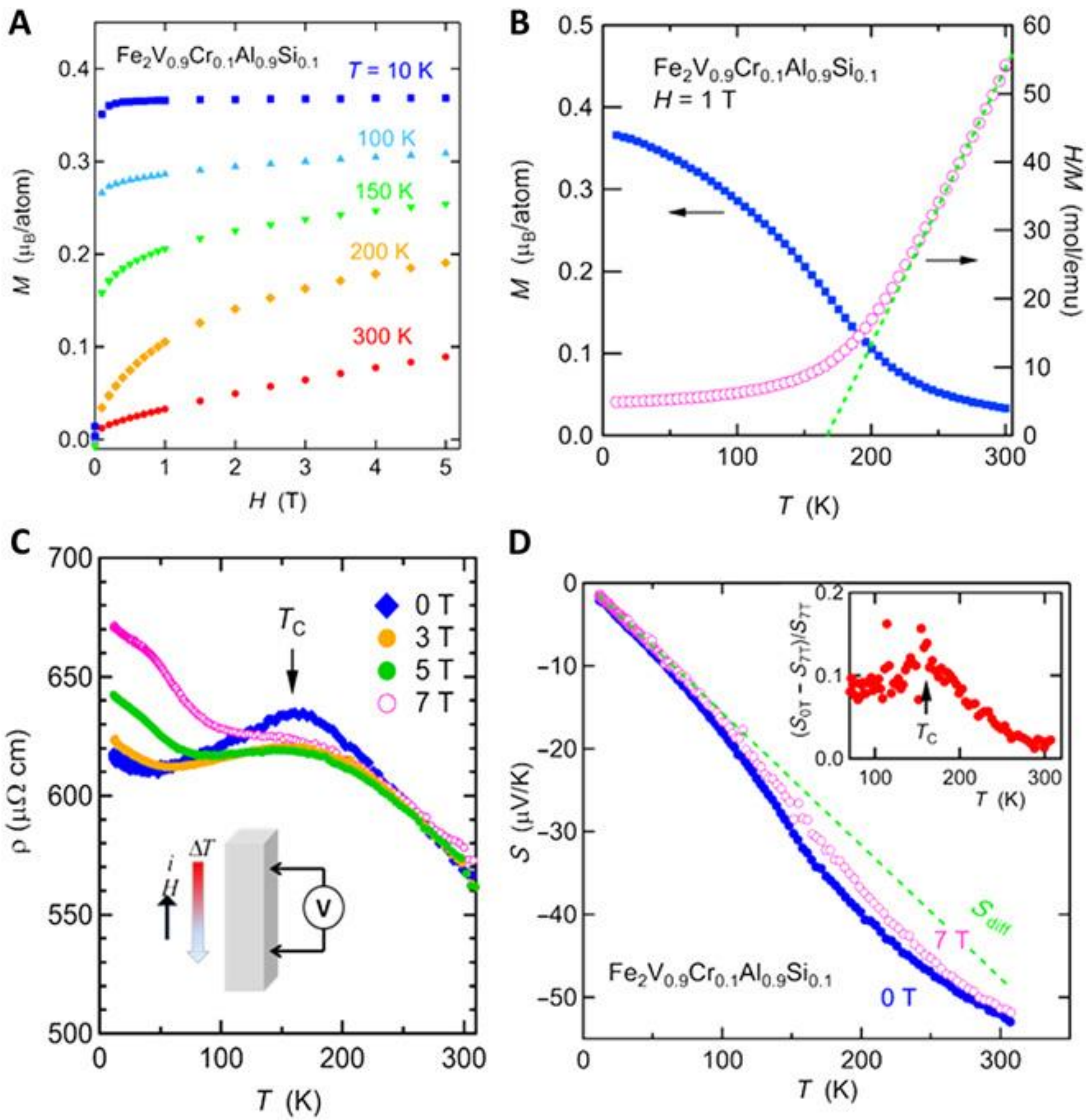


Makoshi & Moriya, JPSJ 38, 10 (1975).



Takeuchi & Masuda, JPSJ **46**, 468 (1979).

Enhanced thermopower due to spin fluctuation

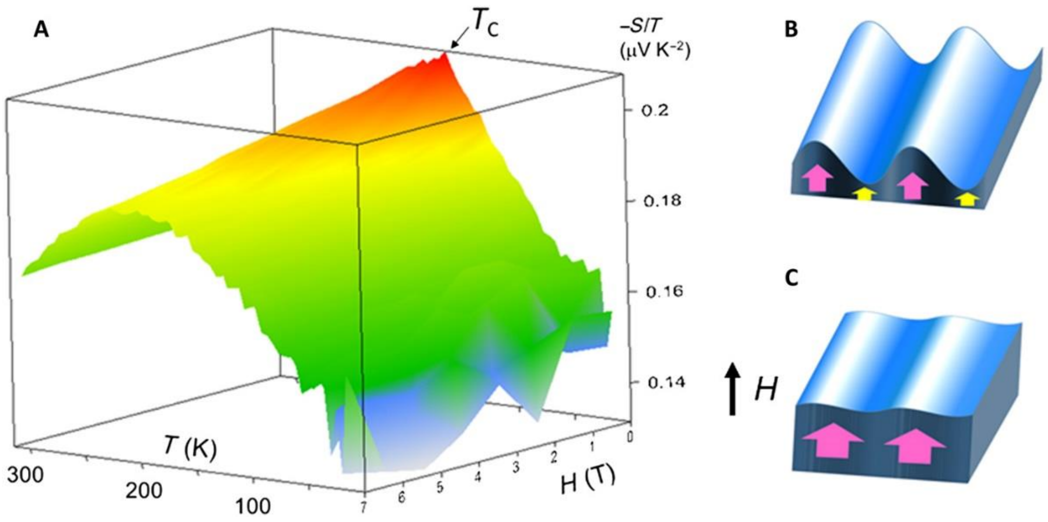


Weak ferromagnet

Spin fluctuation enhancement around T_C

Enhancement of entropy

Magnon drag effect



Tsuji et al. Science Advances **5**, eaat5935 (2019).

Lecture review

Chapter 1 Basic Notions of Magnetism

Breakdown of classical magnetism: cancellation of paramagnetic and diamagnetic terms (Bohr-van Leeuwen theorem)

Quest for the sources of magnetic dipoles in materials.

Spins and spin-orbit interactions

Chapter 2 Magnetism of Localized Electrons

Electronic states of magnetic ions

- LS (j-j) coupling, Hund’s rule
- Ligand field

Magnetic resonance

- Spin Hamiltonian

Lecture review

Chapter 3 Magnetism of conduction electrons

Pauli paramagnetism

Landau diamagnetism

Chapter 4 Interaction between spins

Exchange interaction

- Heisenberg Hamiltonian
- Hubbard model

Superexchange interaction

- Spin Hamiltonian

Chapter 5 Theory of magnetic insulators

Chapter 6 Magnetism of itinerant electrons


Thank you
Have a nice summer vacation

Notification

Deadline for exercise 0629 is now 21st July.

Problems for the final report will be uploaded in the evening of 14 July.
The deadline for the submission of report is 2nd August.