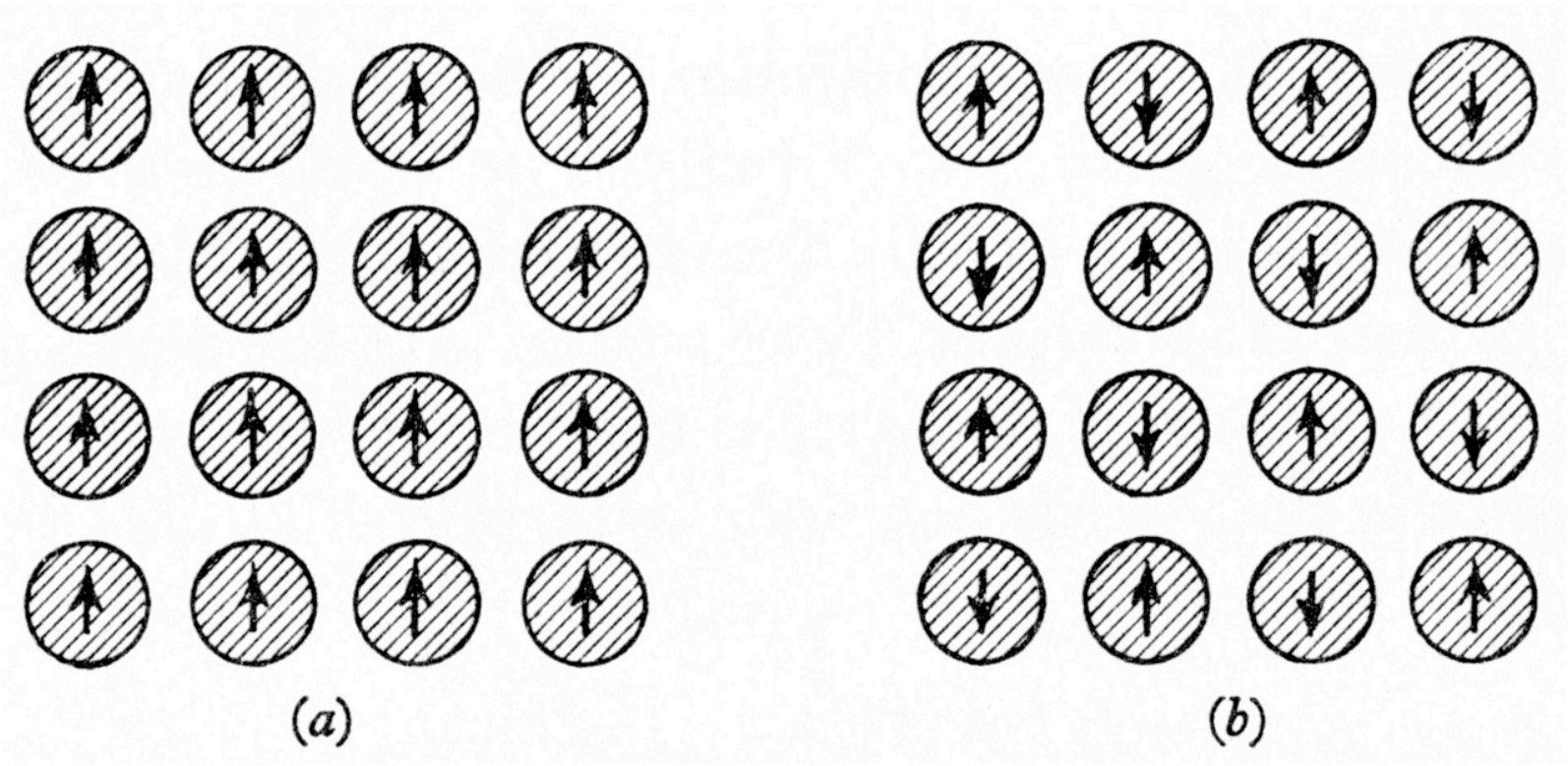
Magnetically ordered solids

- Types of magnetic structure: ferromagnetism, antiferromagnetism, ferrimagnetism, helical order
- Experimental observation of magnetic structures: magnetization, magnetic susceptibility, neutron scattering, nuclear magnetic resonance
- Heisenberg and Ising models
- Spin waves
- Mean field theory, the Curie–Weiss law
- Ferromagnetic domains

Types of magnetic structure: ferromagnetism, antiferromagnetism, ferrimagnetism, helical order

(a) Ferromagnetic ordering. (b) Antiferromagnetic ordering.



[from J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, 1979)]

Ferromagnetism in the mean-field approximation

In the mean field approximation each magnetic atom experiences effective field (from exchange with neighbor sites) proportional to magnetization:

$$B_E = \lambda M$$

The magnetization itself is proportional to the total field $M = \chi_p(B_a + B_E)$

where the paramagnetic susceptibility is given by the Curie law $\chi_p = C/T$,

$$MT = C(B_a + \lambda M)$$

and the total susceptibility

$$\chi = \frac{M}{B_a} = \frac{C}{(T - C\lambda)} = \frac{C}{T - T_c}; \qquad T_c = C\lambda$$

What is the magnitude of effective exchange field B_E and of λ?

$$\frac{M}{B} \cong \frac{NJ(J+1)g^2\mu_B^2}{3k_BT} = \frac{Np^2\mu_B^2}{3k_BT} = \frac{C}{T} \quad \Rightarrow \quad \lambda = \frac{T_c}{C} = \frac{3k_BT_c}{Ng^2S(S+1)\mu_B^2}$$

For iron $Tc = 1000\ K$, $g = 2$, and $S = 1$; => we have $\lambda = 5000$. With saturation magnetization $M_S = 1700$ we have $B_E = \lambda M = 10^7 G = 1000\ T$.

Magnitude of exchange interaction

Energy of interaction of atoms i, j bearing electron spins S_i, S_j contains a term,

$$U = -2JS_i \cdot S_j \quad (1)$$

where J is the exchange integral and is related to the overlap of the charge distributions of the atoms i, j. Equation (1) is called the **Heisenberg model**.

We can establish an approximate connection between the exchange integral J and the Curie temperature Tc. Suppose that the atom has z nearest neighbors, each connected with the central atom by the interaction J. For more distant neighbors we take J as zero. The energy need to flip this spin is $U = 4JzS^2 = 2\mu B_E = 2\mu(\lambda M_s) = 2\mu(\lambda\mu/\Omega)$,

где S — среднее значение $\boldsymbol{S}$ в направлении намагниченности, Ω — объем, приходящийся на один атом. Средний магнитный момент электрона, обусловленный его спином, есть $\mu = gS\mu_B$,

$$\lambda = \frac{2Jz\Omega}{g^2\mu_B^2},$$

The mean field theory result is

$$J = \frac{3k_BT_c}{2zS(S+1)} \quad (2)$$

Better statistical approximations give somewhat different results. For the sc, bcc, and fcc structures with S = 1, Rushbrooke and Wood give kT/Jz = 0.28; 0.325; and 0.346, as compared to 0.500 from (2) for all three structures. If iron is described by the Heisenberg model with S = 1, then the observed Curie temperature corresponds to J = 11.9 meV.

Saturation magnetization in ferromagnetic crystals

Substance	Magnetization M_s, in gauss		Number of Bohr magnetons n_B(0 K), per formula unit	Curie temperature, in K
	Room temperature	0 K		
Fe	1707	1740	2.22	1043
Co	1400	1446	1.72	1388
Ni	485	510	0.606	627
Gd	—	2060	7.63	292
Dy	—	2920	10.2	88
MnAs	670	870	3.4	318
MnBi	620	680	3.52	630
MnSb	710	—	3.5	587
CrO_2	515	—	2.03	386
$MnOFe_2O_3$	410	—	5.0	573
$FeOFe_2O_3$	480	—	4.1	858
$NiOFe_2O_3$	270	—	2.4	858
$CuOFe_2O_3$	135	—	1.3	728
$MgOFe_2O_3$	110	—	1.1	713
EuO	—	1920	6.8	69
$Y_3Fe_5O_{12}$	130	200	5.0	560

Temperature dependence of magnetization in ferromagnet below Curie temperature

Above Curie temperature, at T>Tc, susceptibility of ferromagnetic is

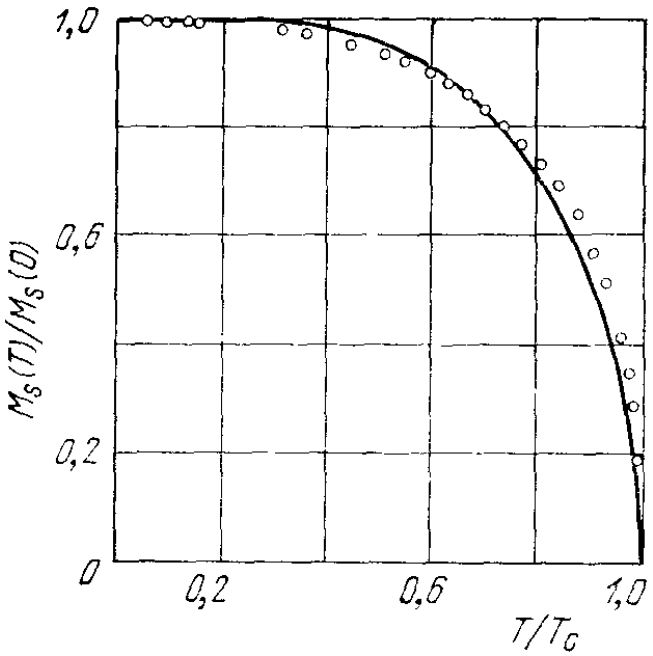
$$\chi = \frac{C}{T - T_c}; \qquad T_c = C\lambda \qquad B_E = \lambda M$$

Below the Curie temperature, at T<Tc, one would expect magnetization M(T)

$$M = N\mu \,\mathrm{th}\,(\mu B/k_B T)$$

where the total field B is mainly due to exchange field $B_E = \lambda M$, so that we obtain an equation on M:

$$M = N\mu \,\mathrm{th}\,(\mu\lambda M/k_B T)$$



The mean field theory does not give a good description of the variation of M at low temperatures. For T <<Tc the argument of tanh is large, and $\mathrm{th}\,\xi \approx 1 - 2e^{-2\xi} + \ldots$

To lowest order the magnetization deviation

$$\Delta M \equiv M(0) - M(T) \approx 2N\mu \exp(-2\lambda N\mu^2/k_B T)$$

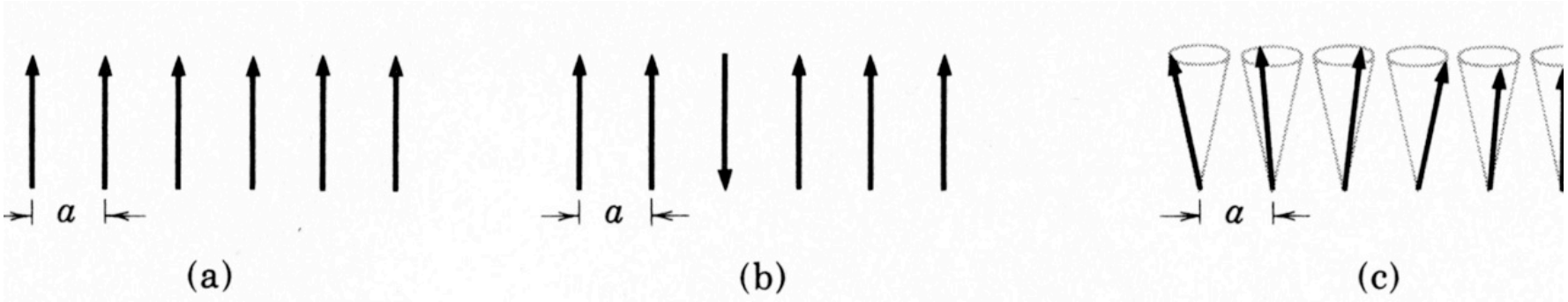
On experiment, $\Delta M/M(0) = AT^{3/2}$

Fig: Saturation magnetization of nickel as a function of temperature, together with mean-field theoretical curve for S = 1/2.

Spin waves

The ground state of a ferromagnet – classical picture:
(a) All spins parallel, (b) An excitation; one spin is reversed,
(c) The low-lying elementary excitations (spin waves).

The spin vectors precess on the surfaces of cones.
Successive spins advanced in phase by a constant angle.

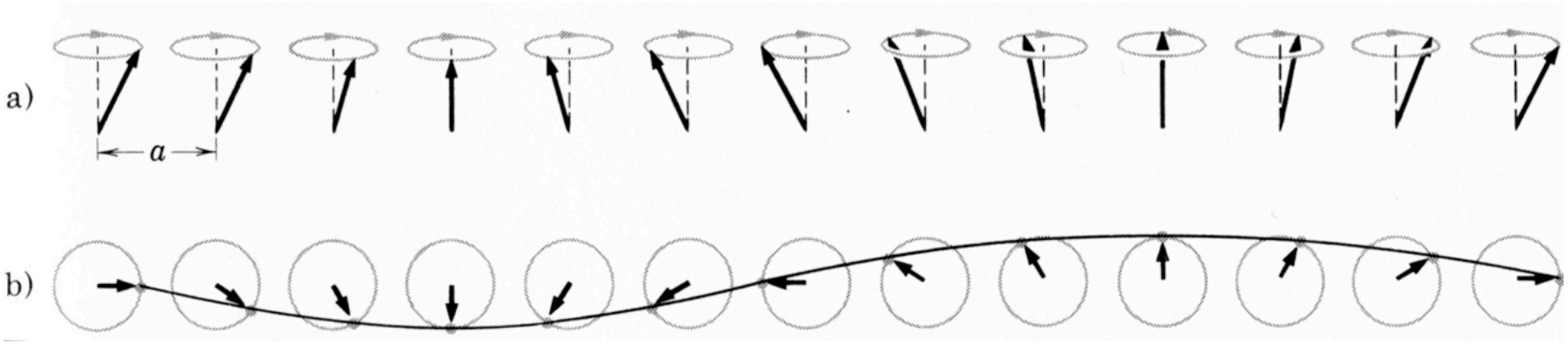


[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

A spin wave on a line of spins:

(a) The spins viewed in perspective,

(b) Spins viewed from above, showing one wavelength.
The wave is drawn through the ends of the spin vectors.



[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

The Heisenberg Hamiltonian is the spin Hamiltonian for the two-spin case, summed over all pairs of ions:

$$H_{\text{spin}} = -\sum_{\substack{i,j \\ i \neq j}} J_{ij}\,\mathbf{S}_i \cdot \mathbf{S}_j - g\mu_B \sum_i \mathbf{B} \cdot \mathbf{S}_i$$

The exchange coupling constant J_{ij} depends on the relative positions of the sites i and j.

Magnetic ions are far enough apart that the overlap of their electronic wave functions is small.

If the angular momentum contains both an orbital and a spin part, the coupling may depend on the absolute and the relative spin orientations.

Spin waves in ferromagnet

(classical theoretical description, dispersion relation)

Consider N spins each of magnitude S on a line or a ring, with nearest neighbor spins coupled by the Heisenberg interaction: $U = -2J \sum_{p=1}^{N} \boldsymbol{S}_p \cdot \boldsymbol{S}_{p+1},$

The effective magnetic field or exchange field that acting on the p-th spin is $\boldsymbol{B}_p = (-2J/g\mu_B)(\boldsymbol{S}_{p-1} + \boldsymbol{S}_{p+1})$

The equations of motion for spins are

$$\hbar \frac{d\boldsymbol{S}_p}{dt} = \boldsymbol{\mu}_p \times \boldsymbol{B}_p = -\frac{g\mu_B}{\hbar} \boldsymbol{S}_p \times \boldsymbol{B}_p = \frac{2J}{\hbar}(\boldsymbol{S}_p \times \boldsymbol{S}_{p-1} + \boldsymbol{S}_p \times \boldsymbol{S}_{p+1})$$

In the spin components these equations are $\frac{dS_p^x}{dt} = \frac{2J}{\hbar}[S_p^y(S_{p-1}^z + S_{p+1}^z) - S_p^z(S_{p-1}^y + S_{p+1}^y)],$

and similarly for dS_p^y/dt and dS_p^z/dt.

These equations involve products of spin components and are nonlinear

If the amplitude of the excitation is small (if $S^x, S^y \ll S$), we may obtain an approximate set of linear equations by taking all $S^z = S$ and by neglecting terms $\sim S^x S^y$ which appear in the equation for dS^z/dt. Then one obtains:

$$dS_p^x/dt = (2JS/\hbar)(2S_p^y - S_{p-1}^y - S_{p+1}^y) ;$$

$$dS_p^y/dt = -(2JS/\hbar)(2S_p^x - S_{p-1}^x - S_{p+1}^x)$$

$$dS_p^z/dt = 0 .$$

Dispersion relation of spin waves in ferromagnet

By analogy to finding phonon dispersion we substituting the traveling wave solutions

$$S_p^x = u\, e^{i\,(pka-\omega t)}, \quad S_p^y = v\, e^{i\,(pka-\omega t)}$$

to the linearized equations of motion:
(neglecting the time evolution of S^z=S)

$$dS_p^x/dt = (2JS/\hbar)(2S_p^y - S_{p-1}^y - S_{p+1}^y) \; ;$$

$$dS_p^y/dt = -(2JS/\hbar)(2S_p^x - S_{p-1}^x - S_{p+1}^x)$$

This gives:

$$-i\omega u = (2JS/\hbar)(2 - e^{-ika} - e^{ika})v = (4JS/\hbar)(1 - \cos ka)v \; ;$$

$$-i\omega v = -(2JS/\hbar)(2 - e^{-ika} - e^{ika})u = -(4JS/\hbar)(1 - \cos ka)u$$

These linear equations have a zon-zero solution for the amplitudes u and v if the determinant of coefficients is zero:

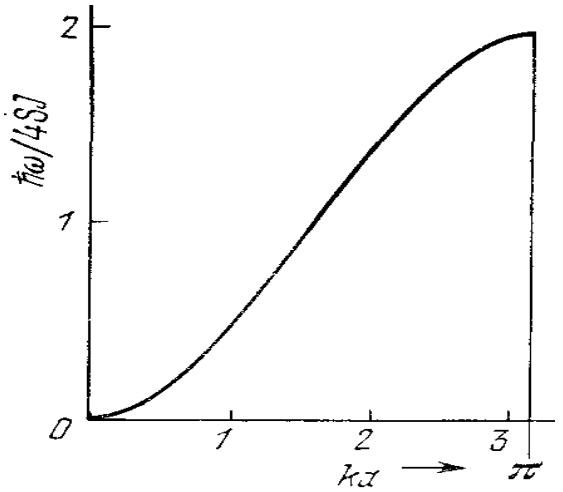
$$\begin{vmatrix} i\omega & (4JS/\hbar)(1 - \cos ka) \\ -(4JS/\hbar)(1 - \cos ka) & i\omega \end{vmatrix} = 0$$

This give the magnon dispersion in 1D ferromagnet: $\hbar\omega = 4JS\,(1 - \cos ka)$

At long wavelengths $ka << 1$, and $\hbar\omega \approx (2JSa^2)\,k^2$

In 3D crystal $\hbar\omega = 2JS\left[z - \sum_{\delta} \cos\,(\boldsymbol{k}\cdot\boldsymbol{\delta})\right]$

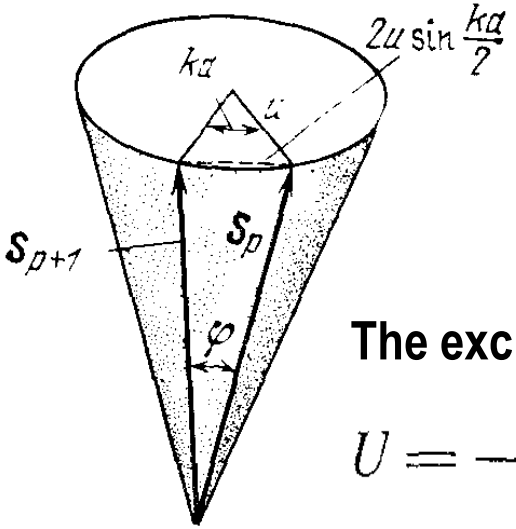
where the summation is over the z vectors denoted by δ which join the central atom to its nearest neighbors.



Quantization of spin waves in ferromagnet. Magnons.

The z-axis projection of total spin S_z^{tot} is an integer number. One quantum of spin wave (magnon) in ferromagnet changes this projection by 1, => $S_z^{tot}=NS-n_k$, where n_k is the number of magnons. Since for one spin $S_z = (S^2 - u^2)^{1/2} \approx S - \frac{u^2}{2S}$

the quantization of spin waves gives $n_k \approx \frac{Nu_k^2}{2S}$, или $u_k^2 \approx \frac{2Sn_k}{N}$ (1)



Assume that the angle between any two adjacent spins φ<<1. This angle is related to the amplitude u and wave vector k of the spin wave: $\sin(\varphi/2) = (u/S)\sin(ka/2)$

or $\cos\varphi = 1 - 2(u/S)^2 \sin^2(ka/2)$

The exchange interaction energy is than reduced by $NJ\,(1-\cos\varphi)$:

$$U = -2J\sum_{p=1}^{N} \boldsymbol{S}_p \cdot \boldsymbol{S}_{p+1} \approx -2JNS^2 + 4Ju^2\sin^2(ka/2) = \\ = -2JNS^2 + 2JNu^2(1-\cos ka)$$

Substituting (1) one obtains the energy of the spin wave: $\varepsilon_k = 4JS(1-\cos ka)\,n_k = n_k\hbar\omega_k$

where in a 3D crystal $\hbar\omega = 2JS\left[z - \sum_{\delta}\cos(\boldsymbol{k}\cdot\delta)\right]$

Thermal Excitation of Magnons

In thermal equilibrium the average number of magnons excited in the mode k is given by the Planck distribution (Bose-Einstein distribution at μ=0) :

$$\langle n_k \rangle = \frac{1}{\exp\left(\hbar\omega_k / k_B T\right) - 1}$$

The total number of magnons excited at a temperature T is

$$\sum_k n_k = \int d\omega \, \mathcal{D}(\omega) \langle n(\omega) \rangle,$$

Magnons have a single polarization for each value of k. In three dimensions the number of modes of wavevector less than k is $(1/2\pi)^3(4\pi k^3/3)$ per unit volume, whence the number of magnons $D(\omega)d\omega$ with frequency in $d\omega$ at ω is $(1/2\pi)^3(4\pi k^2)(dk/d\omega)\, d\omega$

The magnon dispersion gives

$$\frac{d\omega}{dk} = \frac{4JSa^2k}{\hbar} = 2\left(\frac{2JSa^2}{\hbar}\right)^{1/2} \omega^{1/2}$$

The density of magnon modes in ferromagnet is

$$D(\omega) = \frac{1}{4\pi^2}\left(\frac{\hbar}{2JSa^2}\right)^{3/2} \omega^{1/2}$$

The total number of magnons

$$\sum_k n_k = \frac{1}{4\pi^2}\left(\frac{\hbar}{2JSa^2}\right)^{3/2} \int_0^\infty d\omega \frac{\omega^{1/2}}{e^{\beta\hbar\omega} - 1} = \frac{1}{4\pi^2}\left(\frac{k_B T}{2JSa^2}\right)^{3/2} \int_0^\infty dx \frac{x^{1/2}}{e^x - 1}$$

and the temperature dependence of the deviation from saturation magnetization

$$\frac{\Delta M}{M(0)} = \frac{0.0587}{SQ} \cdot \left(\frac{k_B T}{2JS}\right)^{3/2}$$

Ferromagnetic domains

In real ferromagnetic samples the magnetization at zero temperature is much less than in mean-field theory because of the creation of ferromagnetic domains.

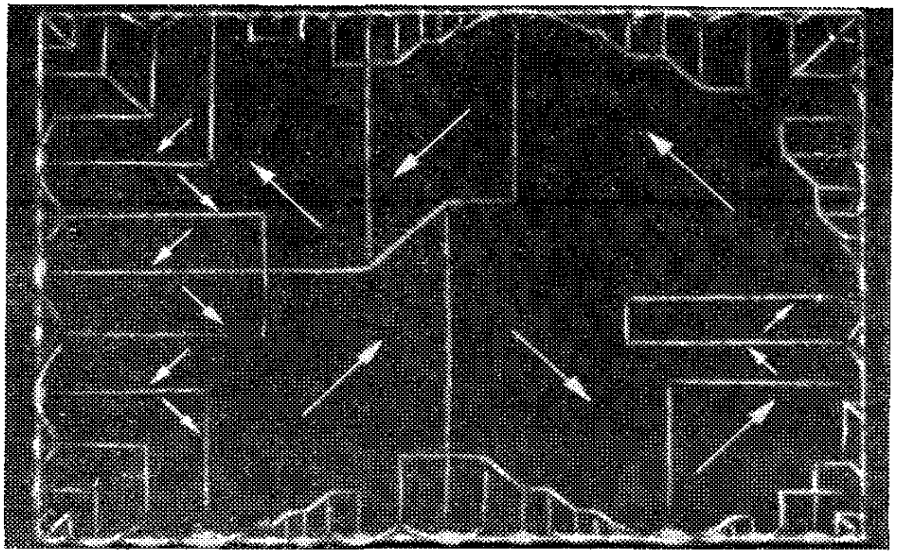
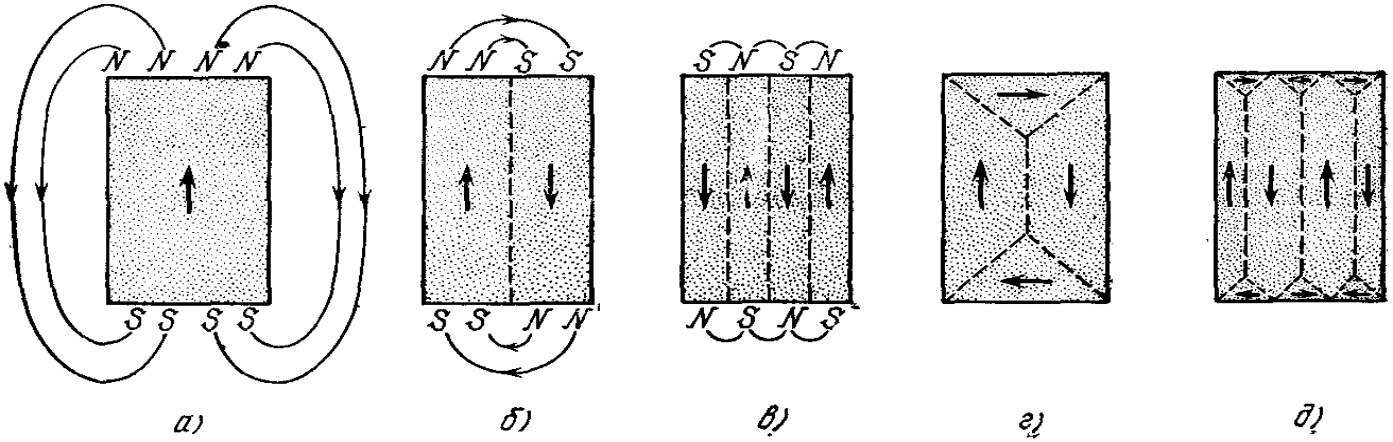
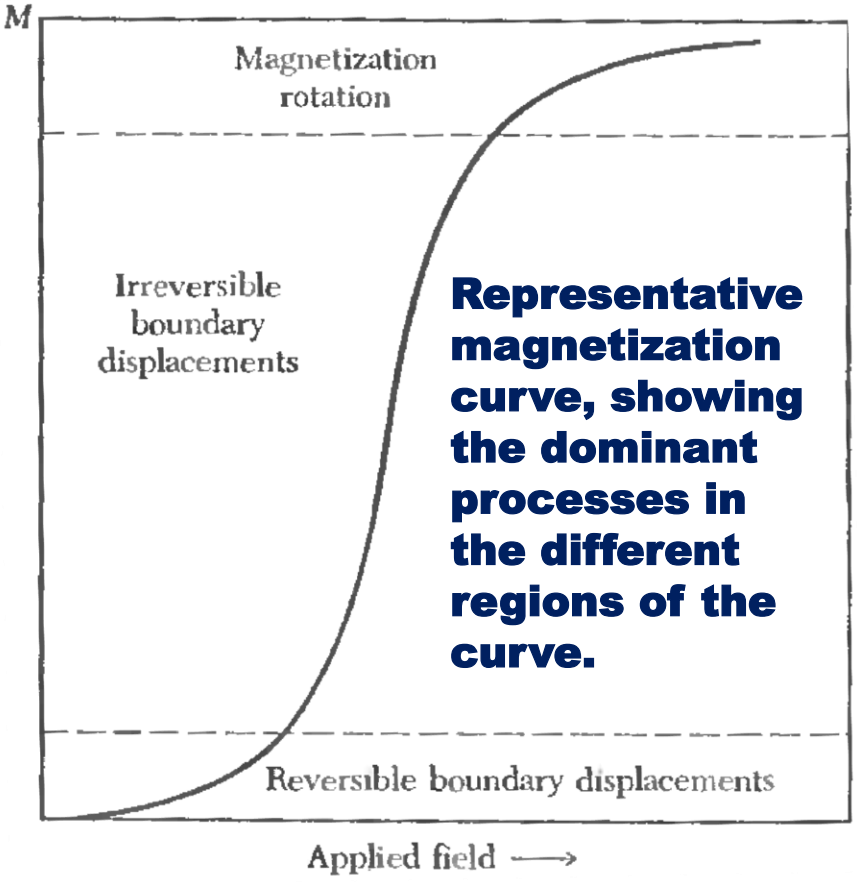


Fig. Ferromagnetic domain pattern on a single crystal platelet of nickel. The domain boundaries are made visible by the Bitter magnetic powder pattern technique. The direction of magnetization within a domain is determined by observing growth or contraction of the domain in a magnetic field.

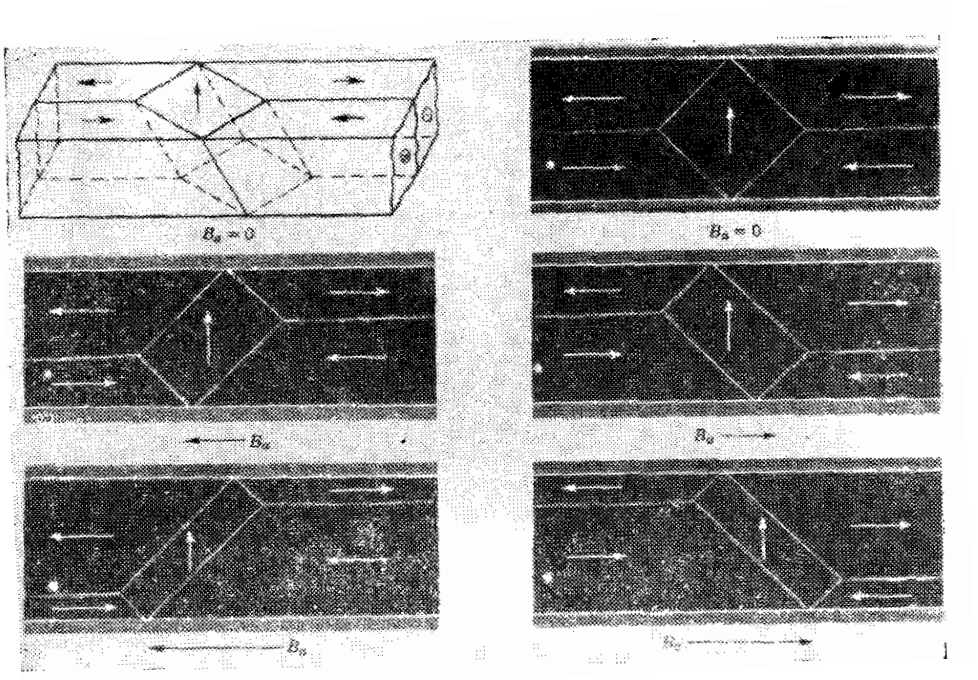


Domains reduce the energy of magnetic field $\int dV B^2/8\pi$.

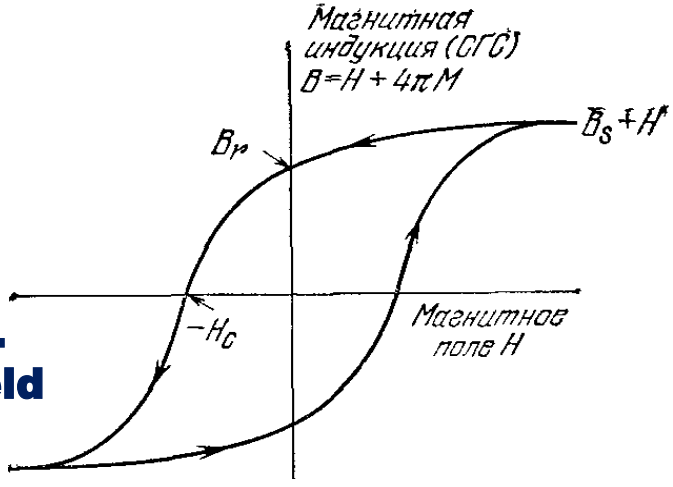
Ferromagnetic domains (2)



Representative magnetization curve, showing the dominant processes in the different regions of the curve.



Reversible boundary displacements of magnetic domains in iron.



The technical magnetization curve. The coercivity Hc is the reverse field that reduces B to zero.

Ferromagnetic domains

Domain structure is a consequence of the various contributions to the energy of a ferromagnetic sample:

- Exchange
- Anisotropy
- Magnetic

The energy of a ferromagnetic sample in a (multi) domain configuration is lower than that of a uniformly magnetized ferromagnetic sample in single domain configuration.

Coercive force and hysteresis

Magnetic anisotropy in crystals

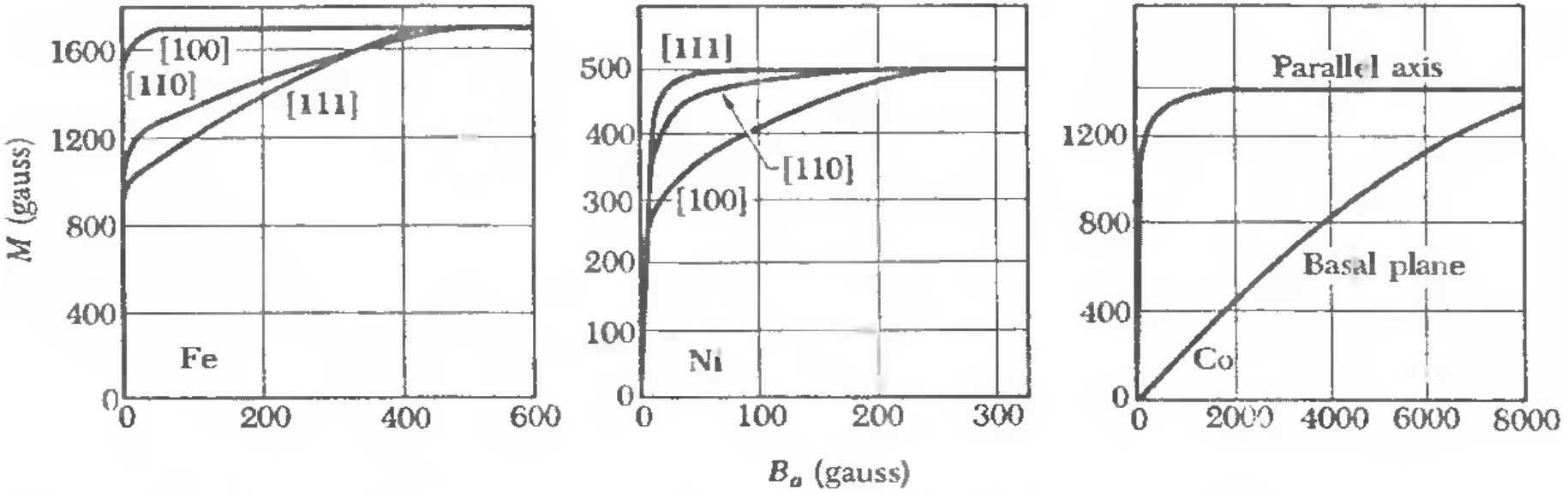
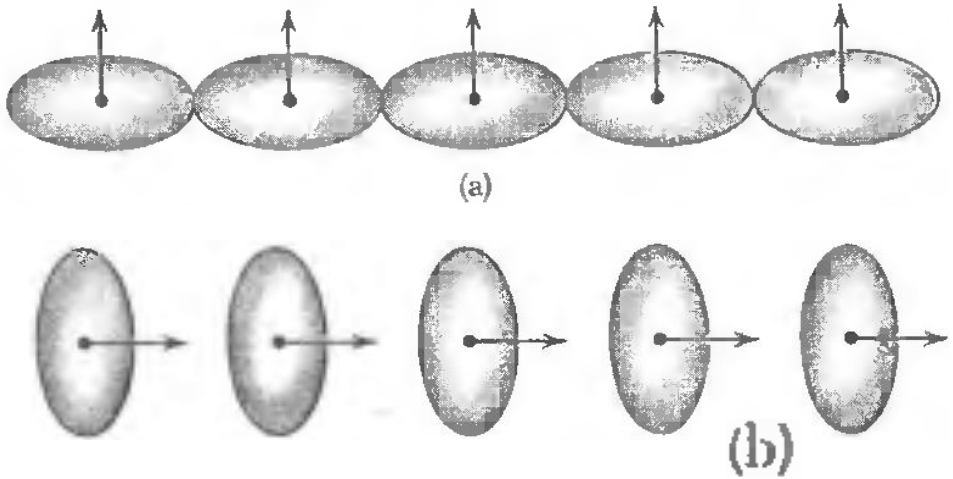


Fig. 1. Magnetization curves for single crystals of iron, nickel, and cobalt. From the curves for iron we see that the [100] directions are easy directions of magnetization and the [111] directions are hard directions The applied field is B„. (After Honda and Kaya.)



Asymmetry of the overlap of electron distributions on neighboring ions provides one mechanism of magneto-crystalline anisotropy.

Strip domains, domains of closure

Bubble domains

Domains in antiferromagnets (MnF_2)

Magnetocrystalline or anisotropy energy (the spin interacts with orbital motion via the spin-orbit coupling).

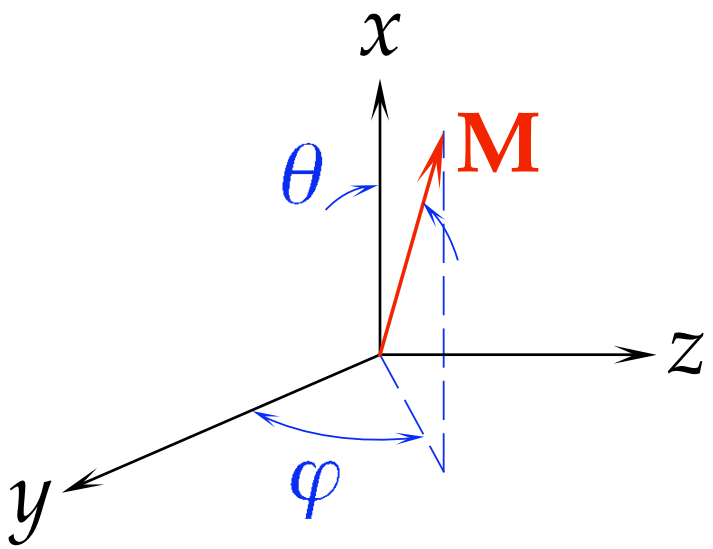
Anisotropy energy density:

- Hexagonal $U_K = K_1' \sin^2\theta + K_2' \sin^4\theta$
- Cubic $U_K = K_1\left(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2\right) + K_2\alpha_1^2\alpha_2^2\alpha_3^2$

Domain walls

Néel walls – exchange and anisotropy energies.

Bloch walls – also magnetic energy, because $\operatorname{div}\mathbf{M} \neq 0$.



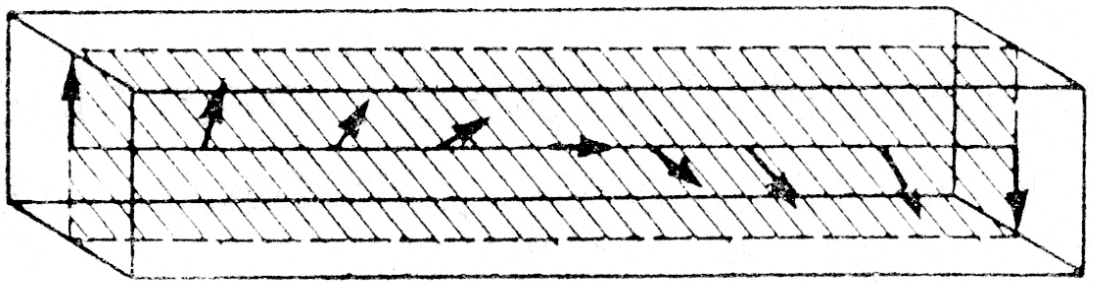
The free energy density

$$\sigma(z) = K\sin^2\theta + A\left[\left(\frac{\partial\theta}{\partial z}\right)^2 + \sin^2\theta\left(\frac{\partial\varphi}{\partial z}\right)^2\right],$$

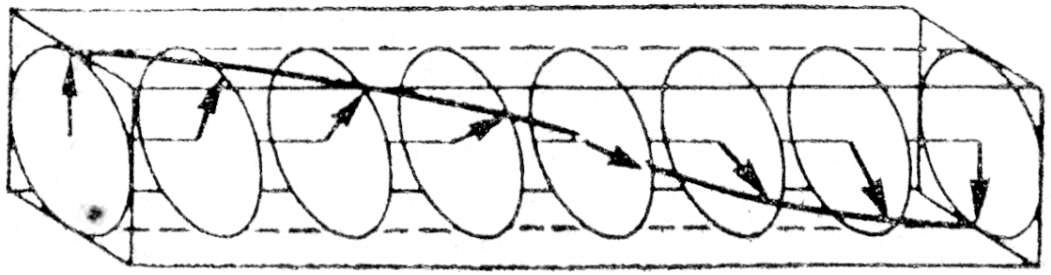
where K is the anisotropy parameter and A is the exchange parameter. For the Néel wall $\varphi = \pi/2$, for the Bloch wall $\varphi = 0$.

The wall structure is $\theta(z) = 2\arctan\left[\exp\left(\sqrt{K/A}\, z\right)\right]$.

The Néel wall



The Bloch wall



[from Robert M. White and Theodore H. Geballe, *Solid State Physics Advances in Research: Long Range Order in Solids* (*Solid state physics: Supplement 15*) (Academic Press, New York, 1979)]

Ground state of the Heisenberg ferromagnet, spin waves

The ferromagnetic Heisenberg Hamiltonian:

$$H = -\frac{1}{2}\sum_{\mathbf{R},\mathbf{R}'} J(\mathbf{R}-\mathbf{R}')\mathbf{S}(\mathbf{R})\cdot\mathbf{S}(\mathbf{R}') - g\mu_B H\sum_{\mathbf{R}} \mathbf{S}_z(\mathbf{R}),$$

$$J(\mathbf{R}-\mathbf{R}') = J(\mathbf{R}'-\mathbf{R}) \geq 0.$$

Ground state of the Heisenberg antiferromagnet

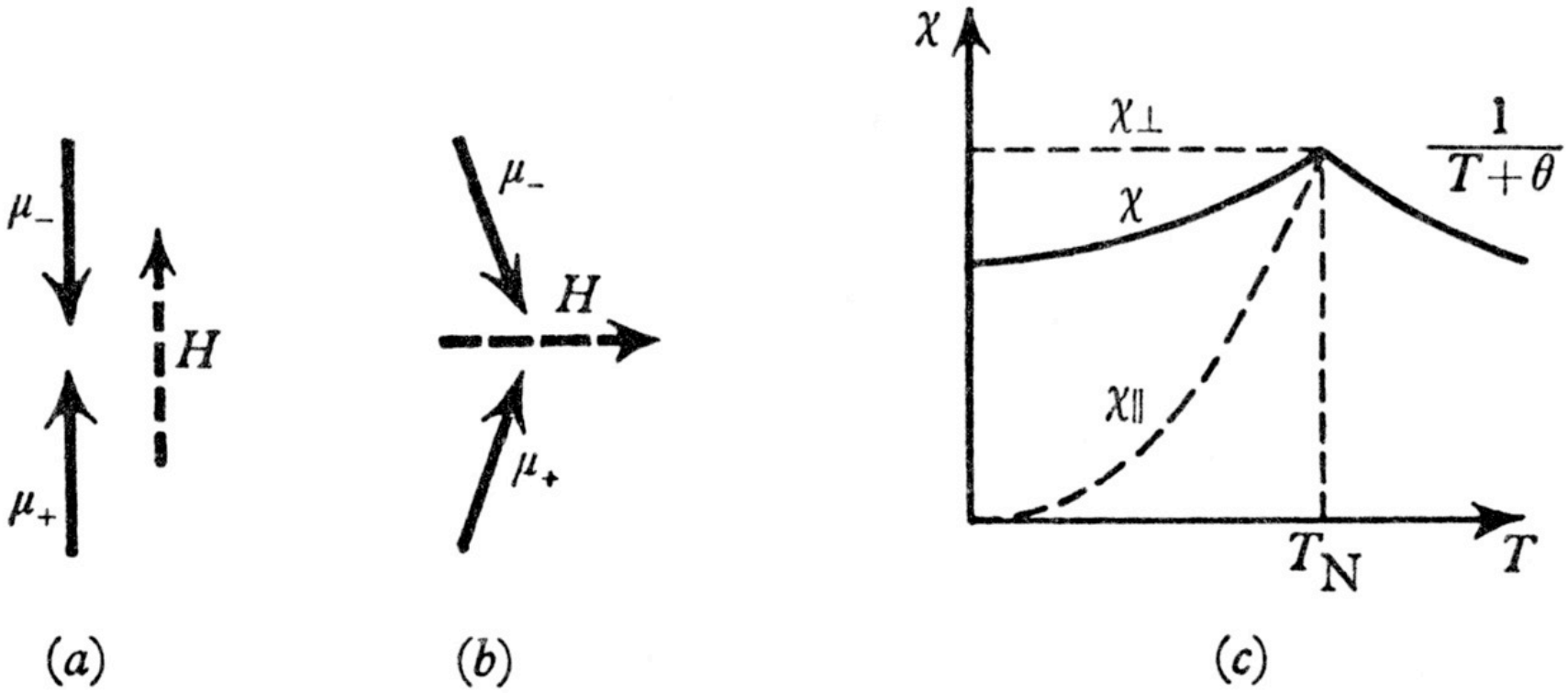
The antiferromagnetic Heisenberg Hamiltonian:

$$H = \frac{1}{2}\sum_{\mathbf{R},\mathbf{R}'} \left|J(\mathbf{R}-\mathbf{R}')\right| \mathbf{S}(\mathbf{R})\cdot\mathbf{S}(\mathbf{R}').$$

One-dimensional array of spin 1/2 ions (Bethe, 1931)

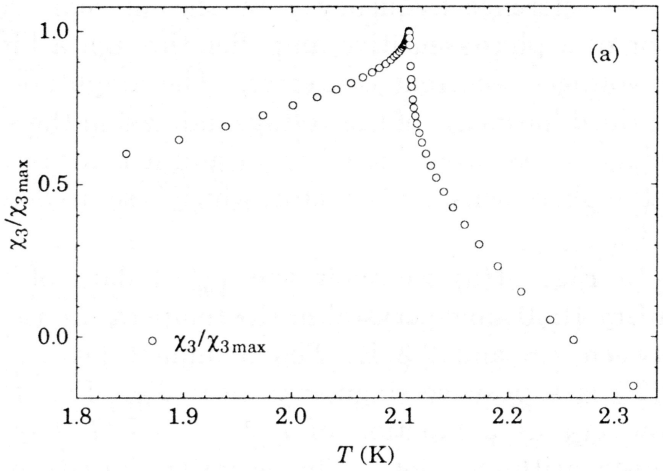
Magnetic susceptibility of an antiferromagnet:

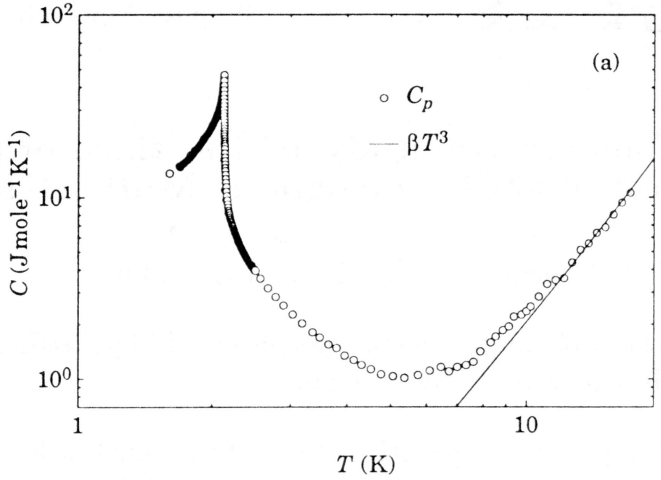
(a) $\chi_{\parallel} \to 0$; (b) $\chi_{\perp} \approx \text{const}$; (c) $\langle \chi \rangle = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp}$

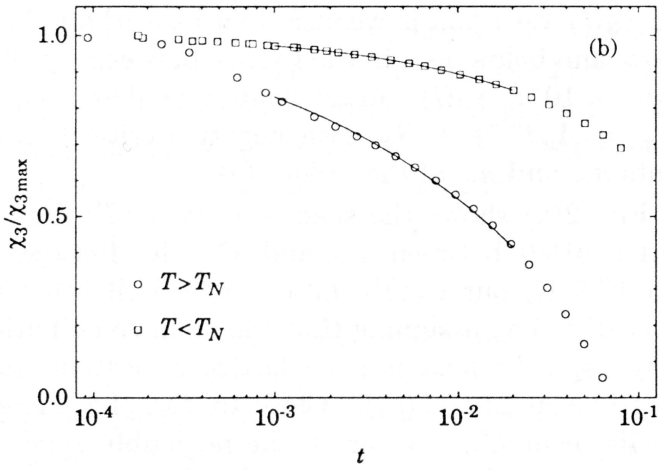


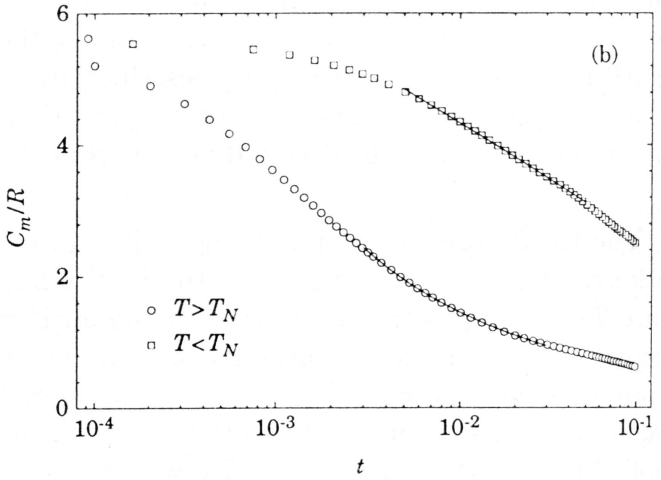
[from J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, 1979)]

Antiferromagnetic $MnBr_2 \cdot 4H_2O$: $\chi_3(T)$ and $C_p(T)$

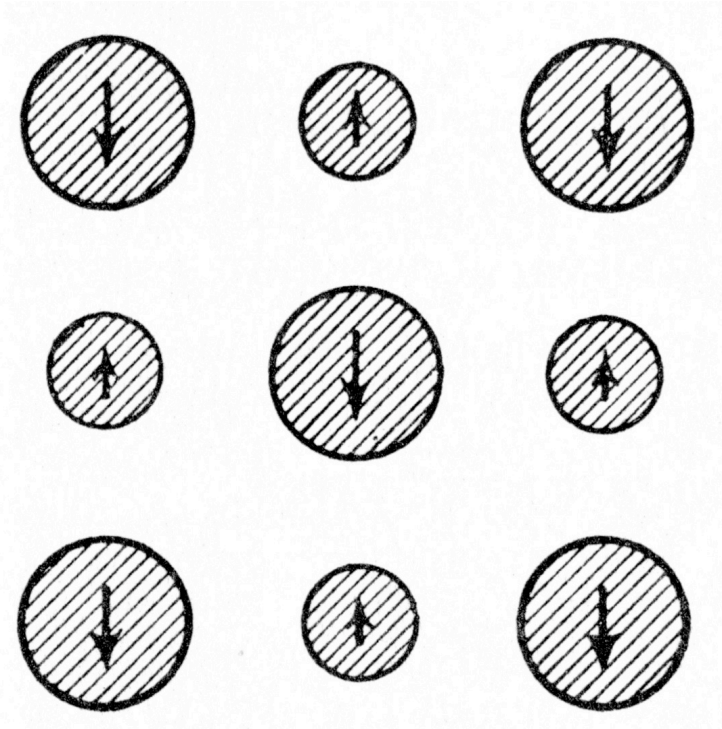






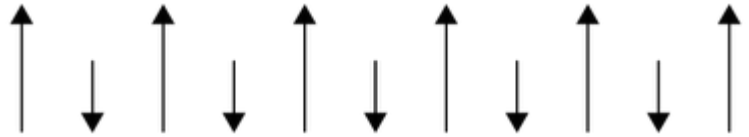


Ferrimagnetic ordering:



[from J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, 1979)]

Ferrimagnetism in the mean-field approximation



The mean exchange fields acting on the A and B spin sublattices may be written as

$$\boldsymbol{B}_A = -\lambda \boldsymbol{M}_A - \mu \boldsymbol{M}_B, \quad \boldsymbol{B}_B = -\mu \boldsymbol{M}_A - \nu \boldsymbol{M}_B;$$

To show that antifferomagnetic exchange may result to ferrimagnetism, we take all mean field constants λ,μ,ν to be positive. The interaction energy density is

$$U = -\frac{1}{2}(\boldsymbol{B}_A \cdot \boldsymbol{M}_A + \boldsymbol{B}_B \cdot \boldsymbol{M}_B) = \frac{1}{2}\lambda M_A^2 + \mu \boldsymbol{M}_A \cdot \boldsymbol{M}_B + \frac{1}{2}\nu M_B^2;$$

This is lower when M_A is antiparallel to M_B than when M_A is parallel to M_B. The energy when antiparallel should be compared with zero, because a possible solution is $M_A = M_B = 0$. Thus the ground state will have M_A directed oppositely to M_B when

$$\mu M_A M_B > \frac{1}{2}(\lambda M_A^2 + \nu M_B^2)$$

(Under certain conditions there may be noncollinear spin arrays of still lower energy.)

Large μ >> λ,ν is reasonable, because the distance between A and B spins is smaller than between two A or two B spins.

Magnetic susceptibility of ferrimagnetic above Tc

At $\lambda=\nu=0$, i.e. when interaction is only between nearest neighbours

$$B_A = -\mu M_B, \quad B_B = -\mu M_A,$$

Then we have in the mean field approximation (where B_A is the applied field):

$$M_A T = C_A (B_a - \mu M_B), \quad M_B T = C_B (B_a - \mu M_A)$$

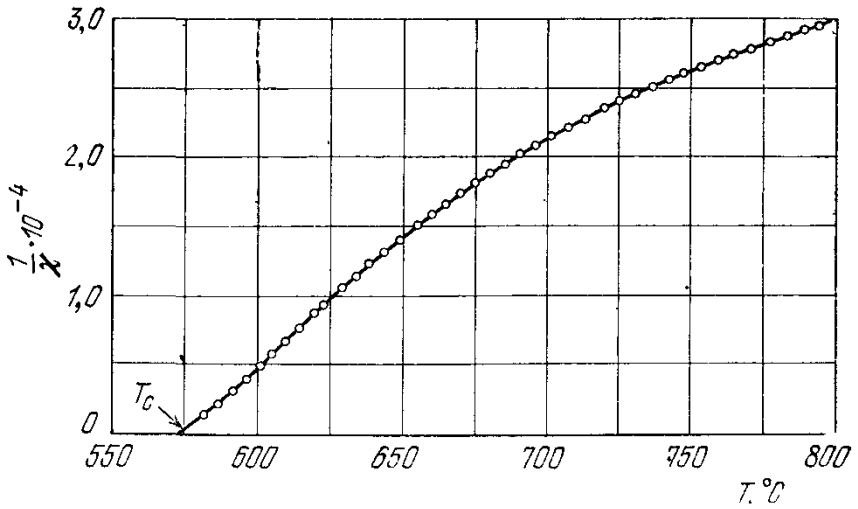
These equations have a nonzero solution for M_A and M_B in zero applied field if

$$\begin{vmatrix} T & \mu C_A \\ \mu C_B & T \end{vmatrix} = 0$$

so that the ferrimagnetic Curie temperature is given by $T_c = \mu(C_A C_B)^{1/2}$.

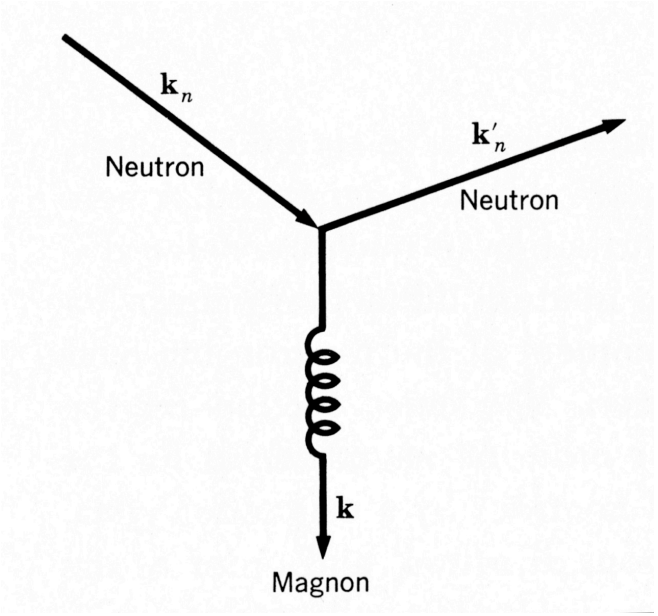
Magnetic susceptibility

$$\chi = \frac{M_A + M_B}{B_a} = \frac{(C_A + C_B)\,T - 2\mu C_A C_B}{T^2 - T_c^2}$$



Reciprocal susceptibility of magnetite, $FeO \bullet Fe_2O_3$

Inelastic neutron scattering



[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

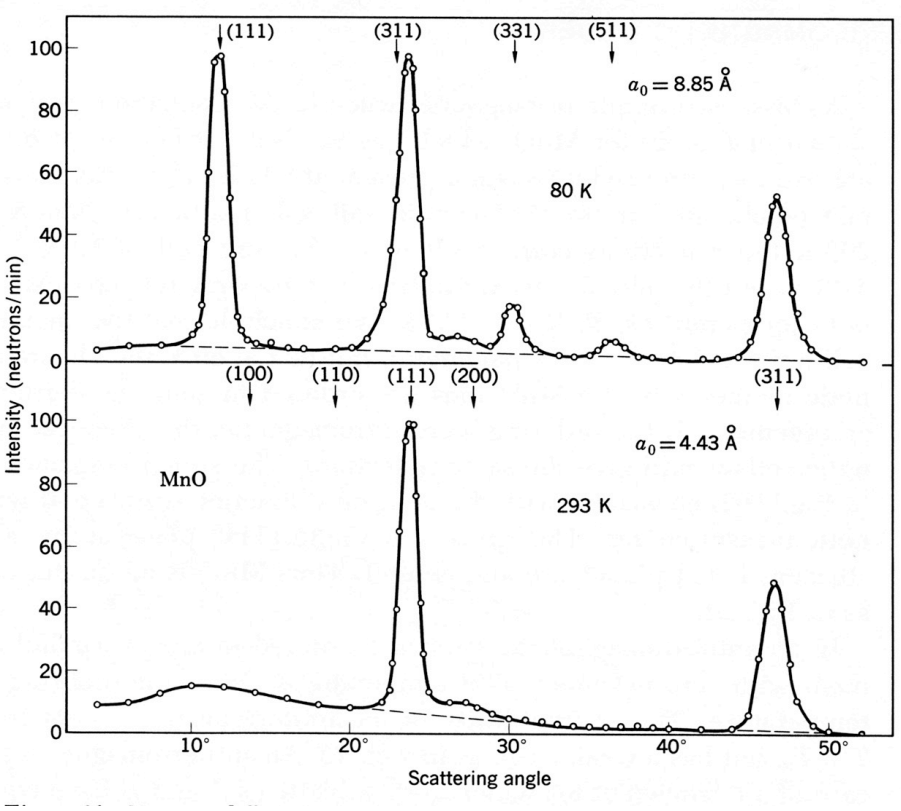
In an inelastic scattering event a neutron may create or destroy a magnon.

Conservation of crystal momentum; conservation of energy.

Experimental observation of magnetic structures: neutron magnetic scattering

The magnetic moment of the neutron interacts with the magnetic moment of the electron.

Diffraction of neutrons by a magnetic crystal allows us to determine the order of the magnetic moments.



[from Charles Kittel, *Introduction to Solid State Physics* (Wiley, 2004)]

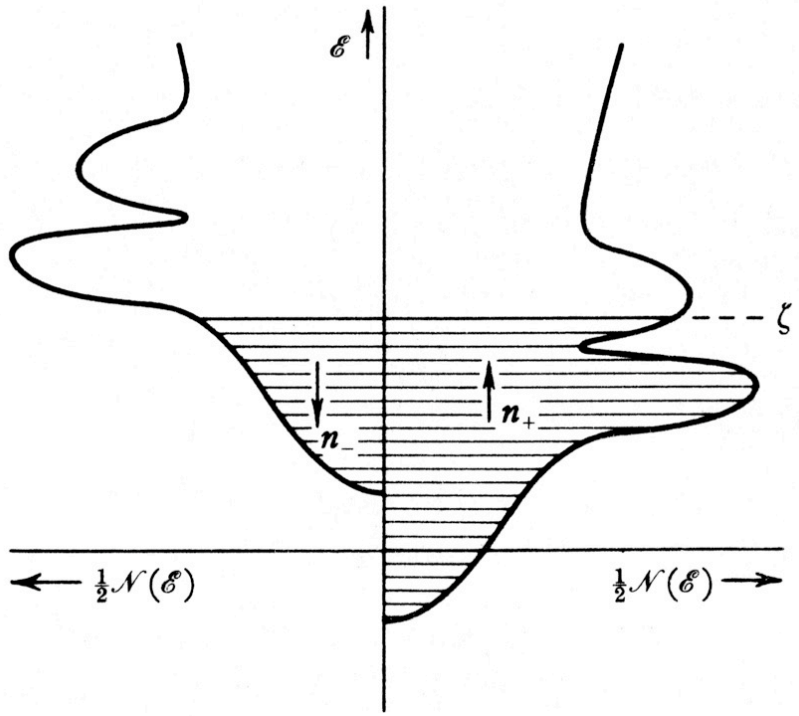
(a) Band ferromagnetism

Stoner model:

$$H_{\text{int}} = \frac{U}{N}\sum_{\mathbf{k},\mathbf{k}'} n_{\mathbf{k}+} n_{\mathbf{k}'-}.$$

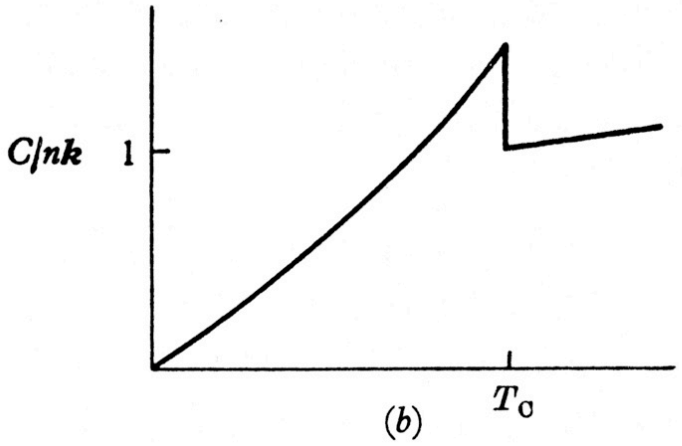
$$\chi_{H\to 0,\,T\to 0} = \frac{\mu_0^2 n\left(E_F\right)}{1-\frac{1}{2}Un\left(E_F\right)}.$$

Transition to FM: $\frac{1}{2}Un\left(E_F\right) > 1$



(a)

(b) Electronic specific heat of a ferromagnetic metal



(b)

[from J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, 1979)]

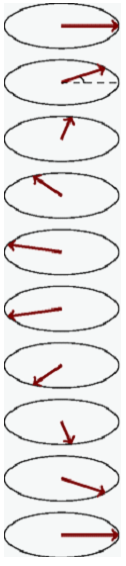
Antiferromagnetic helical order (terbium and dysprosium)

Tb and Dy order ferromagnetically below 219 and 85 K, resp.

Above T_C these two elemental metals slip into a helical antiferromagnetic state, in which all the atomic moments in a basal plane layer are parallel, and oriented at a certain angle to the moments of adjacent layers.

In a transect along the hexagonal axis the moments would be observed to rotate around the transect line in a helical pattern. There is no net spontaneous magnetization.

Transitions from a helical antiferromagnetic state to a paramagnetic state occur at 230 and 179 K, respectively.



Helical or conical ferromagnetism

Erbium below 19.5 K also exhibits a helical magnetic order.

Each atom, however, has a component of magnetization parallel to the hexagonal axis, and, consequently, there is a net magnetic moment.

Between 19.5 and 80 K erbium displays modulated antiferromagnetism (hex. axis components vary continuously in magnitude in a sinusoidal pattern from layer to layer).

Sinusoidal AF ordering (thulium between 32 and 56 K).

Modulated ferromagnetism (thulium below 32 K).