2022.6.8 Lecture 9

10:25 – 11:55

Lecture on

Magnetic Properties of Materials

磁性 (Magnetism)

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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

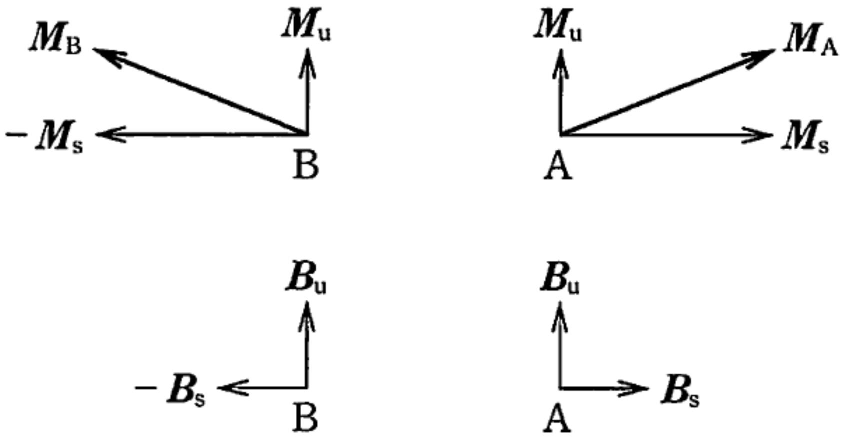
- Spin wave

Antiferromagnetic Heisenberg model

Antiferromagnetic Heisenberg Hamiltonian

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

$J < 0$



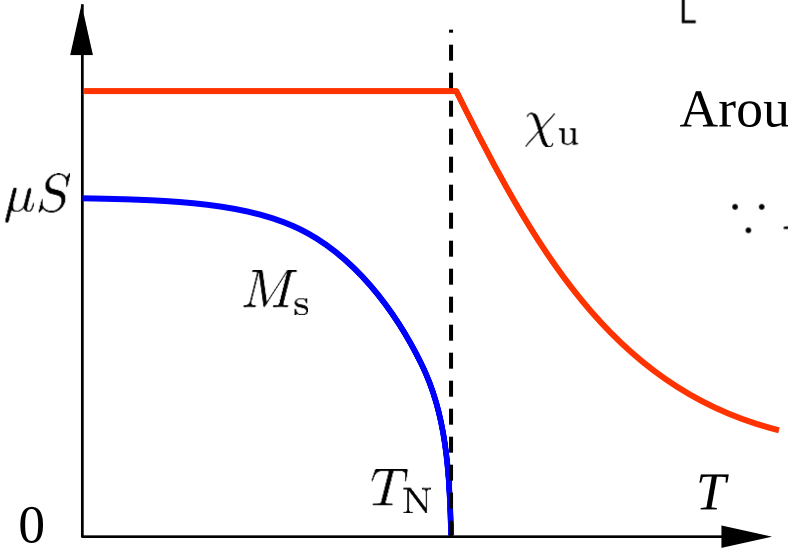
Sublattice magnetic field

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

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

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

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

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

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

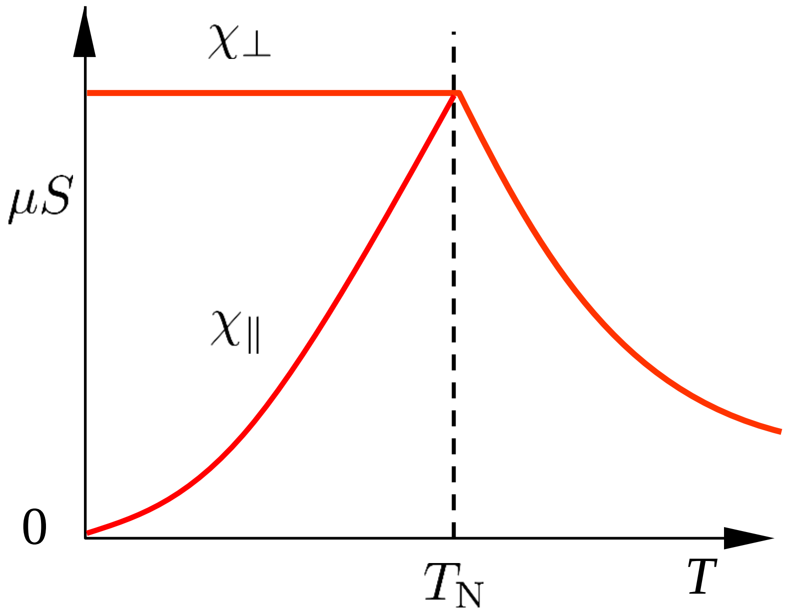
Antiferromagnetic Heisenberg model: parallel field

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

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

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

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



This set of equations should be solved numerically.

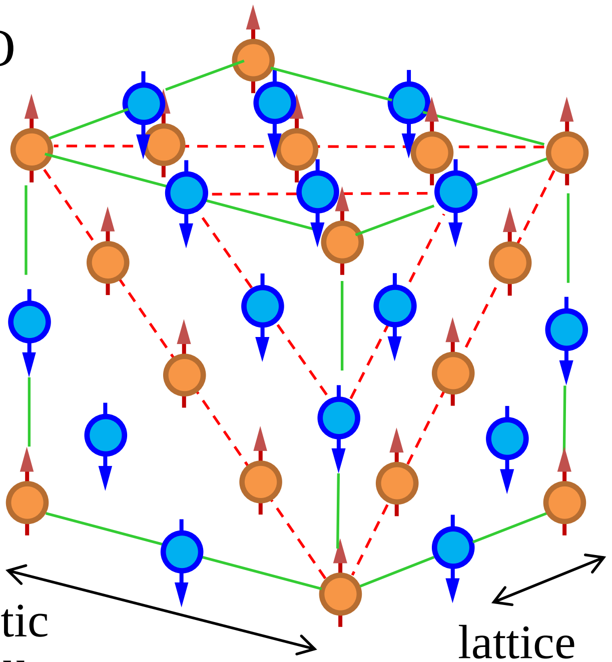
Then the parallel susceptibility is given by $\chi_\parallel = \lim_{B\to 0} \frac{M_A + M_B}{B}$

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

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

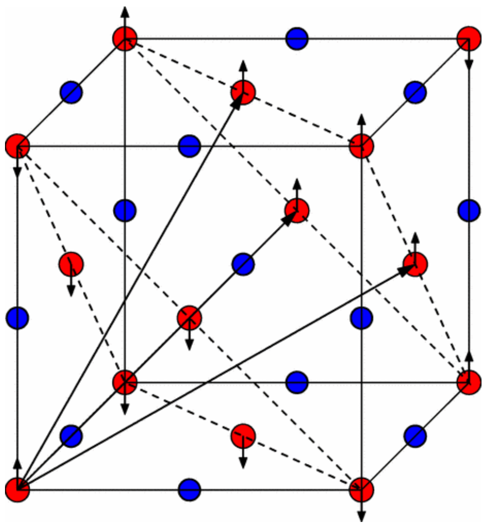
Examples of spin configuration in metal-oxide antiferromagnets

MnO

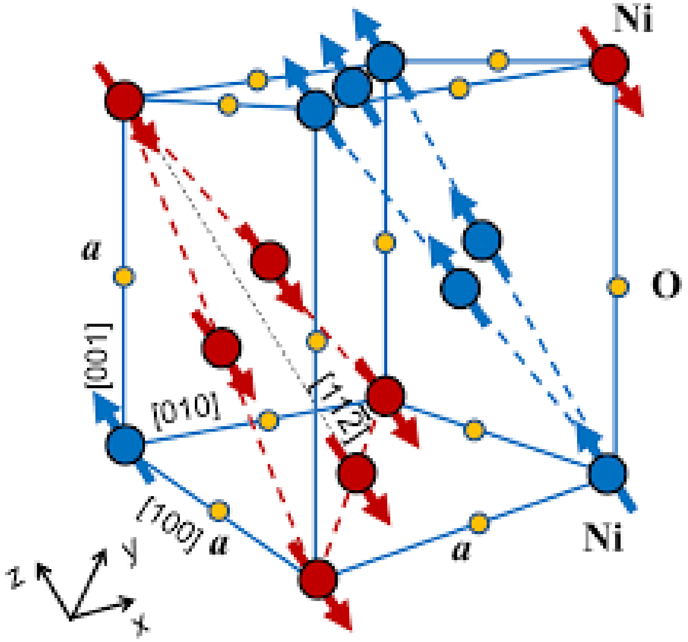


magnetic unit cell

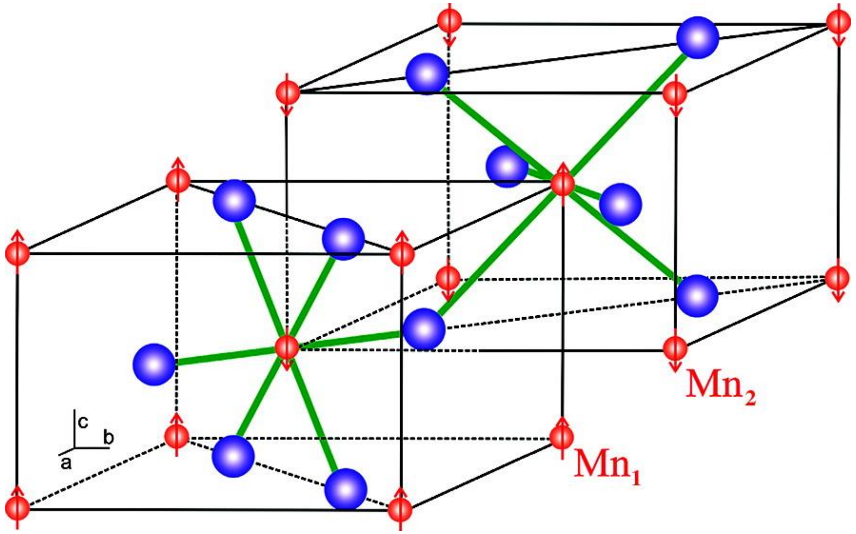
lattice unit cell



FeO

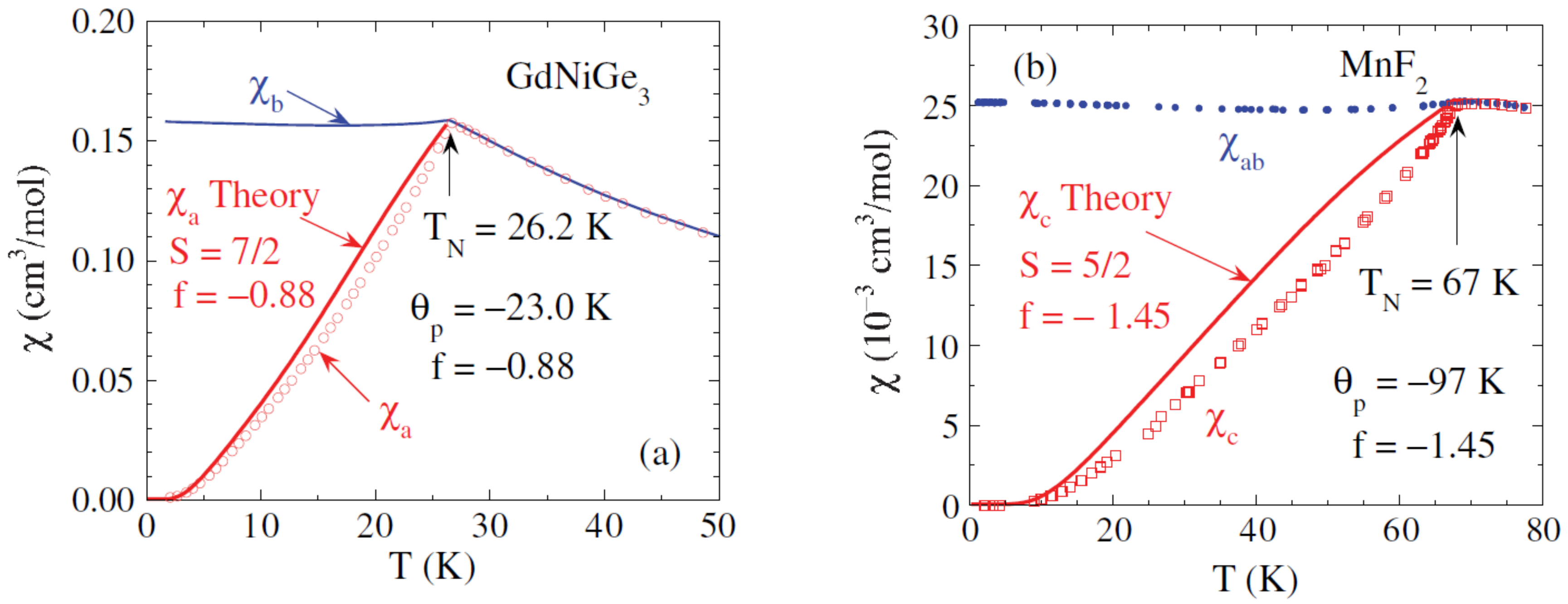


NiO



MnF_2

Temperature dependence of susceptibility



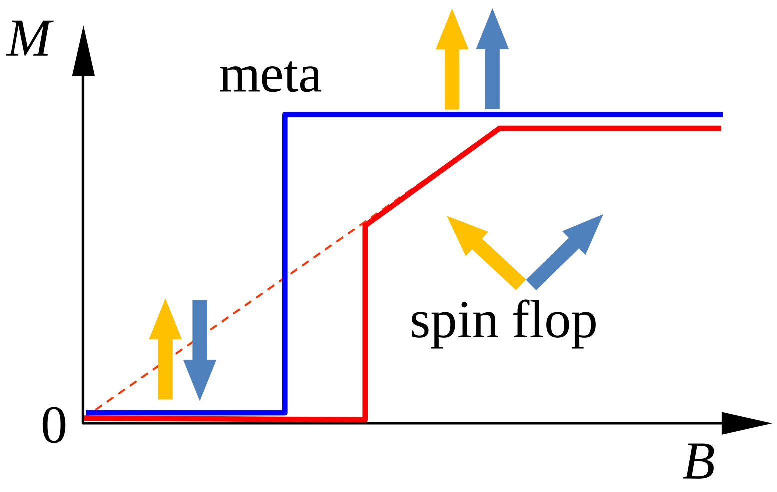
High temperature side ($T > T_{\mathrm{N}}$) $\chi_{\mathrm{u}} \propto \dfrac{1}{T+\theta}$ θ: Weiss temperature

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

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

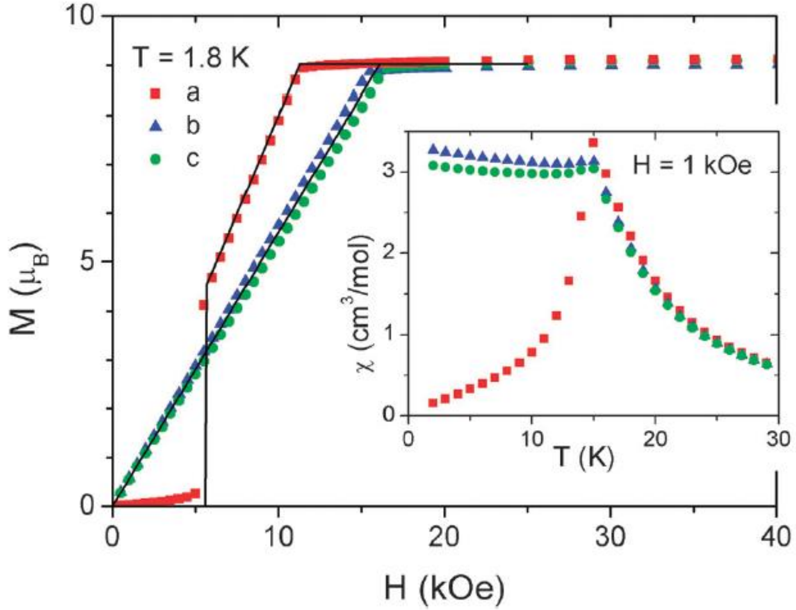
However crystals often have magnetic anisotropy. Let *K* be the anisotropic energy.

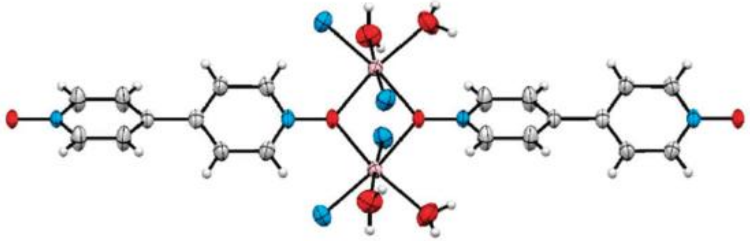
The anisotropic energy is overcome by the Zeeman energy at $\frac{\chi_{\perp} - \chi_{\parallel}}{2\mu_0^2}B_{\mathrm{c}}^2 = K$ Spin flop transition

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

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

Spin flop transition, metamagnetic transition

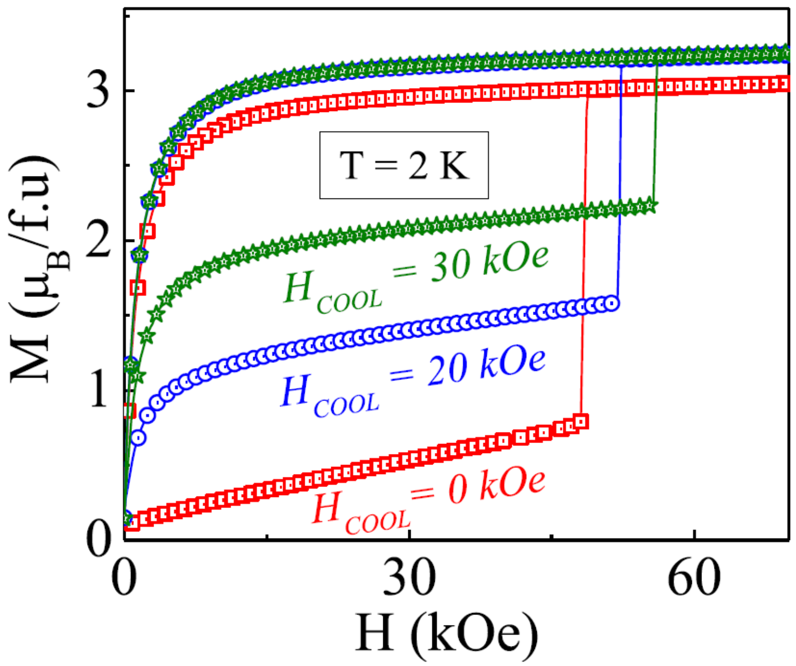




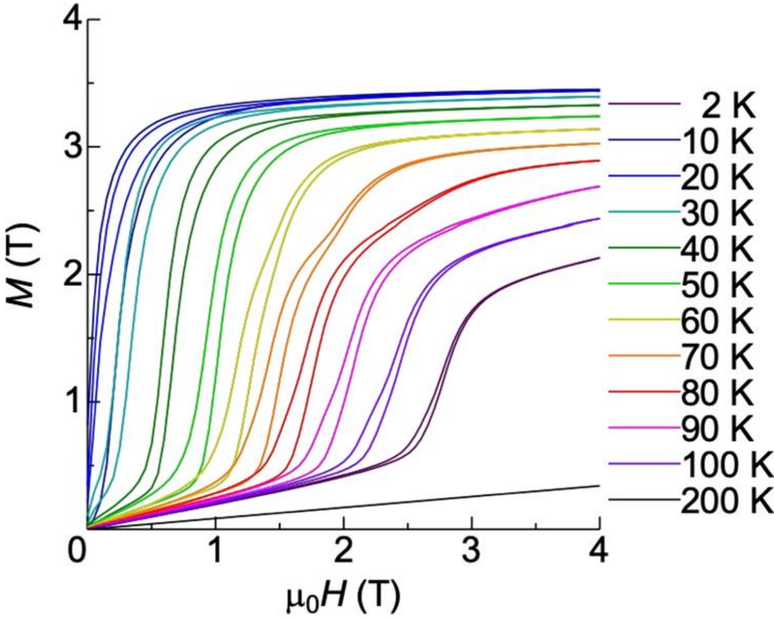
$\{[Mn_2(bpdo)(H_2O)_4][Nb(CN)_8] \cdot 6H_2O\}_n$

Spin flop transition in polymer anti-ferromagnet

Metamagnetic transition



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



Helical magnet Ho single crystal

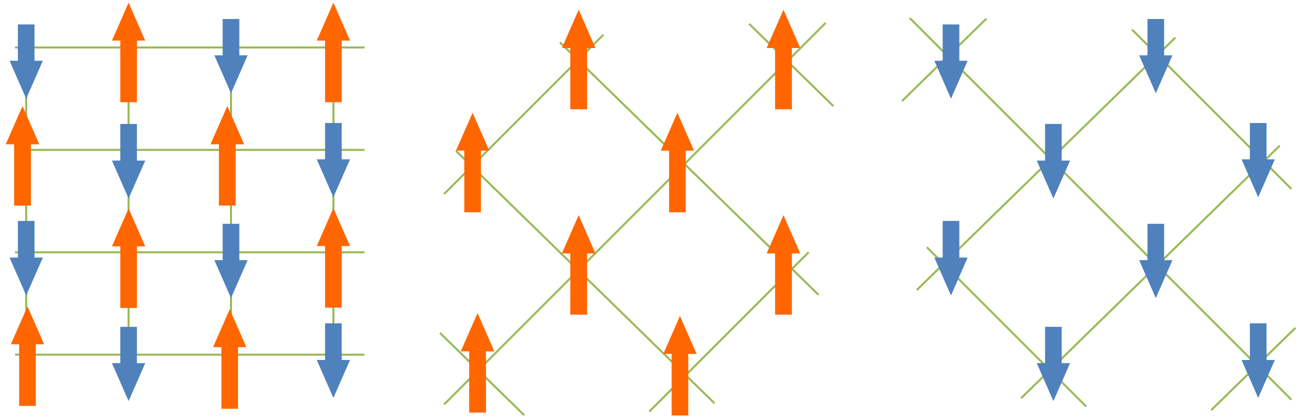
Remember in magnetic refrigeration, to have a good efficiency

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

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

Ferrimagnetism

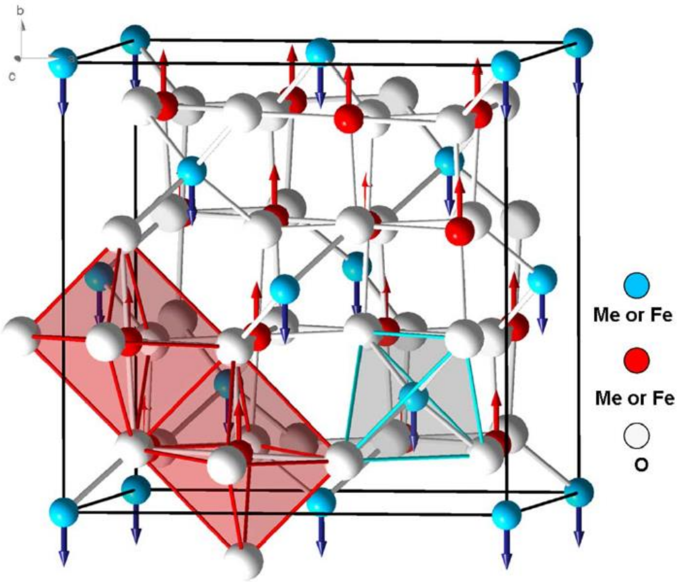
Ferrimagnetism ⟵ Magnetism in ferrites



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

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

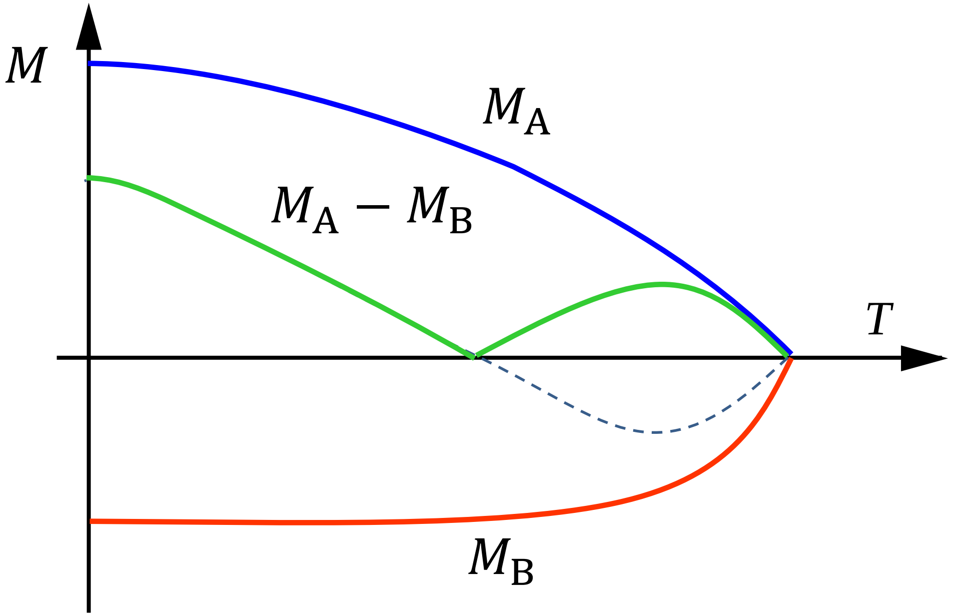
Molecular fields: intra-sublattice interaction is included

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

Self-consistent set of equations

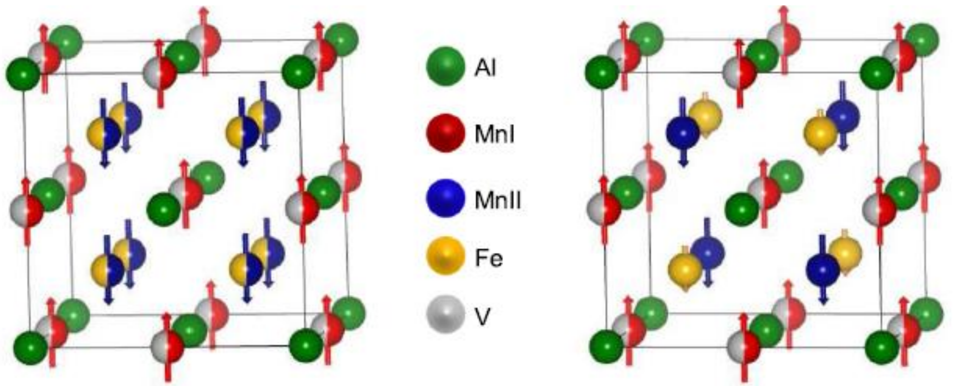
$\mathcal{B}_S(x)$: Brillouin function

Compensated ferrimagnetism

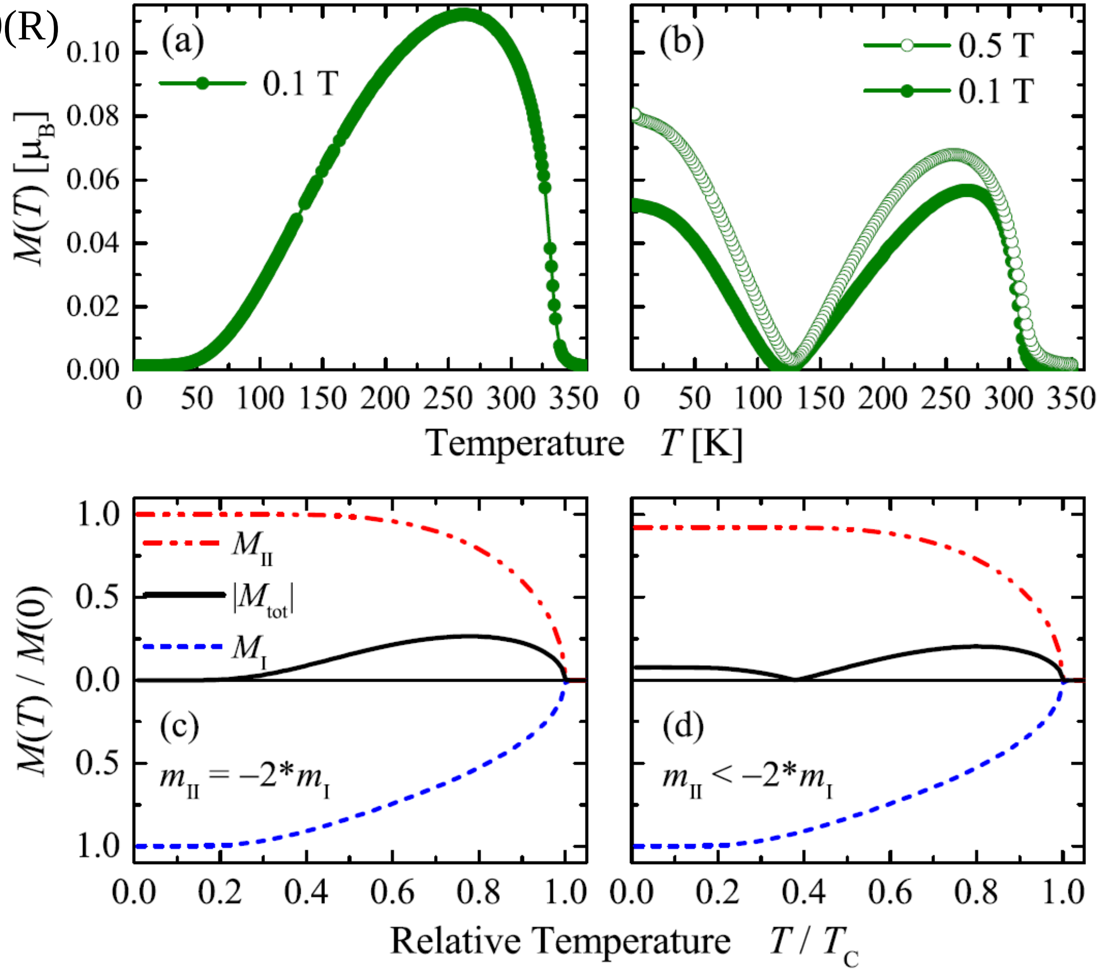


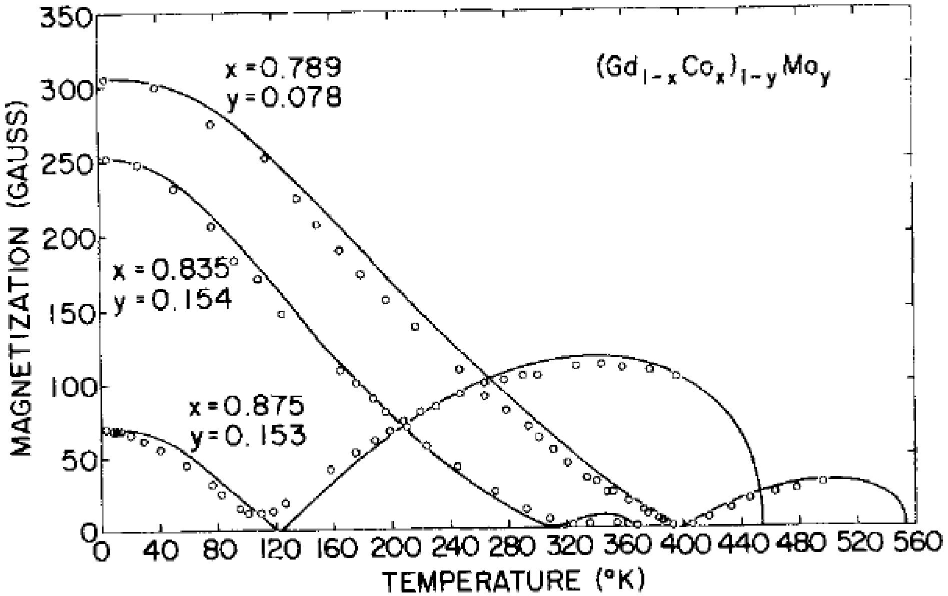
$Mn_{1.5}V_{0.5}FeAl$
Cubic Heusler
$L2_1$
$Fm\bar{3}m$

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



X
$F\bar{4}3m$





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

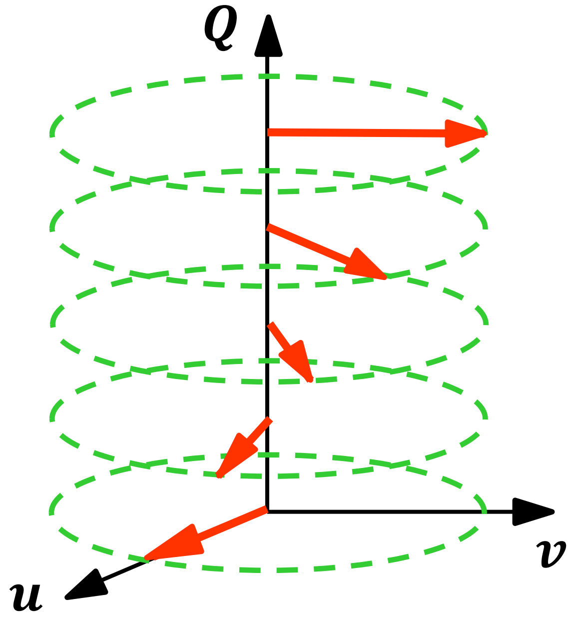
Helimagnetism

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)

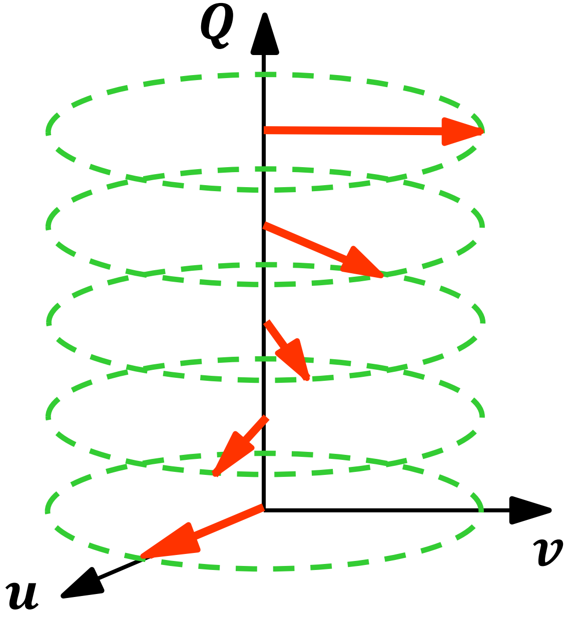
Then we can write with taking ***u*** and ***v*** as orthogonal unit vectors as

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

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

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

Self consistent equation

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

Helical susceptibility

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

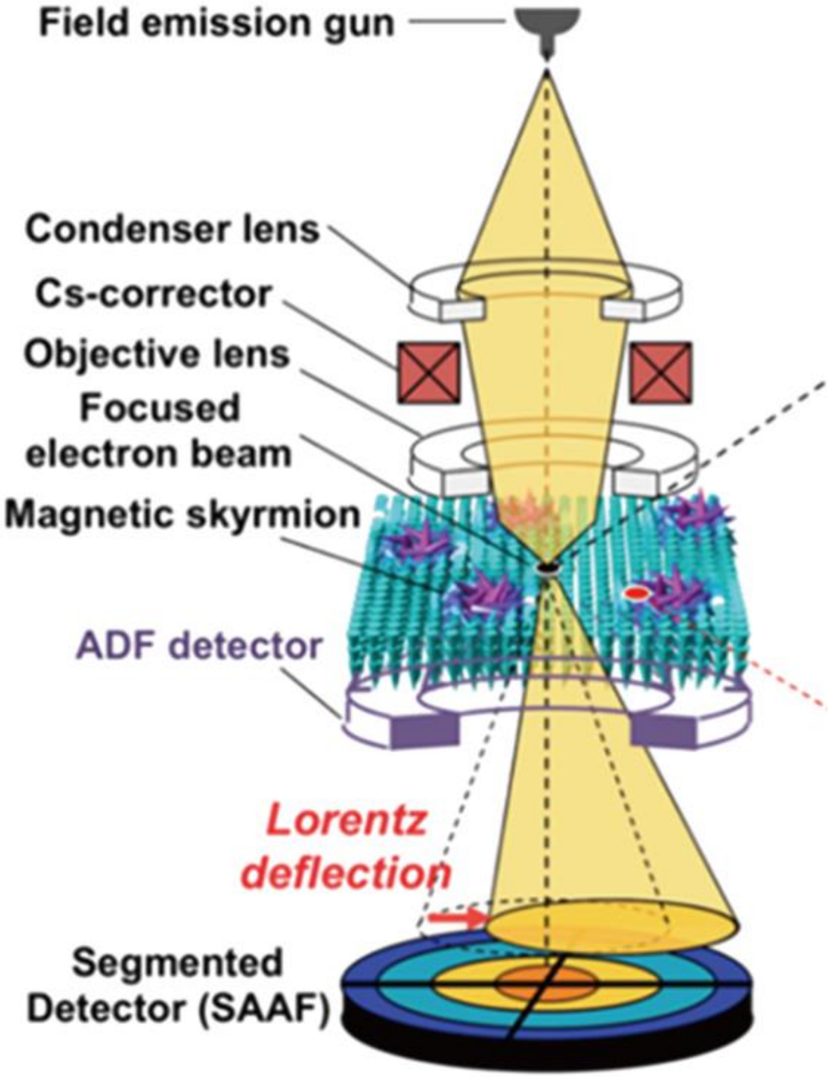
Helical order temperature

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

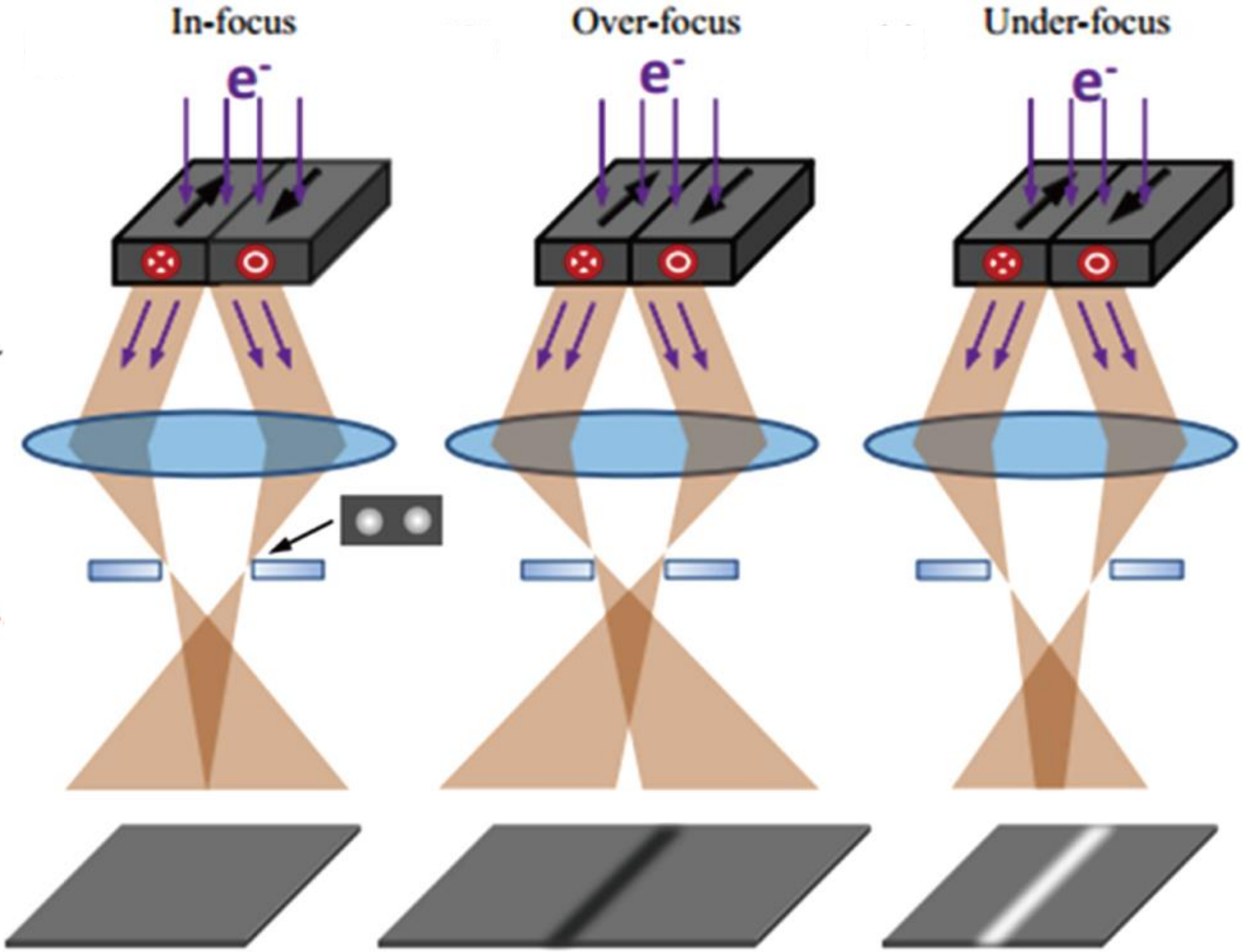
Lorentz transmission microscope

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

Overview

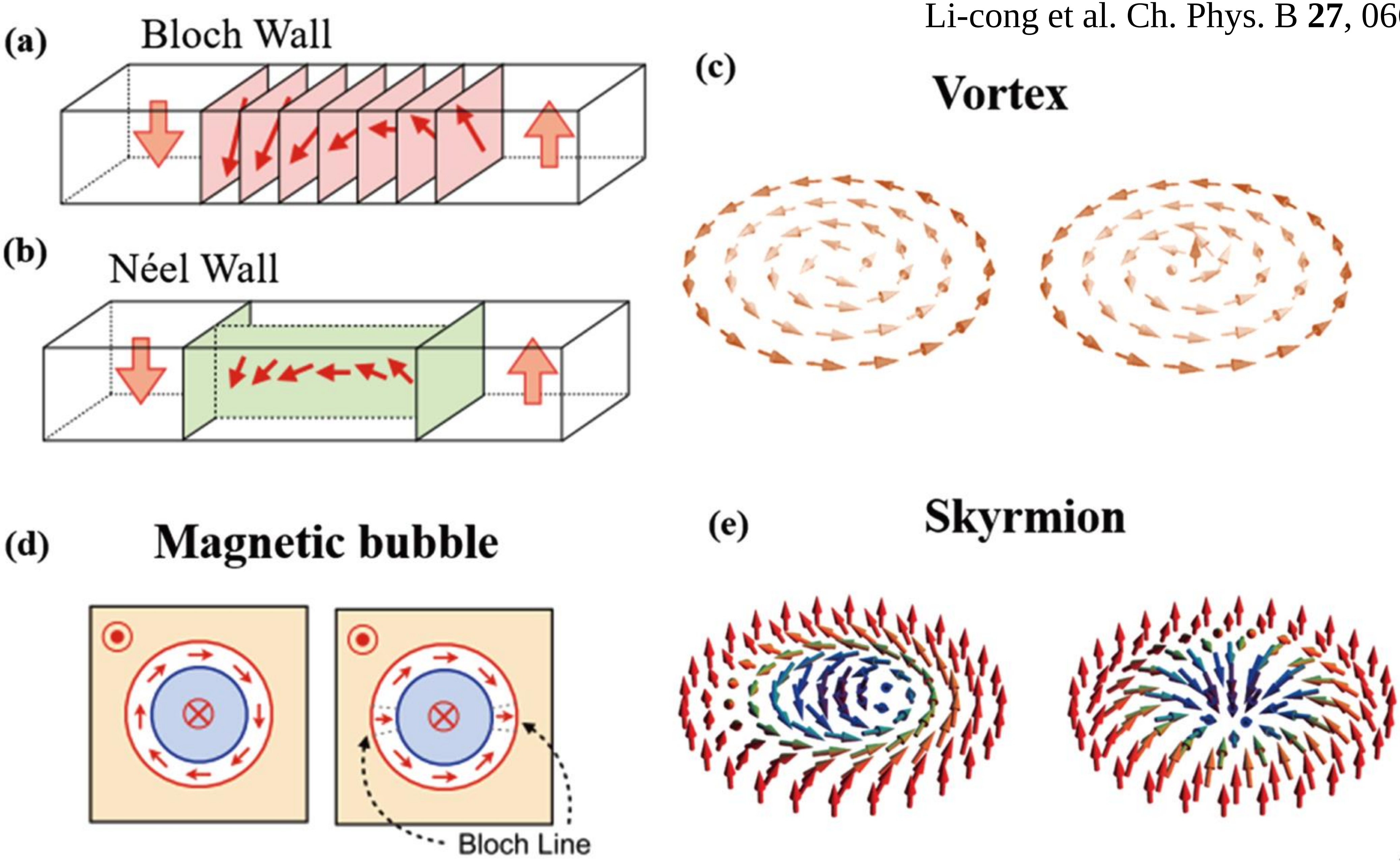


Effect of defocusing

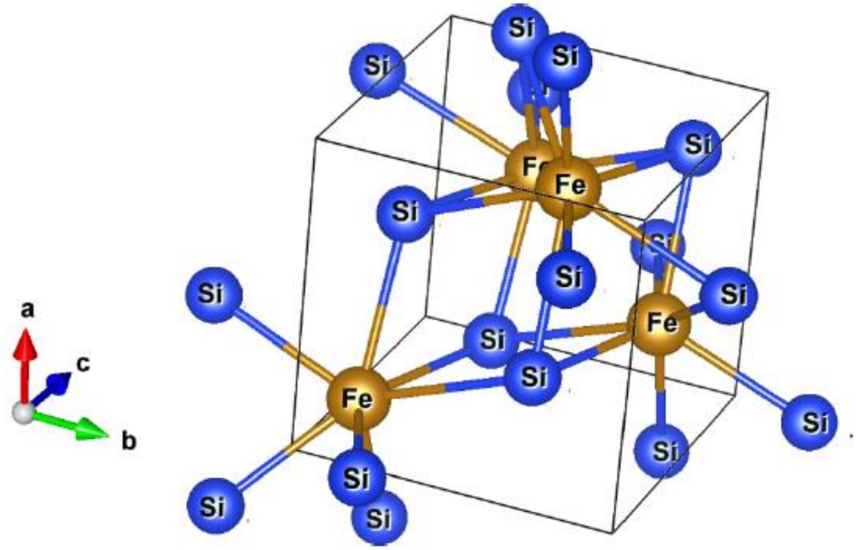


Spatially localized magnetic structures

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



Real space observations of spin structures by Lorentz microscope



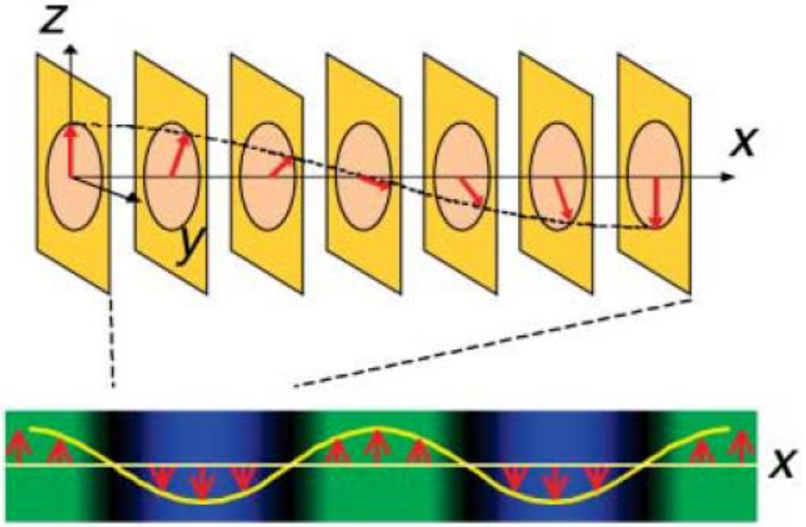
ε-FeSi B20-type cubic non-centro-symmetric lattice

↓

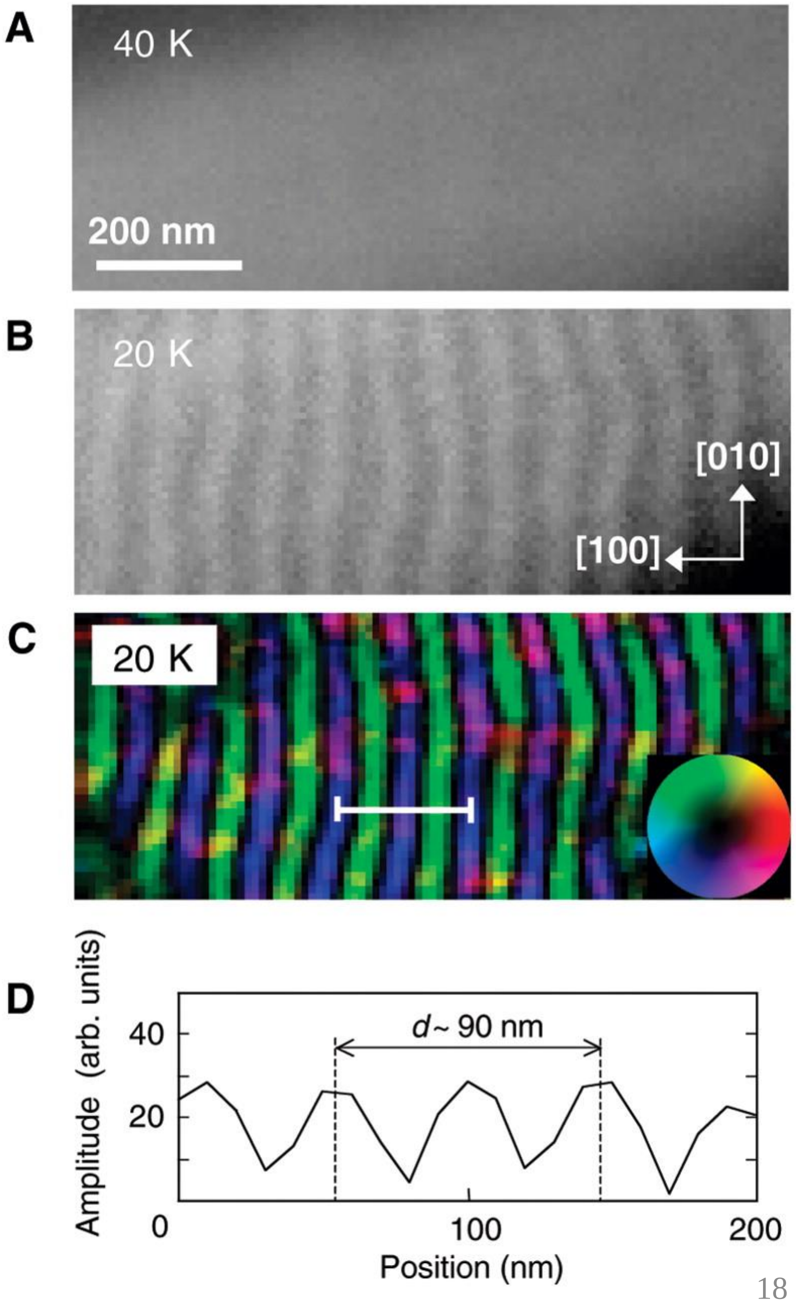
Dzyalosinsky-Moriya interaction causes helimagnetism

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

$Fe_{1-x}Co_xSi$



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

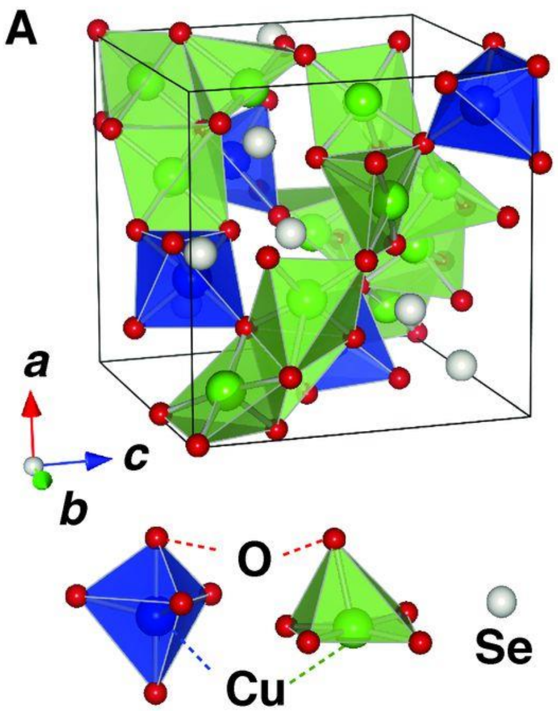


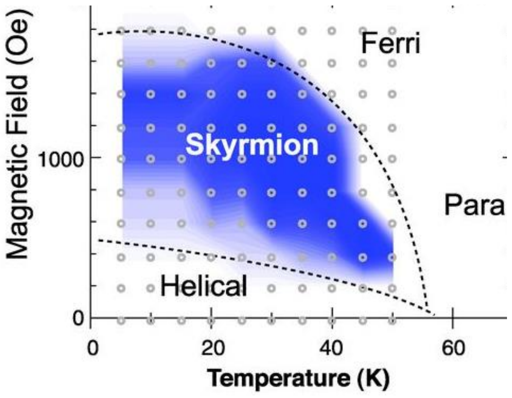
Observation of skyrmions by Lorentz microscope

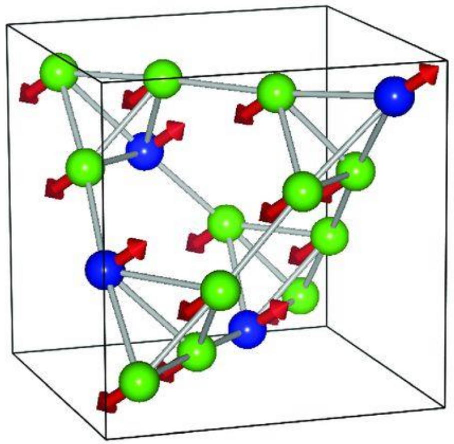
Cu_2OSeO_3

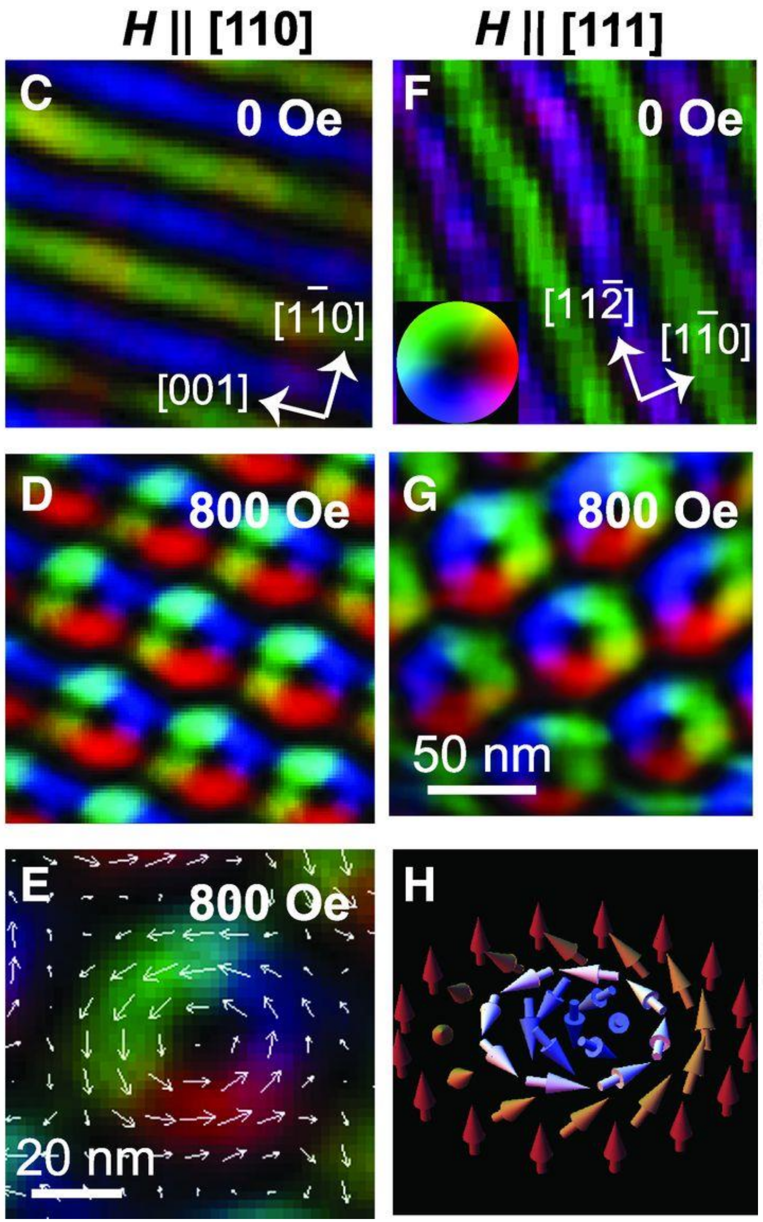
The DM interaction causes helimagnetism.

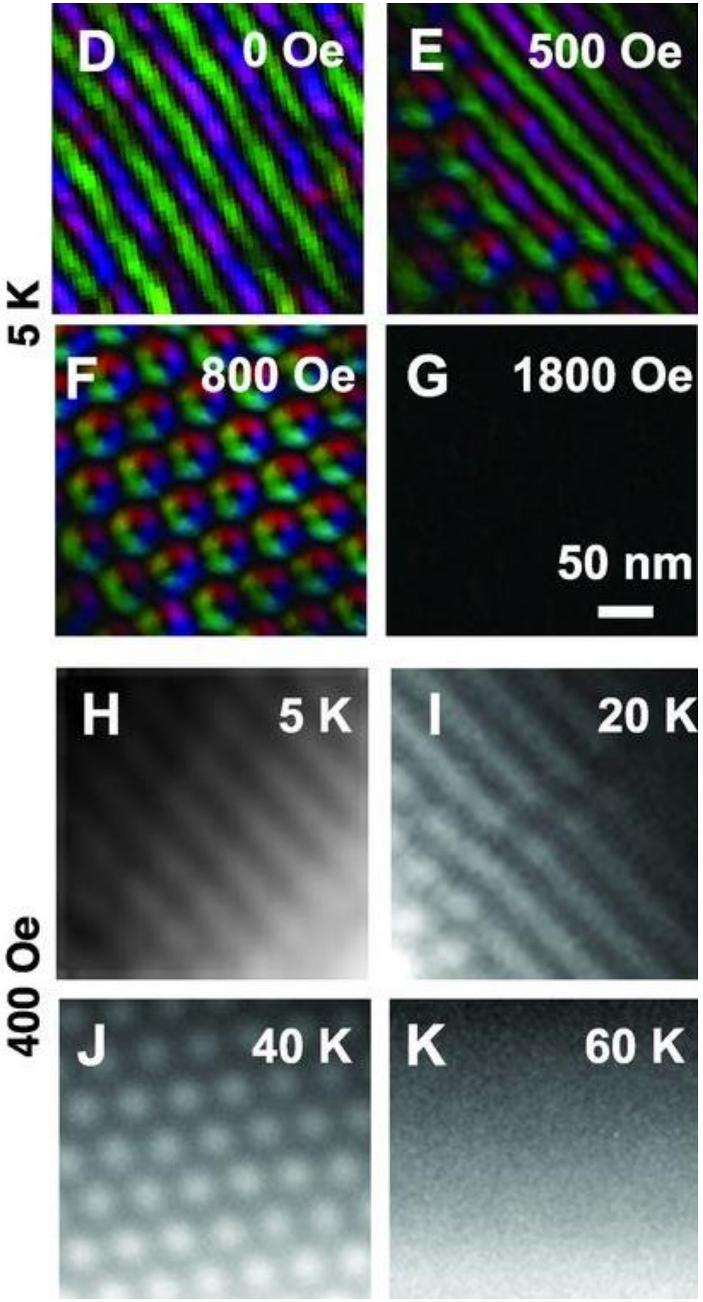
Seki et al.
Science **336**, 198 (`12)











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)

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

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

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

Holstein-Primakoff transformation

Summary

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

- Ferrimagnetism
- Molecular-field approximation

- Helimagnetism

- Spin wave