



2022.7.13 Lecture 14

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

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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.

- 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)

- Paramagnon theory
- Self-consistent renormalization spin-fluctuation theory

Why and how we consider magnons in marginally paramagnetic metals?

Itinerant electron magnetism

26	27	28
Fe	Co	Ni
$3d^64s^2$	$3d^74s^2$	$3d^84s^2$

- 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

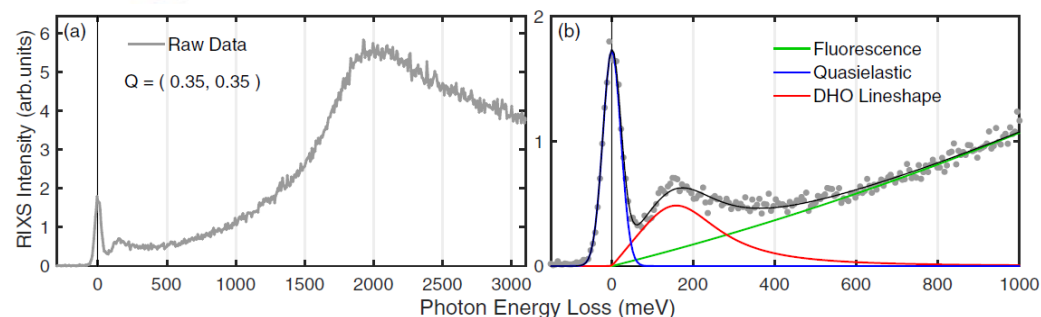
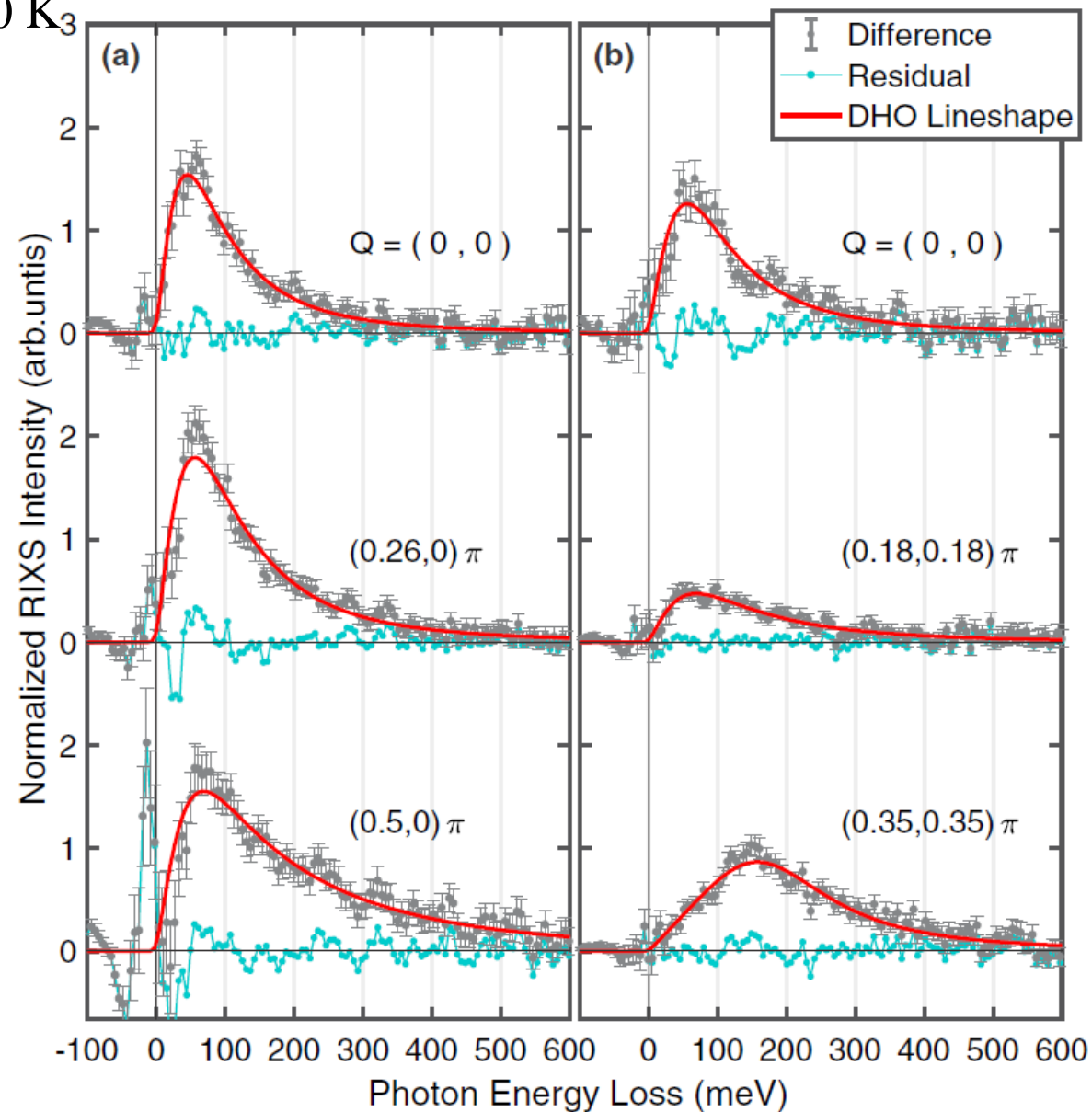
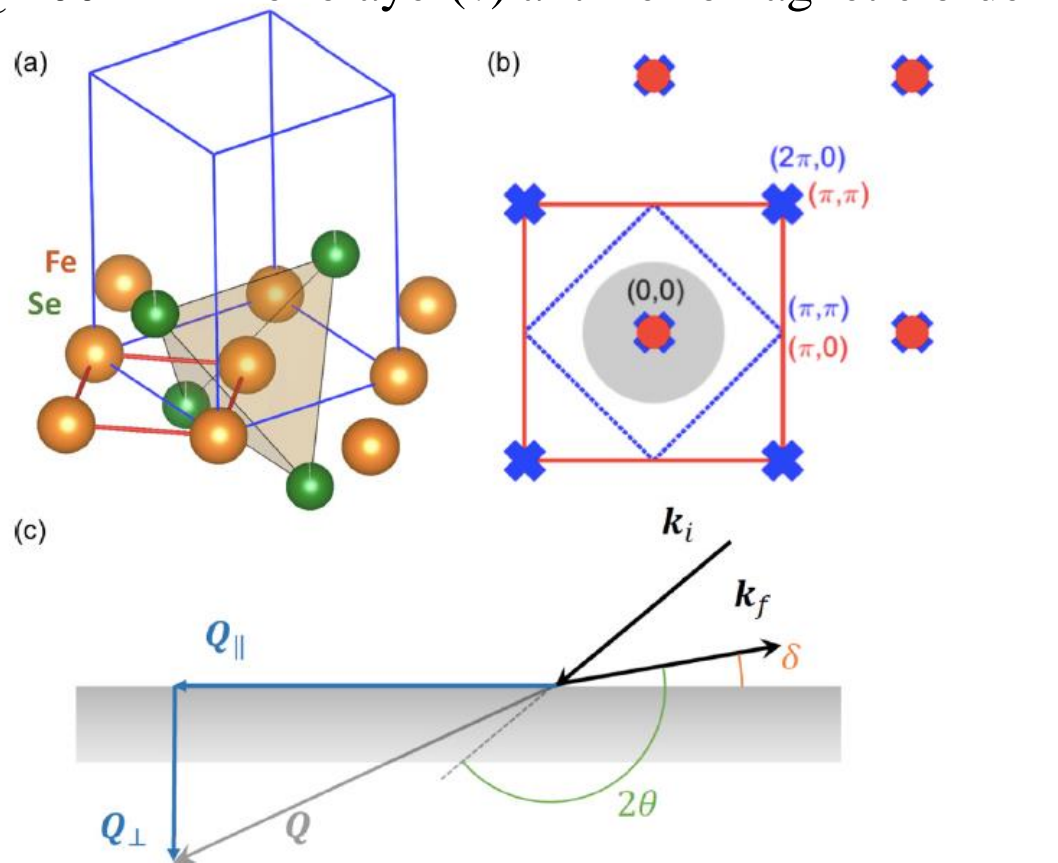
Paramagnons in “nearly ferromagnetic” materials

β -FeSe iron-based superconductor

Resonant inelastic x-ray scattering

Rhan et al., PRB **99**, 014505 (2019).

T_C 100 K in monolayer(?) anti-ferromagnetic order at 90 K₃



Hellmann-Feynman theorem

Hamiltonian with parameter p $\mathcal{H}(p) = \mathcal{H}_0 + \mathcal{H}_1(p)$

Normalized eigenstates $|p, n\rangle$ 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 $C_m = c_m \delta p$

Then taking the inner product $\langle p + \delta p, n | p + \delta p, n \rangle = |1 + c_n \delta p|^2 \langle p, n | p, n \rangle + \sum_{m \neq n} |c_m|^2 |\delta p|^2 \langle p, m | p, m \rangle$

Therefore $c_n = 0$ from the normalization condition. Hence $C_n = 0$ within the linear approximation in δp .

Within linear in δp $\langle p + \delta p | \mathcal{H}(p) | p + \delta p \rangle = \langle p | \mathcal{H}(p) | p \rangle = E_n(p)$

(Other contribution should be in the second order of δp .)

Hellmann-Feynman theorem (2)

Then the shift in the eigenenergy is given by

$$\begin{aligned} E_n(p + \delta p) &= \langle p + \delta p, n | \mathcal{H}(p + \delta p) | p + \delta p, n \rangle \\ &= \left\langle p + \delta p, n \left| \mathcal{H}(p) + \delta p \frac{\partial \mathcal{H}(p)}{\partial p} \right| p + \delta p, n \right\rangle \\ &= E_n(p) + \delta p \left\langle p, n \left| \frac{\partial \mathcal{H}(p)}{\partial p} \right| p, n \right\rangle \end{aligned}$$

Hellmann-Feynman theorem

$$\frac{dE_n(p)}{dp} = \left\langle p, n \left| \frac{\partial \mathcal{H}_1(p)}{\partial p} \right| p, n \right\rangle$$

Free energy of the system under consideration: $F(p)$

$$\frac{\partial F(p)}{\partial p} = \frac{1}{Z} \sum_n \exp \left[\frac{-E_n(p)}{k_B T} \right] \frac{\partial E_n(p)}{\partial p}$$

Paramagnon theory

Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I$ Interaction Hamiltonian with interaction parameter I

Introduction of interaction $I': 0 \rightarrow I$ $F(I) = F(0) + \int_0^I \left\langle \frac{\partial \mathcal{H}_{I'}}{\partial I'} \right\rangle dI'$

We consider paramagnon (spin-fluctuation) contribution to specific heat

Hubbard Hamiltonian $\mathcal{H} = \sum_{\mathbf{k},s} \epsilon_{\mathbf{k}} a_{\mathbf{k}s}^\dagger a_{\mathbf{k}s} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} = \mathcal{H}_0 + \mathcal{H}_I$

Fourier expansion $c_{is} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{R}_i \cdot \mathbf{k}} a_{\mathbf{k}s}$

$$\mathcal{H}_I = \frac{U}{N} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} a_{\mathbf{k}+\mathbf{q}\uparrow}^\dagger a_{\mathbf{k}\uparrow} a_{\mathbf{k}'-\mathbf{q}\downarrow}^\dagger a_{\mathbf{k}'\downarrow} \quad I = U/N$$

Interaction parameter

Up/down operators $\left. \begin{aligned} S_+(\mathbf{q}) &= \sum_{\mathbf{k}} a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}+\mathbf{q}\downarrow}, \\ S_-(\mathbf{q}) &= \sum_{\mathbf{k}} a_{\mathbf{k}\downarrow}^\dagger a_{\mathbf{k}+\mathbf{q}\uparrow} \end{aligned} \right\}$

Paramagnon theory (2)

The interaction Hamiltonian can be developed as

$$\mathcal{H}_I = I \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}} a_{\mathbf{k}+\mathbf{q}\uparrow}^\dagger a_{\mathbf{k}\uparrow} (\delta_{\mathbf{k}', \mathbf{k}'-\mathbf{q}} - a_{\mathbf{k}'\downarrow} a_{\mathbf{k}'-\mathbf{q}\downarrow}^\dagger)$$

$$= I \left[\sum_{\mathbf{k}, \mathbf{k}'} a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}\uparrow} - \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}} a_{\mathbf{k}+\mathbf{q}\uparrow}^\dagger a_{\mathbf{k}'\downarrow} a_{\mathbf{k}-\mathbf{q}\downarrow}^\dagger a_{\mathbf{k}\uparrow} \right]$$

Fermion commutation relation

Change of summation representation

$$\mathbf{q} \rightarrow -\mathbf{q} + \mathbf{k}' - \mathbf{k}$$

$$\left. \begin{aligned} \mathbf{k} + \mathbf{q} &\rightarrow \mathbf{k} - \mathbf{q} + \mathbf{k}' - \mathbf{k} = \mathbf{k}' - \mathbf{q} \\ \mathbf{k}' - \mathbf{q} &\rightarrow \mathbf{k} + \mathbf{q} \end{aligned} \right\}$$

$$\mathcal{H}_I = I \left[\sum_{\mathbf{k}, \mathbf{k}'} a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}\uparrow} - \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}} a_{\mathbf{k}'-\mathbf{q}\uparrow}^\dagger a_{\mathbf{k}'\downarrow} a_{\mathbf{k}+\mathbf{q}\downarrow}^\dagger a_{\mathbf{k}\uparrow} \right]$$

$$\left. \begin{aligned} S_+(\mathbf{q}) &= \sum_{\mathbf{k}} a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}+\mathbf{q}\downarrow}, \\ S_-(\mathbf{q}) &= \sum_{\mathbf{k}} a_{\mathbf{k}\downarrow}^\dagger a_{\mathbf{k}+\mathbf{q}\uparrow} \end{aligned} \right\}$$

$$= I \left[\sum_{\mathbf{k}, \mathbf{k}'} a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}\uparrow} - \sum_{\mathbf{q}} S_+(-\mathbf{q}) S_-(\mathbf{q}) \right] = I \left[\sum_{\mathbf{k}, \mathbf{k}'} a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}\uparrow} - \sum_{\mathbf{q}} S_+(\mathbf{q}) S_-(\mathbf{-q}) \right]$$

Paramagnon theory (3)

$$\mathcal{H}_I = I \left[\sum_{\mathbf{k}, \mathbf{k}'} a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}\uparrow} - \sum_{\mathbf{q}} S_+(\mathbf{q}) S_-(-\mathbf{q}) \right] \quad \text{does not change by spin inversion in paramagnetic state}$$

Then can be written in a form

$$\mathcal{H}_I = \frac{N_e U}{2} - \frac{I}{2} \sum_{\mathbf{q}} \{S_+(\mathbf{q}), S_-(-\mathbf{q})\}_+$$

$\{A, B\}_+ = AB + BA$
anti-commutation relation

Variation of free energy

$$\Delta F = \frac{N_e U}{2} - \frac{1}{2} \sum_{\mathbf{q}} \int_0^I dI' \langle \{S_+(\mathbf{q}), S_-(-\mathbf{q})\}_+ \rangle$$

Remember retarded Green's function

$$\mathcal{G}_{QP}^+(\omega) = \sum_{n,m} \langle n|Q|m\rangle \langle m|P|n\rangle \frac{e^{-\beta E_n} - e^{-\beta E_m}}{E_n - E_m + \hbar\omega + i\eta}$$

By writing a parallel expression for an advanced Green's function, we can obtain

$$\mathcal{G}_{QP}^+(\omega) - \mathcal{G}_{QP}^-(\omega) = -2i \text{Im}[\chi_{QP}(\omega)]$$

Paramagnon theory (4)

Fluctuation-dissipation $\mathcal{S}_{QP}(\omega) = \frac{2}{1 - e^{-\beta\hbar\omega}} \text{Im}[\chi_{QP}(\omega)]$

Linear response $\chi_{+-}(\mathbf{q}, \omega) = -(g\mu_B)^2 \frac{i}{\hbar} \int_0^\infty dt \langle [S_-(-\mathbf{q}), S_+(\mathbf{q}, t)] \rangle e^{i\omega t}$

Let $|n\rangle$ be a many-body eigenstate with eigenenergy E_n

$$\text{Im}[\chi_{+-}(\mathbf{q}, \omega)] = \frac{\pi(g\mu_B)^2}{\hbar} \sum_{m,n} (\rho_m - \rho_n) \delta(\omega - \Delta E_{mn}/\hbar) \langle n|S_-(-\mathbf{q})|m\rangle \langle m|S_+(\mathbf{q})|n\rangle$$

Boltzmann factor $\rho_n = \frac{1}{Z} \exp\left[-\frac{E_n}{k_B T}\right], \quad \Delta E_{mn} = E_m - E_n$

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)

$$\begin{aligned}
 & \int_{-\infty}^{\infty} d\omega \operatorname{Im} \chi_{+-}(\mathbf{q}, \omega) \coth\left(\frac{\hbar\omega}{2k_B T}\right) \\
 &= \frac{\pi(g\mu_B)^2}{\hbar} \sum_{m,n} (\rho_m - \rho_n) \coth\left(\frac{\Delta E_{nm}}{k_B T}\right) \langle n | S_{-}(-\mathbf{q}) | m \rangle \langle m | S_{+}(\mathbf{q}) | n \rangle \\
 &= \frac{\pi(g\mu_B)^2}{\hbar} \langle \{S_{-}(-\mathbf{q}), S_{+}(\mathbf{q})\}_{+} \rangle
 \end{aligned}$$

Then from
$$\Delta F = \frac{N_e U}{2} - \frac{1}{2} \sum_{\mathbf{q}} \int_0^I dI' \langle \{S_{+}(\mathbf{q}), S_{-}(-\mathbf{q})\}_{+} \rangle$$

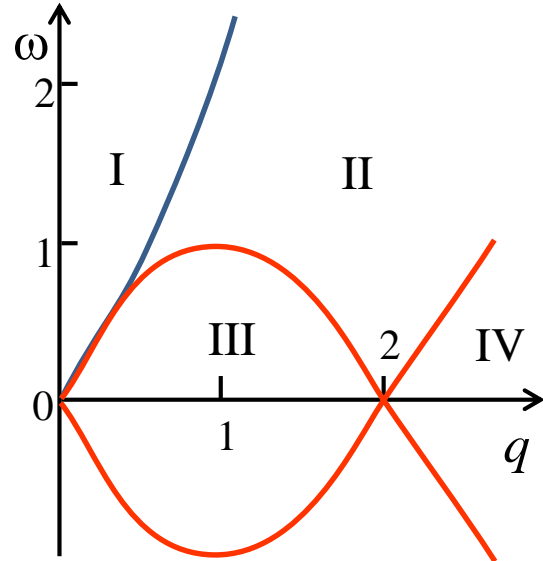
$$\Delta F = \frac{N_e U}{2} - \sum_{\mathbf{q}} \int_0^I dI' \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth\left(\frac{\hbar\omega}{2k_B T}\right) \operatorname{Im}[\chi_{+-}(\mathbf{q}, \omega)]$$

RPA expression
$$\chi_{+-}(\mathbf{q}, \omega) = N(g\mu_B)^2 \frac{2\chi^{(0)}(\mathbf{q}, \omega)}{1 - 2U\chi^{(0)}(\mathbf{q}, \omega)}$$

$$\Delta F = \frac{N_e U}{2} + \sum_{\mathbf{q}} \frac{1}{\pi} \int_0^{\infty} d\omega \coth\left(\frac{\hbar\omega}{k_B T}\right) \operatorname{Im}\{\log[1 - 2U\chi^{(0)}(\mathbf{q}, \omega)]\}$$

Paramagnon theory (6)

In order for calculation of specific heat we pick up temperature-dependent part from the free energy variation.



$$\coth \frac{\hbar\omega}{k_B T} = \underbrace{1 + \frac{2}{e^{\hbar\omega/k_B T} - 1}}_{\text{Paramagnon zero-point motion and ignored}}$$

Contribution from region-III is the largest, where we can expand

$$\chi^{(0)}(q, \omega) = \frac{1}{2} \rho(\epsilon_F) \left[1 - A_0 \left(\frac{q}{k_F} \right)^2 + i C_0 \frac{\hbar\omega}{\epsilon_F} \frac{k_F}{q} \right] \quad A_0 = \frac{1}{12}, \quad C_0 = \frac{\pi}{4}$$

$$\alpha \equiv U \rho(\epsilon_F)$$

$$\begin{aligned} \Delta F(T) &= \frac{N}{2} \rho(\epsilon_F) \epsilon_F^2 \int_0^{q_c} q^2 dq \int_0^\infty d\omega \frac{2}{e^{\beta\omega} - 1} \text{Im} \left[\log \left(1 - \alpha + \alpha A_0 q^2 - i \alpha C_0 \frac{\omega}{q} \right) \right] \\ &= -\frac{N}{2} \rho(\epsilon_F) \epsilon_F^2 \int_0^{q_c} q^2 dq \int_0^\infty d\omega \frac{2}{e^{\beta\omega} - 1} \arctan \left[\frac{\omega}{q} \frac{C_0}{K_0^2 + A_0 q^2} \right] \end{aligned}$$

$$\hbar \rightarrow 1 \quad \text{Wavenumber unit: } k_F \quad \text{Energy unit: } E_F$$

$$\text{Cutoff } q_c \sim 1$$

$$K_0^2 = \frac{1 - \alpha}{\alpha}$$

Paramagnon theory (7)

Low temperature approximation $\omega \ll 1$ $\arctan x \sim x$

$$\frac{\Delta F(T)}{N} = -\frac{2\pi^2}{3} \rho(\epsilon_F) (k_B T)^2 \frac{C_0}{2\pi A_0} \log \frac{K_0^2 + A_0 q_c^2}{K_0^2}$$

Because the free energy is proportional to T^2
we can write

$$C = \gamma T, \quad \gamma_0 \equiv \frac{2\pi^2}{3} k_B^2 \rho(\epsilon_F) \quad \text{Free electron expression}$$

$$\gamma = \gamma_0 \left(1 + \frac{C_0}{\pi A_0} \log \frac{K_0^2 + A_0 q_c^2}{K_0^2} \right)$$

Logarithmic divergence for the Stoner condition $\alpha \rightarrow 1$, $K_0 \rightarrow 0$

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

$$F(M, T) = \underbrace{F_0(M, T)}_{\text{Non-interacting}} + \frac{N_e U}{2} \underbrace{- bM}_{\text{Zeeman}} - \sum_{\mathbf{q}} \int_0^I dI' \frac{1}{2\pi} \int d\omega \coth \frac{\hbar\omega}{2k_B T} \text{Im}[\chi_{+-}(M, I'; \mathbf{q}, \omega)]$$

Magnetic equation of state $\frac{\partial F(M, T)}{\partial M} = 0 \rightarrow$ determines spontaneous magnetization

HF approximation is expressed in these terms $\Delta F_{\text{HF}} = \frac{N_e U}{2} - I \sum_{\mathbf{q}} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth \left(\frac{\hbar\omega}{2k_B T} \right) \text{Im}[\chi_{+-}(M, 0; \mathbf{q}, \omega)]$

Non-interacting starting point derivative:

$$\left\langle \frac{\partial \mathcal{H}}{\partial I} \right\rangle_{I=0} = N \sum_i^N \langle n_{i\uparrow} n_{i\downarrow} \rangle_{I=0} = N \sum_i^N \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle$$

$$= \frac{N^2}{4} (n_+^2 - n_-^2) = \frac{N^2}{4} [n^2 - (2m)^2] = \frac{N_e^2}{4} - M^2$$

where $n_+ = n_\uparrow + n_\downarrow$, $n_- = n_\uparrow - n_\downarrow$, $m = \frac{n_-}{2}$

$$F(M, T) = F_0(M, T) + I \left(\frac{N_e^2}{4} - M^2 \right) - bM \quad : \text{HF Approximation}$$

$$- \sum_{\mathbf{q}} \int_0^I dI' \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth \frac{\hbar\omega}{k_B T} \text{Im}[\chi_{+-}(M, I'; \mathbf{q}, \omega) - \chi_{+-}(M, 0; \mathbf{q}, \omega)] \quad : \text{Correction}$$

We apply RPA to $\chi_{\pm-}$

$$F(M, T) = F_0(M, T) + I \left(\frac{N_e^2}{4} - M^2 \right) - bM$$

$$- \sum_{\mathbf{q}} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth \frac{\hbar\omega}{k_B T} \text{Im}[\log\{1 - 2U\chi^{(0)}(M; \mathbf{q}, \omega)\} + 2U\chi^{(0)}(M; \mathbf{q}, \omega)].$$

$$\chi^{(0)}(M; \mathbf{q}, \omega) = \frac{1}{2N} \chi_{+-}(M, 0; \mathbf{q}, \omega)$$

SCR-SF theory (3)

To obtain magnetic equation of state, we take differentiation by $m = M/N$

$$\frac{\partial F_0}{N \partial m} - 2Um - b - \frac{1}{N} \sum_{\mathbf{q}} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth \frac{\hbar\omega}{2k_B T} \text{Im} \left[\frac{2U\chi^{(0)}(M; \mathbf{q}, \omega)}{1 - 2U\chi^{(0)}(M; \mathbf{q}, \omega)} 2U \frac{\partial \chi^{(0)}(M; \mathbf{q}, \omega)}{\partial m} \right] = 0$$

$$\chi = \frac{\partial m}{\partial b}, \quad \frac{1}{\chi} = \frac{\partial b}{\partial m}$$

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

$$\begin{aligned} \frac{1}{\chi} &= \frac{1}{\chi_0} - 2U \\ &- \frac{1}{N} \sum_{\mathbf{q}} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth \frac{\hbar\omega}{2k_B T} (2U)^2 \\ &\times \text{Im} \left[\chi(\mathbf{q}, \omega) \frac{\partial^2 \chi^{(0)}(\mathbf{q}, \omega)}{\partial m^2} \Big|_{m=0} + \chi^2(\mathbf{q}, \omega) \left\{ \frac{1}{\chi^{(0)}(\mathbf{q}, \omega)} \frac{\partial \chi^{(0)}(\mathbf{q}, \omega)}{\partial m} \Big|_{m=0} \right\}^2 \right] \end{aligned}$$

Square of spin-fluctuation
Ignored
↓

Coupling constant $g = -(2U)^2 \chi_0 \left. \frac{\partial^2 \chi^{(0)}(\mathbf{q}, \omega)}{\partial m^2} \right|_{m=0, q=0, \omega=0}$

$$\frac{\chi_0}{\chi} = 1 - 2U\chi_0 + \frac{g}{N} \sum_{\mathbf{q}} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \coth \frac{\hbar\omega}{2k_B T} \text{Im}[\chi(\mathbf{q}, \omega)]$$

Application of RPA → Breakdown of self-consistency

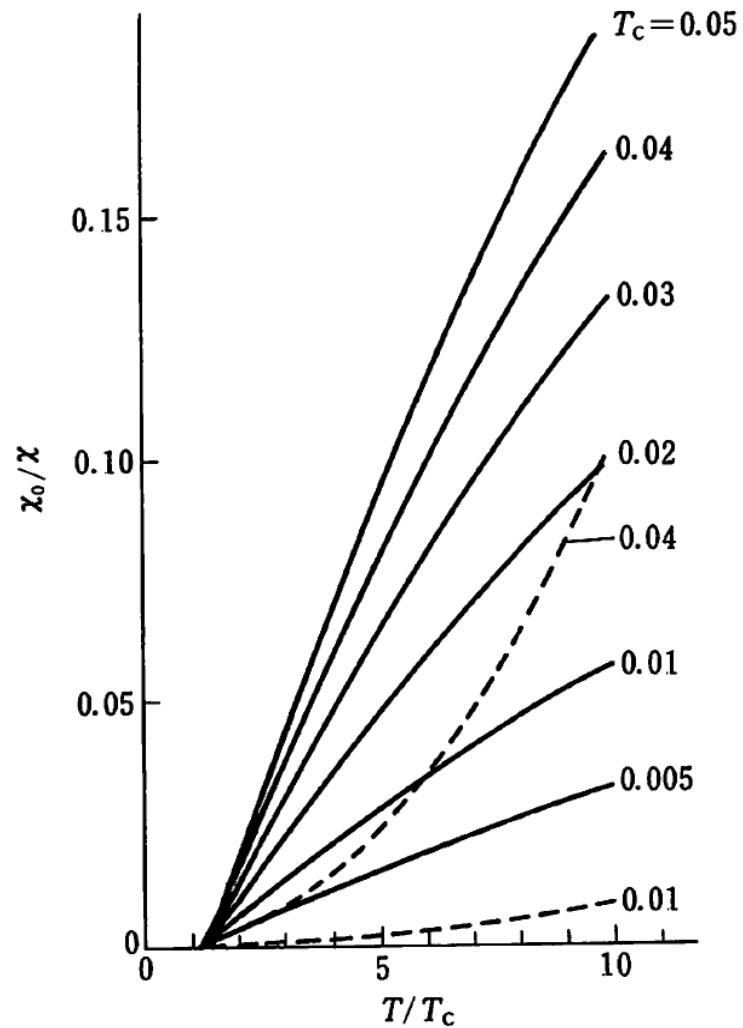
$$T = 0 \quad \frac{\chi_0}{\chi(T=0)} = 1 - 2U\chi_0 + \frac{g}{N} \sum_{\mathbf{q}} \frac{1}{\pi} \int_0^{\infty} d\omega \text{Im}[\chi(\mathbf{q}, \omega)]_{T=0}$$

Correction of overestimation of stability in ferromagnetic state

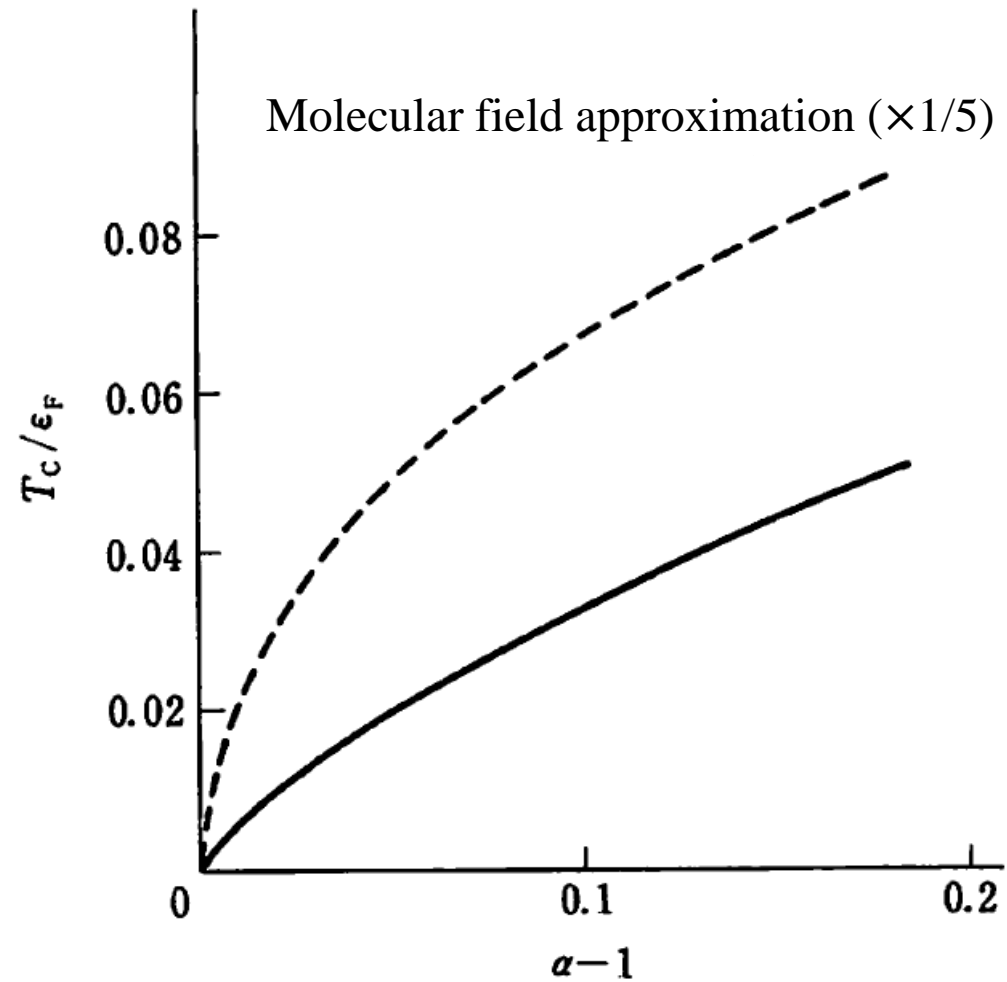
Ignore magnon zero-point motion $\frac{\chi_0}{\chi} = \frac{\chi_0}{\chi(T=0)} + \frac{g}{N} \sum_{\mathbf{q}} \frac{1}{\pi} \int_0^{\infty} d\omega \frac{2}{e^{\hbar\omega\beta} - 1} \text{Im}[\chi(\mathbf{q}, \omega)]$

Expansion around (0,0) $\frac{\chi_0}{\chi(\mathbf{q}, \omega)} = \frac{\chi_0}{\chi(+0, +0)} + A \left(\frac{q}{k_F} \right)^2 - iC \frac{\omega}{\epsilon_F} \frac{k_F}{q}$ Self-consistent determination of χ

Improvements by SCR-SF theory

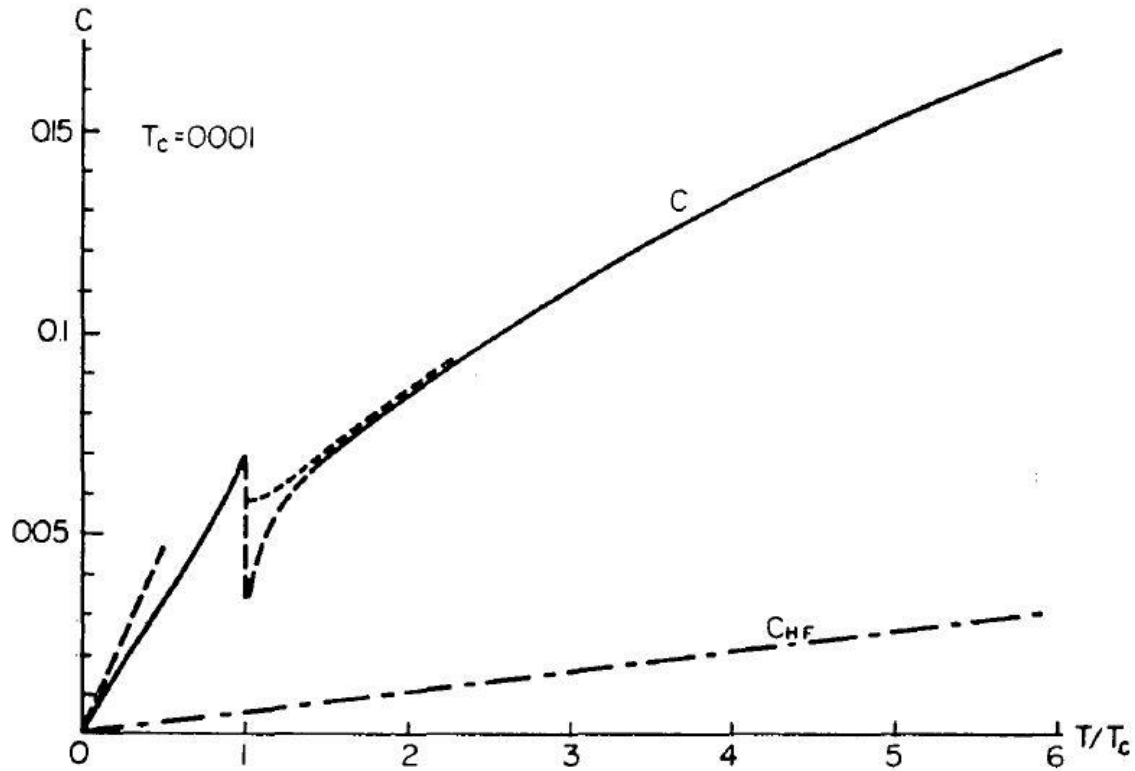


Temperature dependence of susceptibility

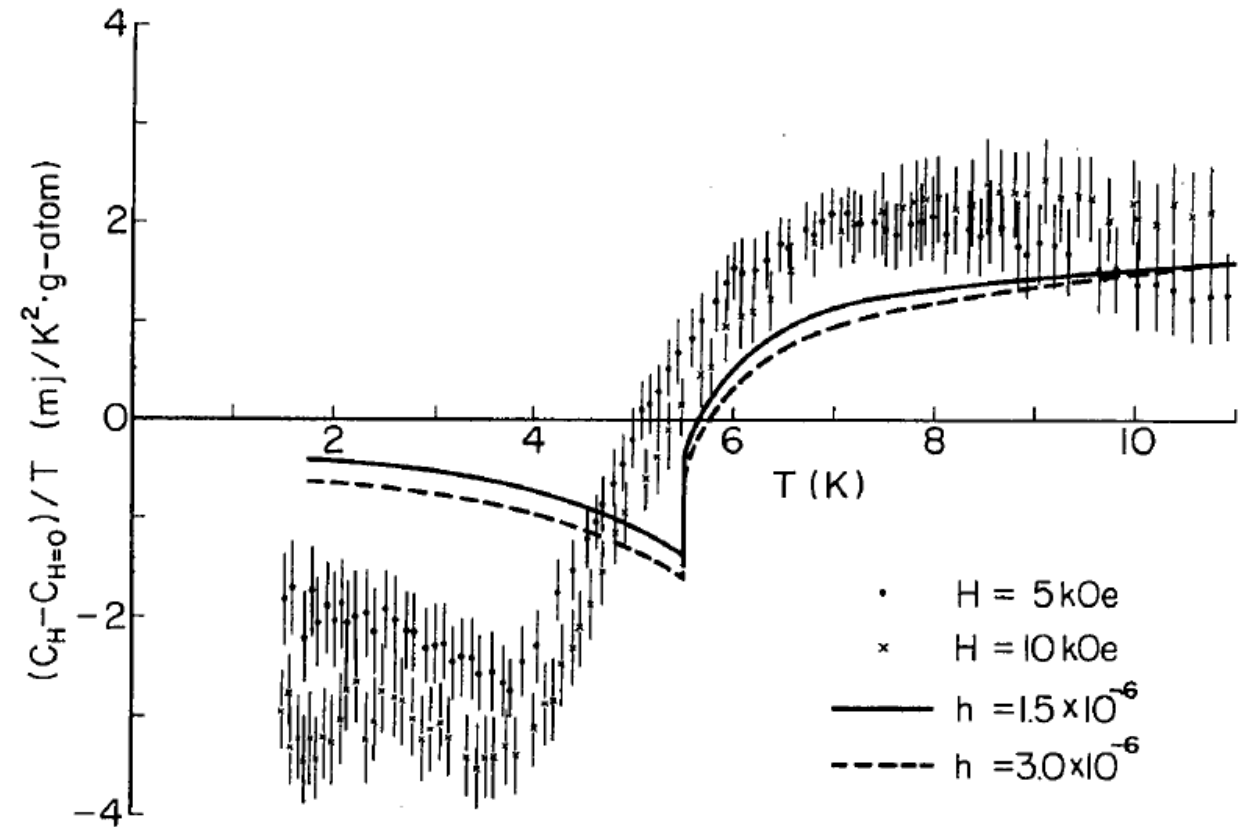


Critical temperature vs interaction parameter

Problems in SCR-SF theory

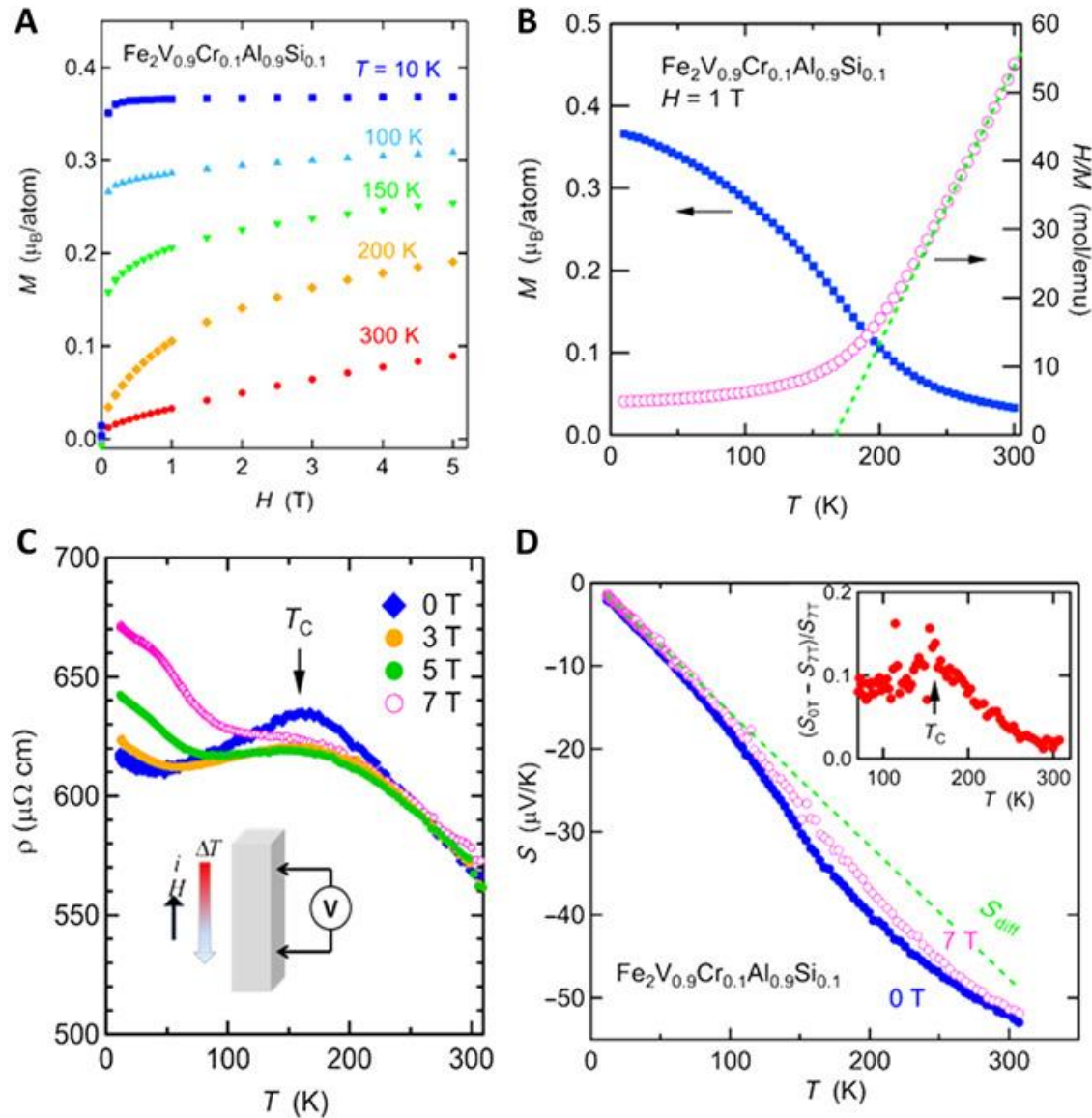


Makoshi & Moriya, JPSJ 38, 10 (1975).



Takeuchi & Masuda, JPSJ 46, 468 (1979).

Enhanced thermopower due to spin fluctuation

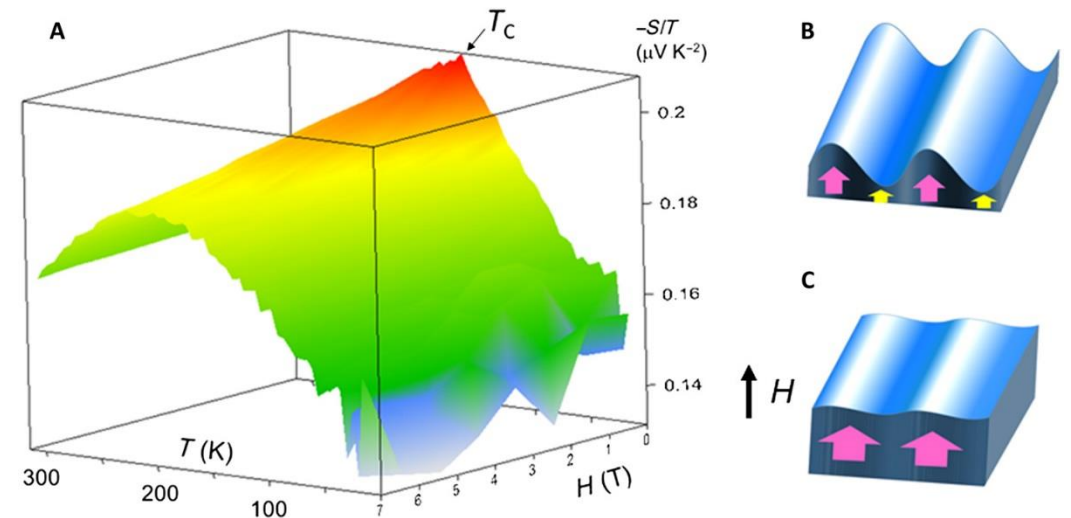


Weak ferromagnet

Spin fluctuation enhancement around T_C

Enhancement of entropy

Magnon drag effect



Tsuji et al. Science Advances **5**, eaat5935 (2019).

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

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.