Magnetochemistry

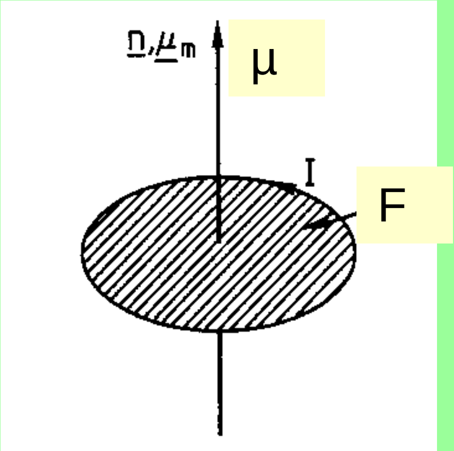
(12.7.06)

H.J. Deiseroth, SS 2006

Magnetochemistry

The magnetic moment of a single atom (μ)

(μ is a vector !)



$\mu = i\,F$ [Am^2], circular current i, aerea F

$\mu_B = eh/4\pi m_e = 0{,}9274\ 10^{-27}\ Am^2$

(h: Planck constant, m_e: electron mass)

μ_B: „Bohr magneton“ (smallest quantity of a magnetic moment)

→ for one unpaired electron in an atom („spin only“):

$$\mu^s = 1{,}73\ \mu_B$$

Magnetochemistry

→ The magnetic moment of an atom has two components a spin component („spin moment“) and an orbital component („orbital moment“).

→Frequently the orbital moment is supressed („spin-only-magnetism“, e.g. coordination compounds of 3d elements)

Magnetisation M and susceptibility χ

$$M = (\sum \mu)/V$$

$\sum \mu$: sum of all magnetic moments μ in a given volume V, dimension: $[\mathrm{Am^2/m^3} = \mathrm{A/m}]$

The actual magnetization of a given sample is composed of the „intrinsic“ magnetization (susceptibility χ) and an external field H:

$$M = H \chi \qquad (\chi\text{: suszeptibility})$$

Magnetochemistry

There are three types of susceptibilities:

χ_V: dimensionless (volume susceptibility)
χ_g: $[cm^3/g]$ (gramm susceptibility)
χ_m: $[cm^3/mol]$ (molar susceptibility)

!!!!! χ_m is used normally in chemistry !!!!

Frequently: $\chi = f(H)$ → complications !!

Magnetochemistry

Diamagnetism

- external field is weakened
- atoms/ions/molecules with closed shells

$$-10^{-4} < \chi_m < -10^{-2}\ \text{cm}^3/\text{mol}$$ (negative sign)

Paramagnetism (van Vleck)

- external field is strengthened
- atoms/ions/molecules with open shells/unpaired electrons

$$+10^{-4} < \chi_m < 10^{-1}\ \text{cm}^3/\text{mol}$$

→ diamagnetism (core electrons) + paramagnetism (valence electrons)

Magnetism of the elements

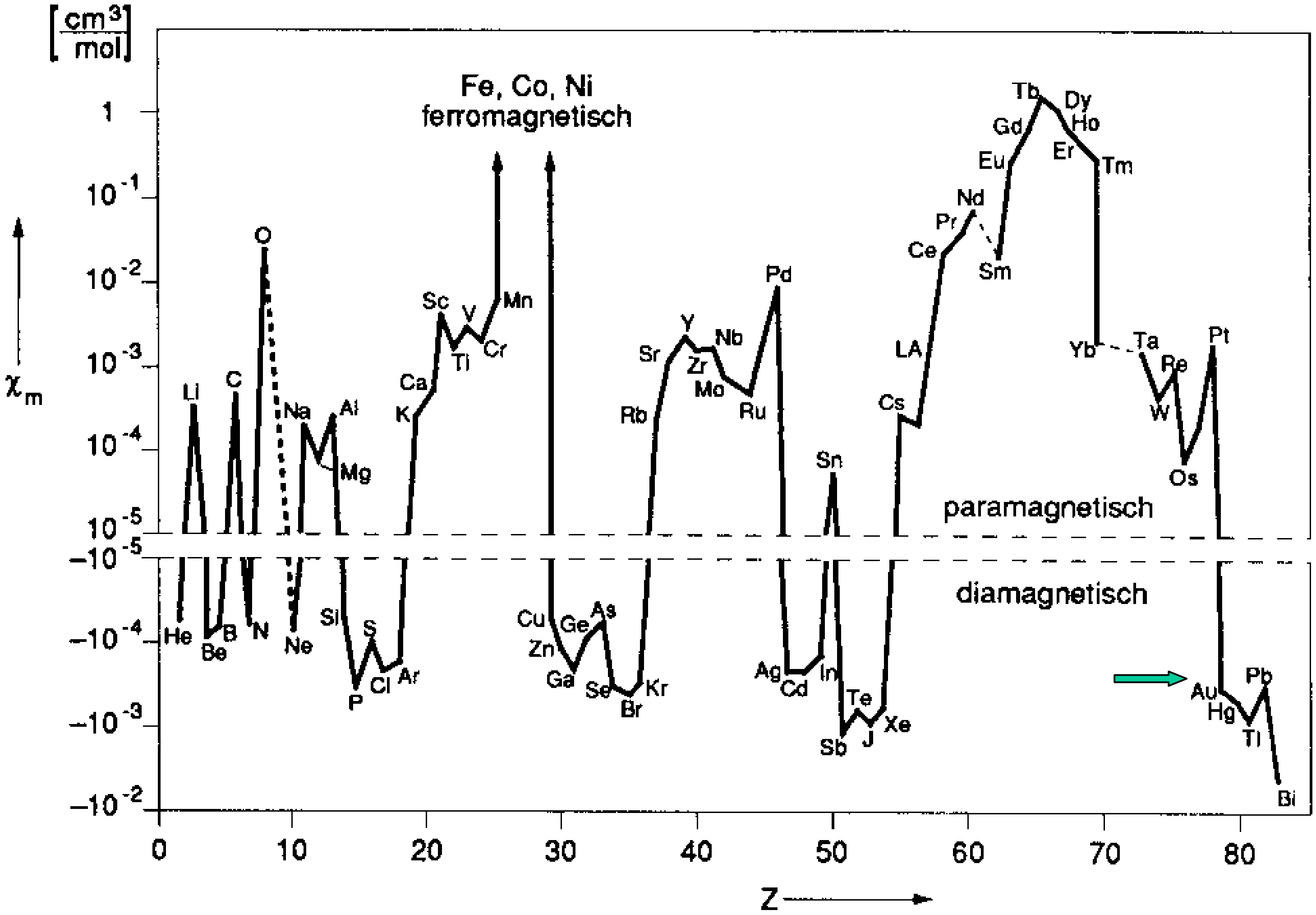


Bild 7.1.3–1: Molare Suszeptibilität der Elemente (nach [15])

Magnetism of the elements

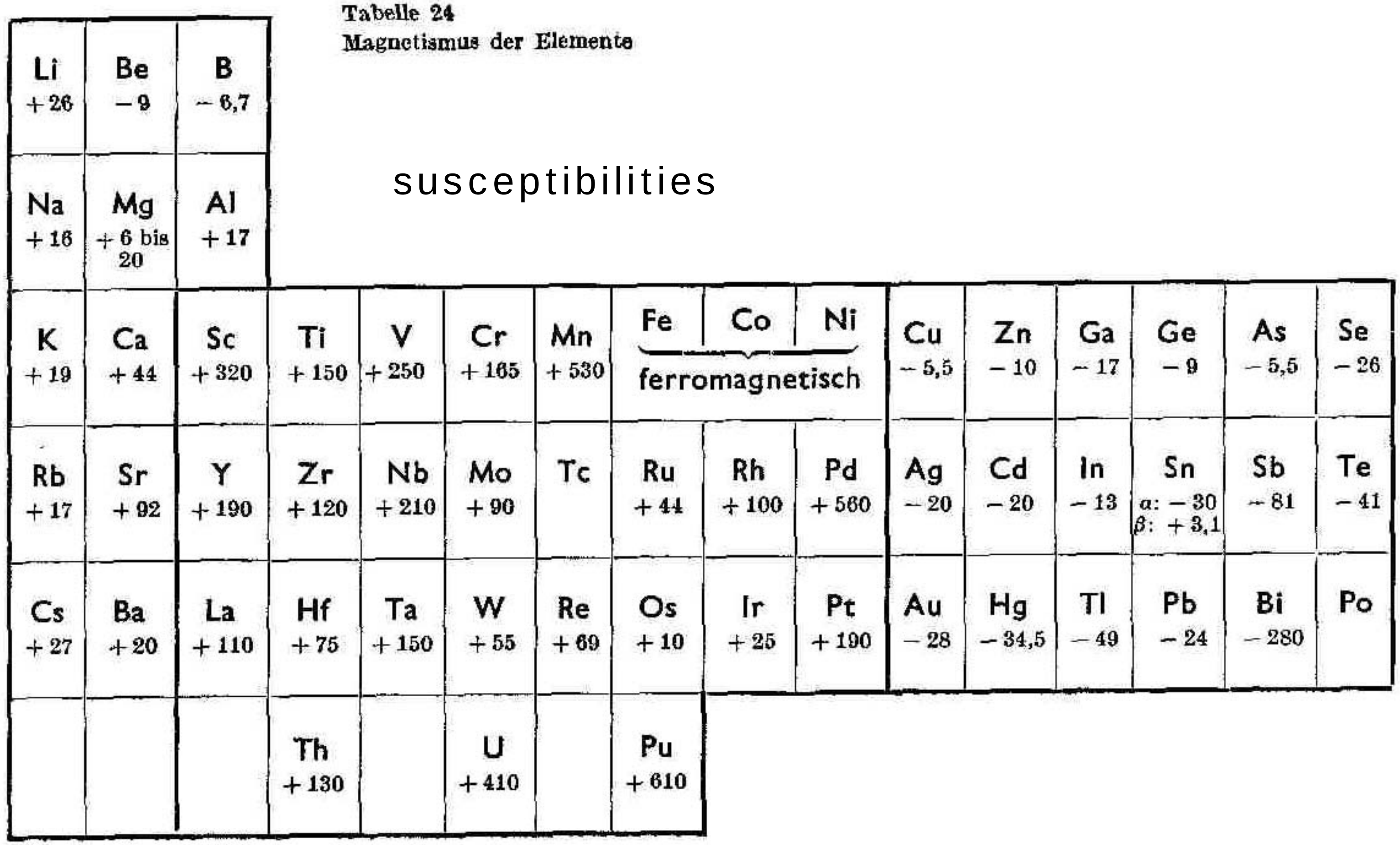


Tabelle 24
Magnetismus der Elemente

susceptibilities

Li +26	Be −9	B −6,7													
Na +16	Mg +6 bis 20	Al +17													
K +19	Ca +44	Sc +320	Ti +150	V +250	Cr +165	Mn +530	Fe ferromagnetisch	Co	Ni	Cu −5,5	Zn −10	Ga −17	Ge −9	As −5,5	Se −26
Rb +17	Sr +92	Y +190	Zr +120	Nb +210	Mo +90	Tc	Ru +44	Rh +100	Pd +560	Ag −20	Cd −20	In −13	Sn α: −30 β: +3,1	Sb −81	Te −41
Cs +27	Ba +20	La +110	Hf +75	Ta +150	W +55	Re +69	Os +10	Ir +25	Pt +190	Au −28	Hg −34,5	Tl −49	Pb −24	Bi −280	Po
			Th +130		U +410		Pu +610								

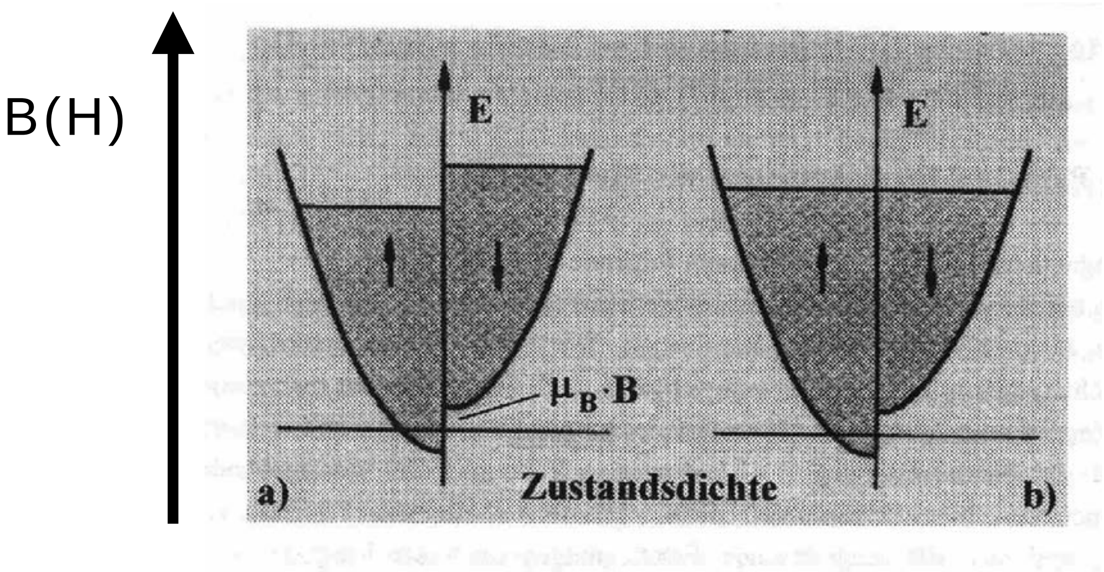
Magnetism of the metals

Pauli-Paramagnetism:

→ special type of magnetism of the conduction electrons in metals

→ refers only to the free electrons in the electron gas of a metallic solid)

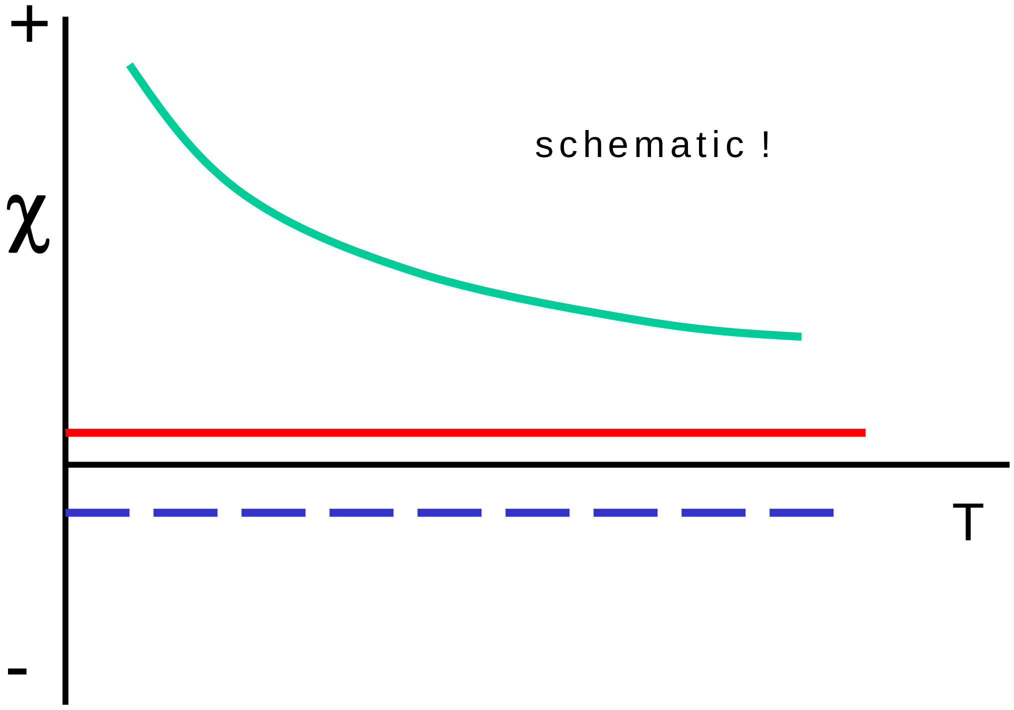
$$+10^{-6} < \chi_m < +10^{-5}\ \mathrm{cm^3/mol}$$



Temperature dependence of the magnetic suszeptibility

General:

1.) Diamagnetism: independent of temperature
2.) Paramagnetism: Curie- or Curie-Weiss-law
3.) Pauli-Paramagnetism: independent of temperature



Curie- und Curie-Weiss-law for paramagnetic samples

Curie: $1/\chi = C \cdot T$;   Curie-Weiss: $1/\chi = C \cdot (T-\Theta)$

H: external field

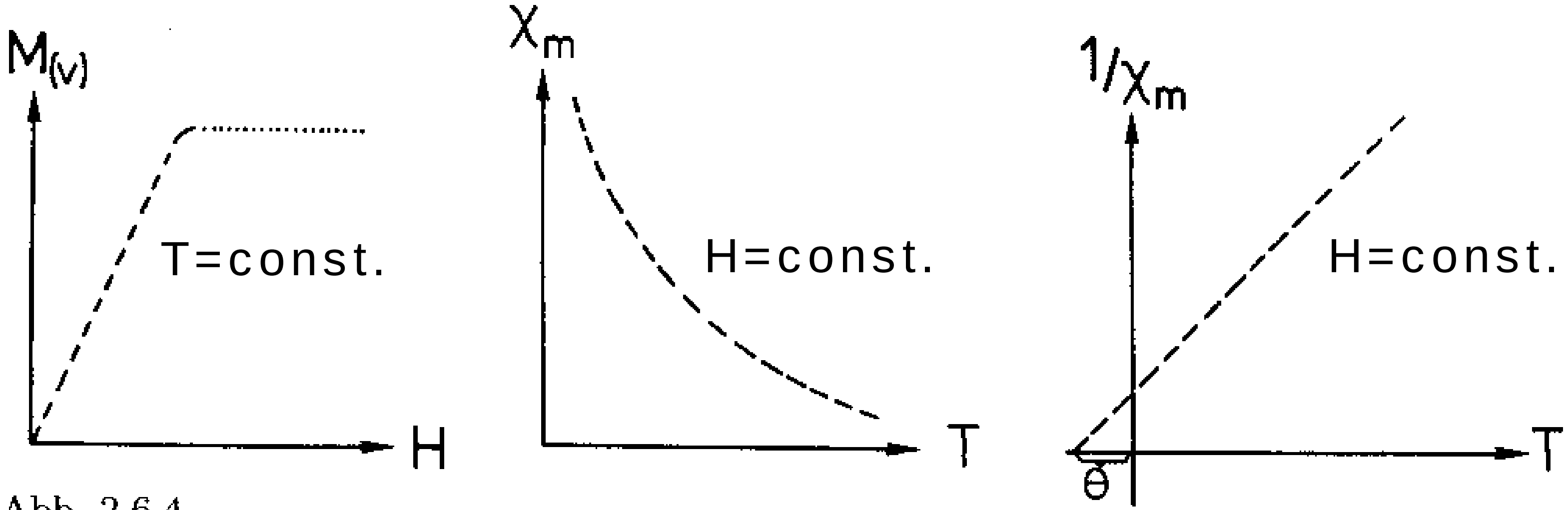
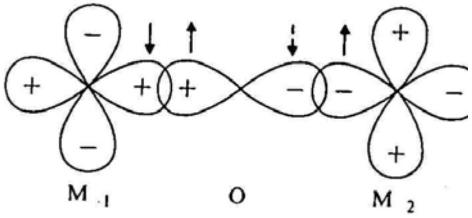


Abb. 2.6.4
$M_{(v)} = f(H)$, $\chi_m = f(T)$ und $\frac{1}{\chi_m} = f(T)$ für paramagnetische Stoffe

Different types of collective magnetism in a solid due to coupling of magnetic moments

Paramagnetism

Ferromagnetism

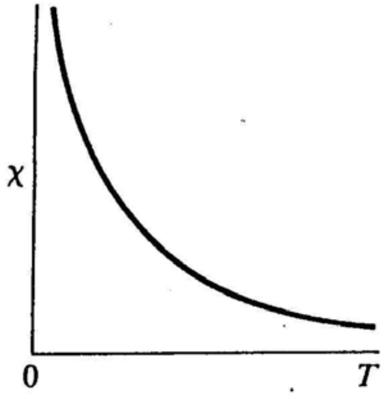


super exchange
(Superaustausch)

Antiferromagnetism

Ferrimagnetism

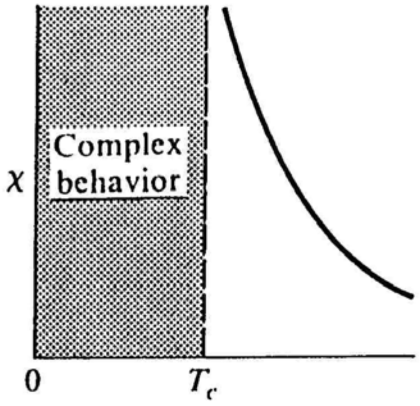
Paramagnetism



$\chi = \frac{C}{T}$

Curie law

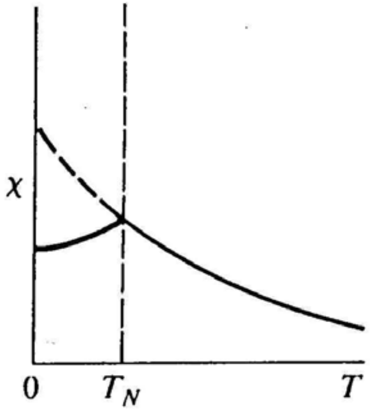
Ferromagnetism and Ferrimagnetism



$\chi = \frac{C}{T - T_c}$

Curie-Weiss law
$(T > T_c)$

Antiferromagnetism



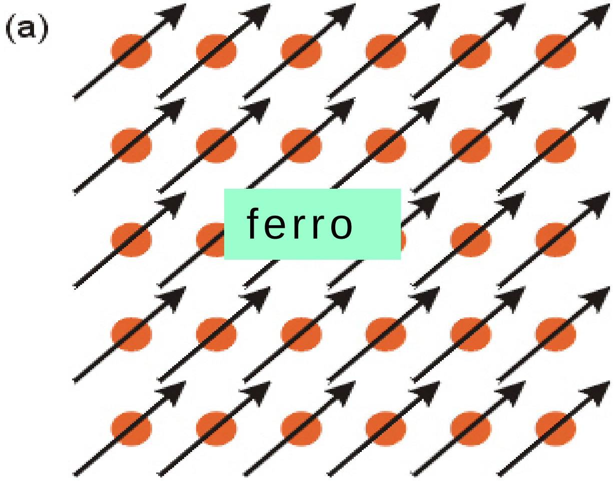
$\chi = \frac{C}{T + \theta}$

$(T > T_N)$

Magnetism in solids
(cooperative magnetism)

- Diamagnetism and paramagnetism are characteristic of compounds with individual atoms which do not interact magnetically (e.g. classical complex compounds)

- Ferromagnetism, antiferromagnetism and other types of cooperative magnetism originate from an intense magnetical interaction between electron spins of many atoms



Magnetochemistry

- magnetic crystal anisotropy: the magnetism of a single crystal may be anisotropic

- magnetic and structural unit cell may be different

- the magnetic structure of a crystalline sample can be determined with „thermal neutrons“ (neutrons with a wavelength in the order of magnitude of interatomic distances): de Broglie equation: $\lambda = h/m_n v_n$
(requires neutron radiation of a nuclear reactor)

Temperatures of magnetic phase transitions:

- Curie-temperature (T_c): ferro- and ferrimagnetism
- Neel-temperature: (T_N): antiferromagnetism

Magnetic structure

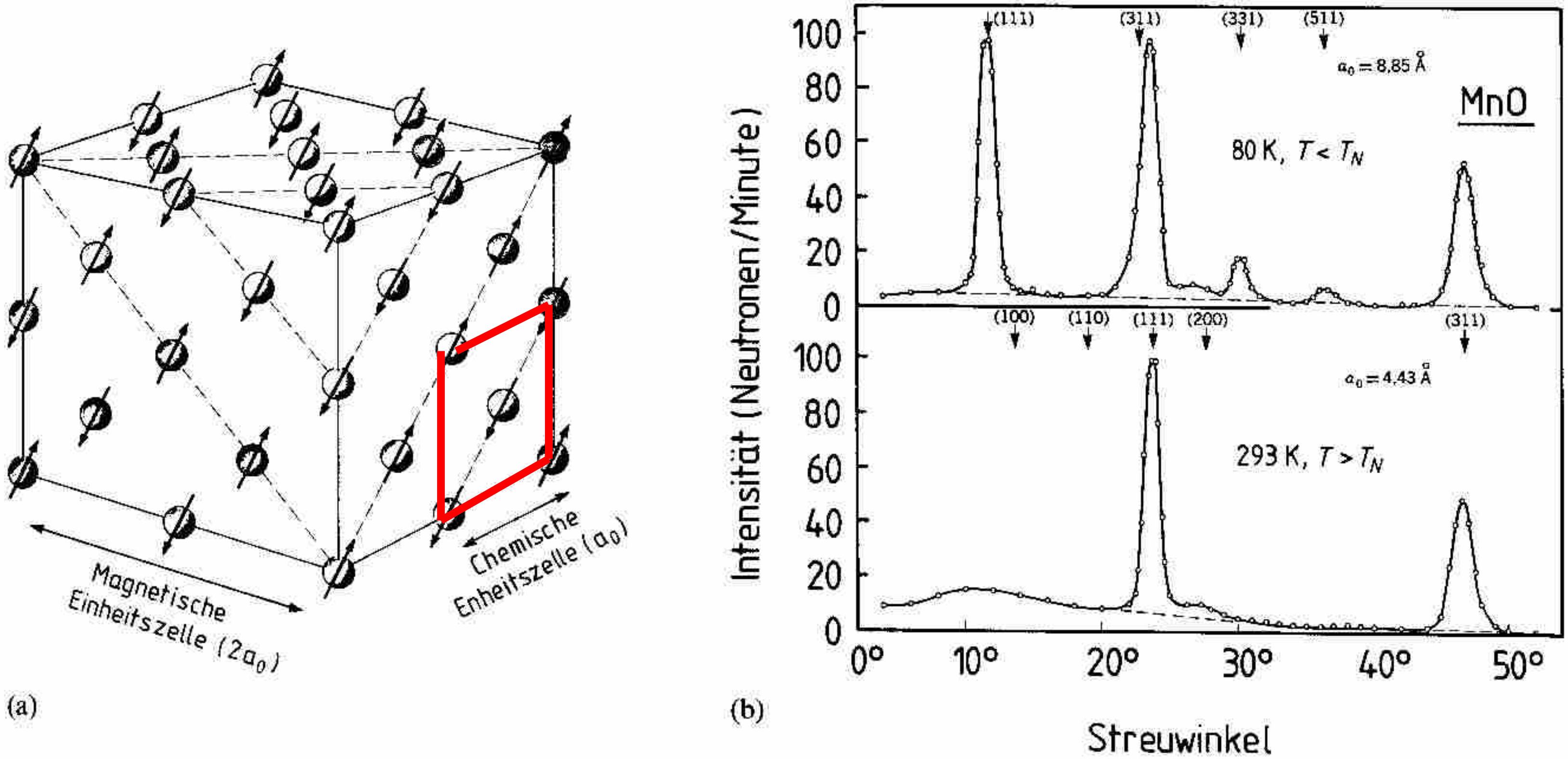
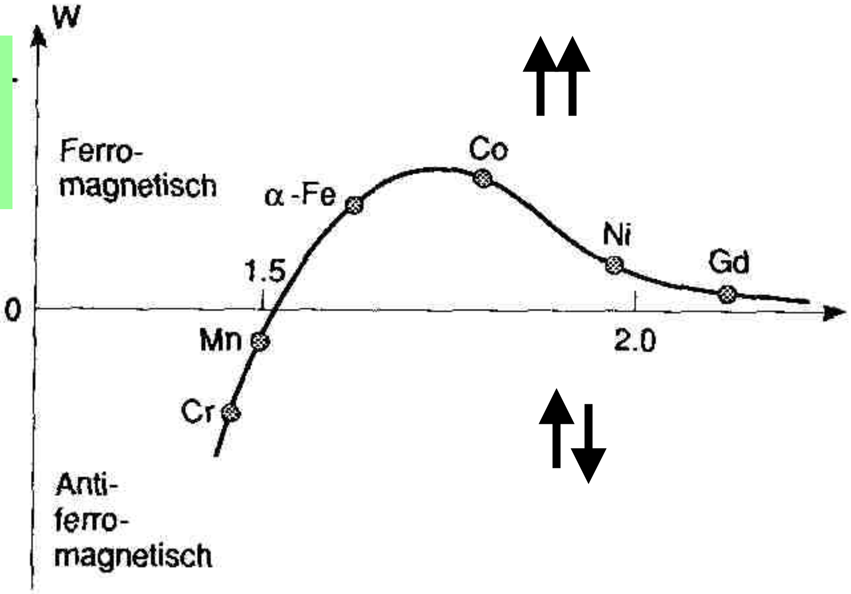


Abb. 18-6. Neutronenbeugung an Manganoxid. (a) Magnetische Struktur von MnO. Es sind nur die Mn-Ionen gezeichnet (nach Kittel 1971). (b) Streuintensität unterhalb und oberhalb der Néel-Temperatur $T_N = 120$ K. Im unteren Teilbild sind die von der magnetischen Ordnung herrührenden Reflexe praktisch verschwunden. Sie entsprechen einer Struktur mit der doppelten Gitterkonstante $2a_0$, weil im Antiferromagnetikum nur jeder zweite Spin in dieselbe Richtung zeigt (siehe Teilbild a), das heißt, sie erscheinen beim halben Streuwinkel ϑ (nach Kittel 1971).

Ferromagnetism

- Fe, Co, Ni, Gd, Tb ... EuO, $CrCl_2$ ...
- without an external magnetic field the atomic moments are oriented parallel in large aereas (Weiß domains) ($T>T_c$)



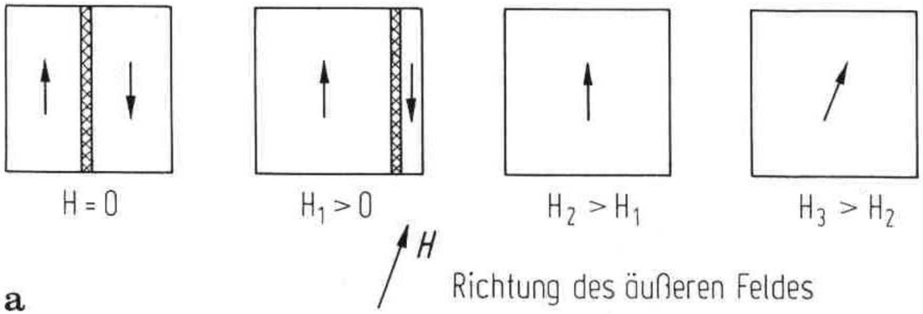
calculated exchange interaction

interatomic distances/radius of 3d orbitals

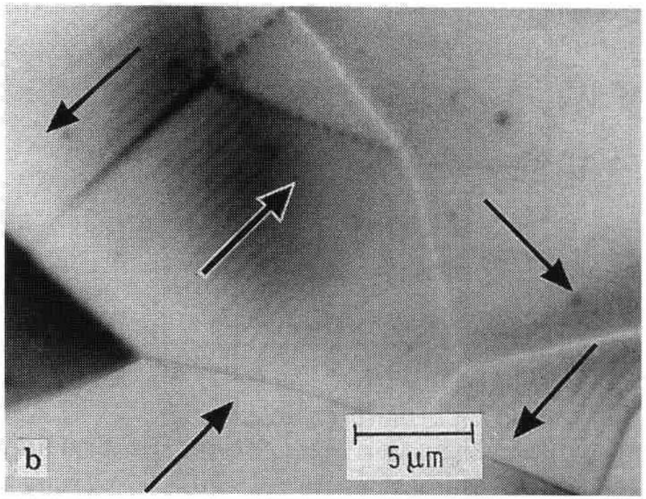
Bild 7.1.4-4: Austauschwechselwirkung der 3d-Elektronen (Bethe-Slater-Kurve): Positive Werte ergeben ein ferromagnetisches–, negative ein antiferromagnetisches Verhalten (nach [63]).

The magnetic domain structure of iron

α-Fe without any magnetic pre-treatment normally does not show any resultant magnetization; exposure to a strong external magnetic field, however, causes it to become ferromagnetic → Weiß domains/Bloch-walls



Shift of a Bloch-wall in an external field



Grain boundaries and Bloch walls in α-Fe

Magnetization of an initially „non-magnetic“ ferro- or ferrimagnet („hysteresis curve“)

$M_{(v)S}$: saturation magnetization
$M_{(v)R}$: remanence
H_C: coercive force

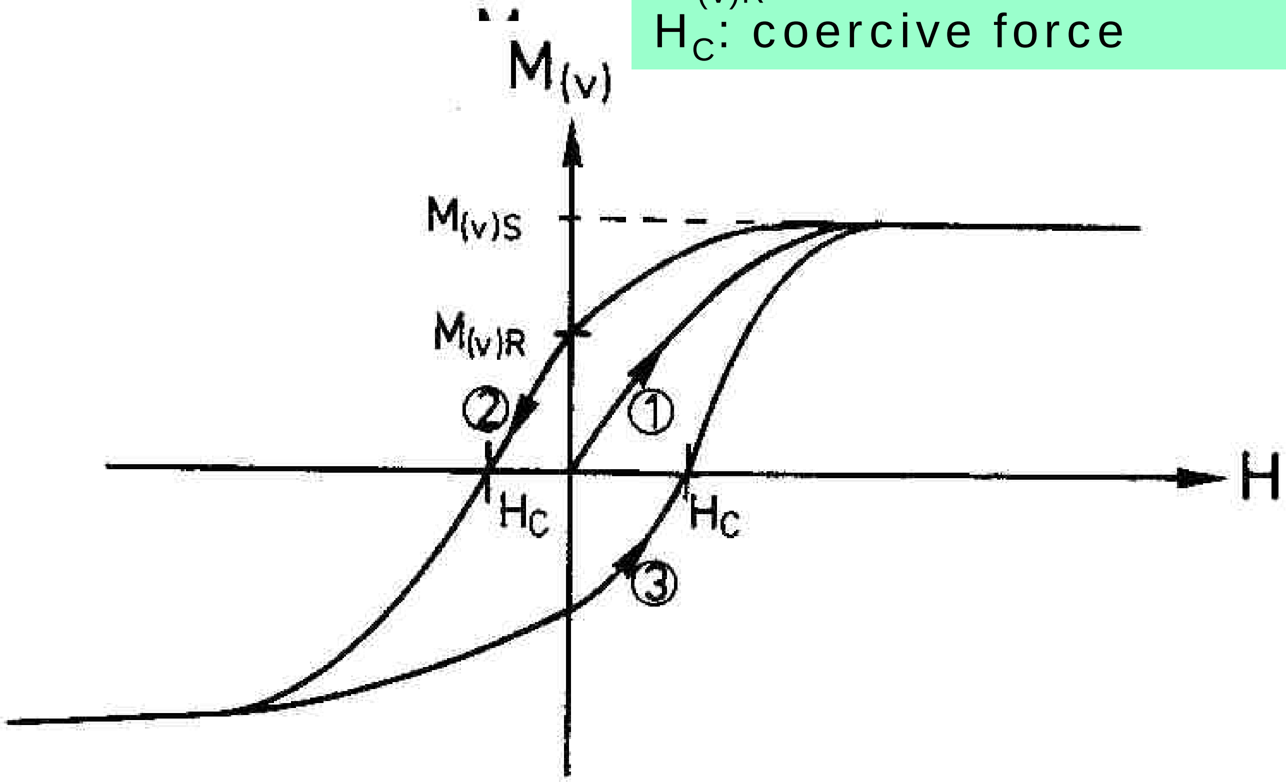
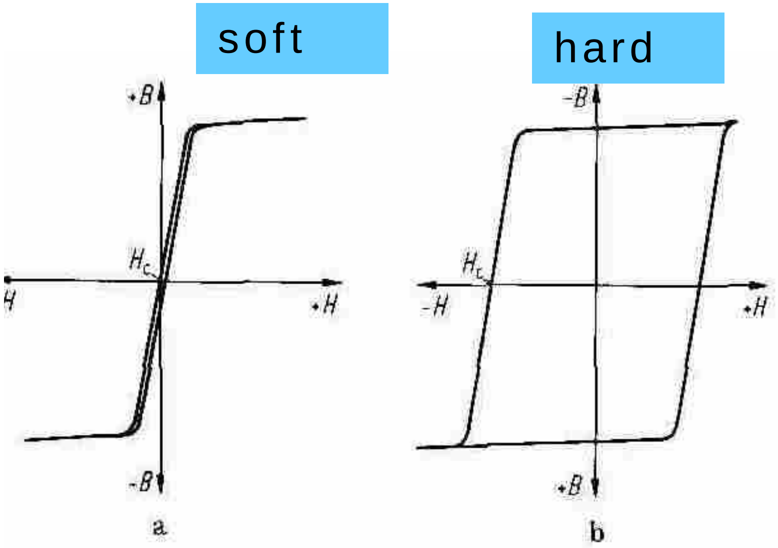


Abb. 2.6.8
$M_{(v)} = f(H)$ für ferro- und ferrimagnetische Stoffe

Soft and hard magnets

Soft magnets: transformers, electromagnets, electric coils…

Hard magnets: sound und video-tapes, permanent magnets …


soft

hard

Metallic soft magnets:

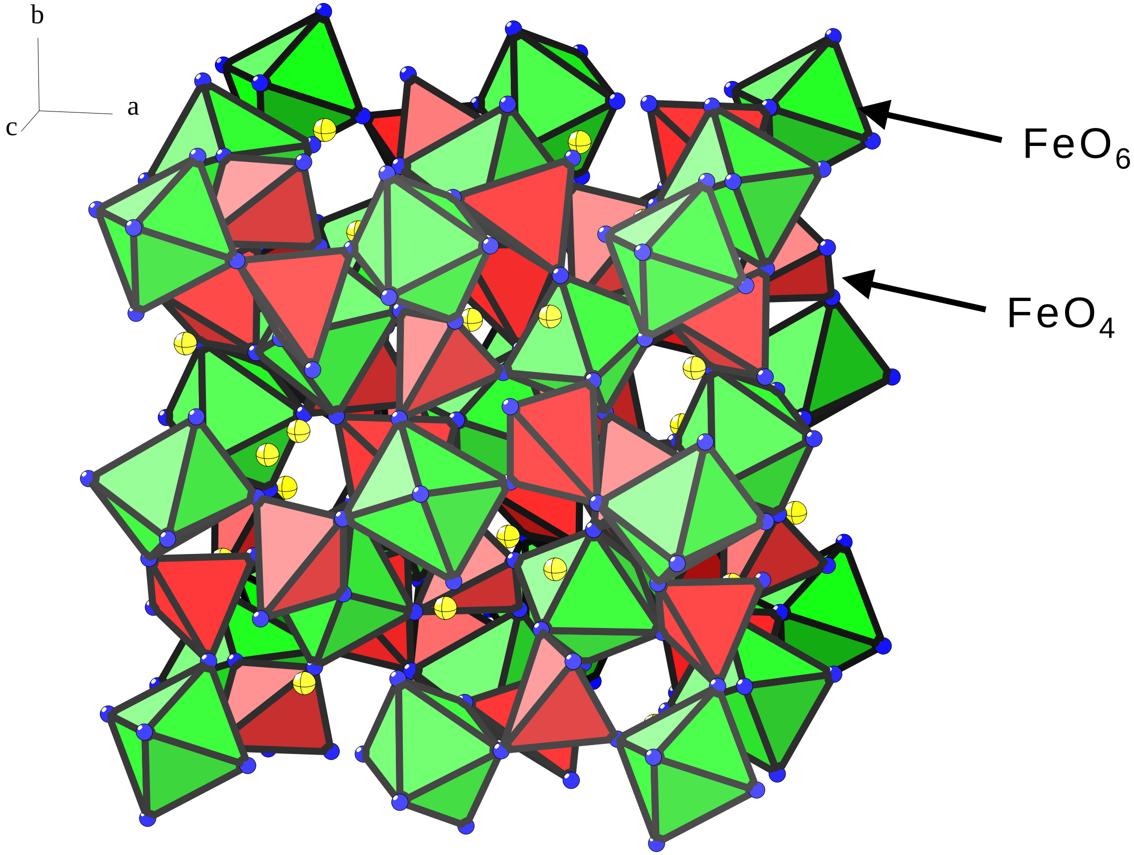
- α-Fe, Ni, Co and some of their alloys
- Fe – Si- und Fe – Ni – compounds and alloys

(e.g. Fe / 6%Si: no α→γ-phase transition up to 1400 ^{0}C)

Ceramic soft magnets:- „Ferrites“: cubic oxide spinels or perowskites, garnets ($Y_3Fe_5O_{12}$)

- spinels: the magnetic moments of ions on tetrahedral and octahedral places are anti-parallel

Y-Fe-garnet: $Y_3Fe_5O_{12}$: Fe^{3+} in tetrahedral and octahedral coordination of O^{2-}



The garnet structure

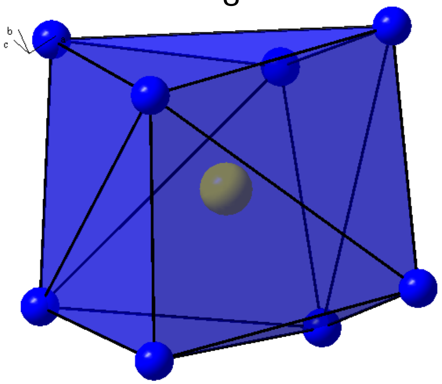
Garnets: $A_3^{2+}B_2^{3+}Si_3O_{12}$: A=Ca, Mg, Fe, Mn ..., B=Al, Fe, Cr

- Orthosilicates with isolated SiO_4-Tetrahedra

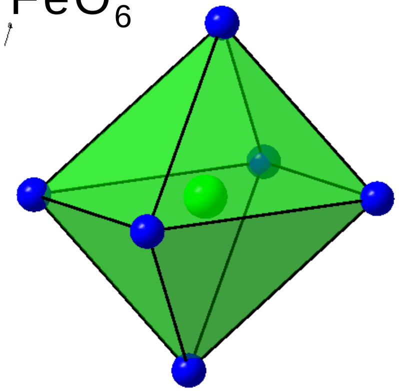
- A^{2+}: larger cations with CN=8
- B^{3+}: smaller cations with CN=6

$Y_3Fe_2Fe_3O_{12}$

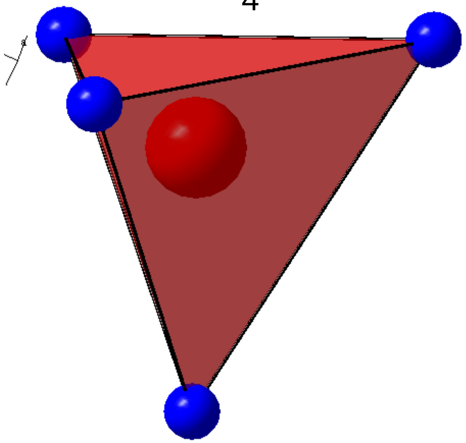
YO_8



FeO_6



FeO_4



Soft and hard magnets

Metallic Hard magnets

(sophisticated materials pre-treatment, e.g. crystallization in srong magnetic fields)

- applications in loud speakers, deflecting magnets ...

- high saturation magnetization, high coercive force

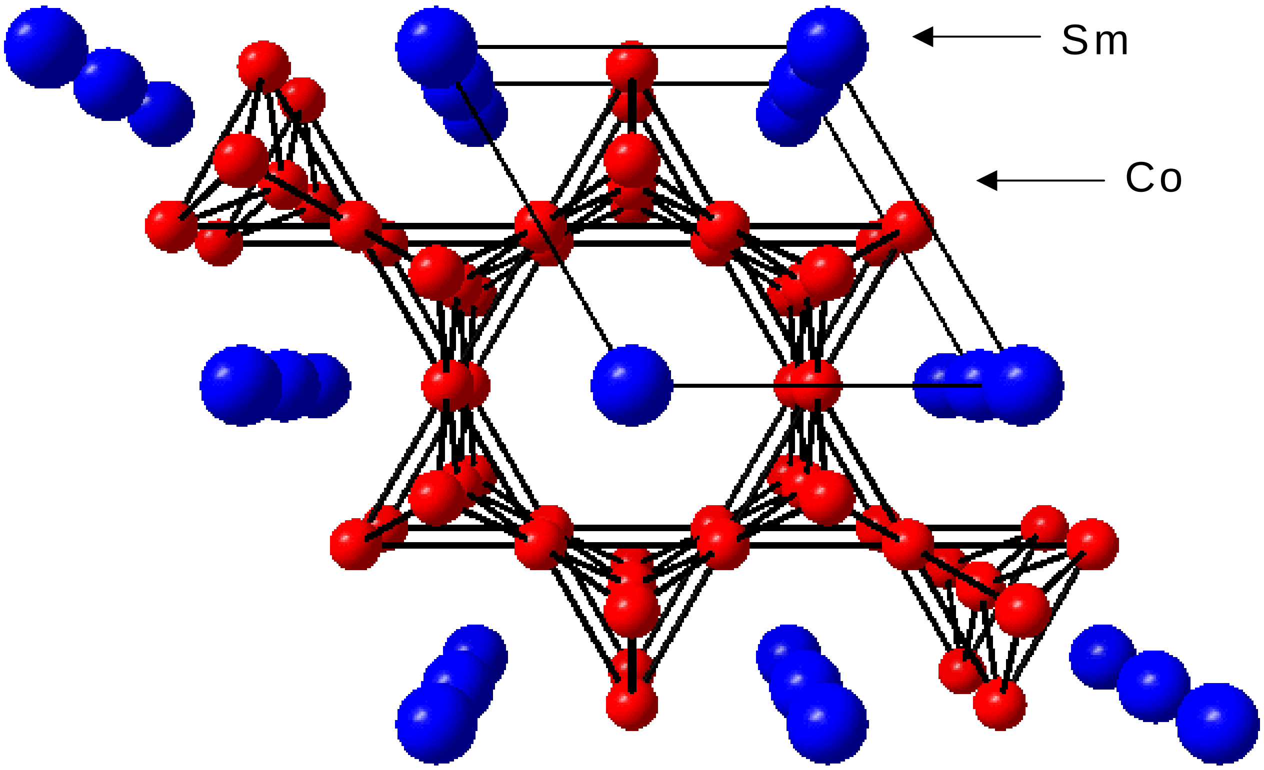
- „pinning“ of Bloch walls by introduction of artificial defects

a) Fe/Co-alloys, „Permalloy“ Fe/Ni alloys)

b) needle shaped magnetic particles with preferred orientation of the magnetization vector in a matrix (e.g. Al/Ni/Co „Alnico“)

c) - $SmCo_5$ hexagonal structure with strong magnetic anisotropy

Crystal structure of $SmCo_5$ ($CaZn_5$-Typ)



Soft and hard magnets

Non-metallic hard magnets

c) hexagonal spinels with preferred orientation of the magnetization vector

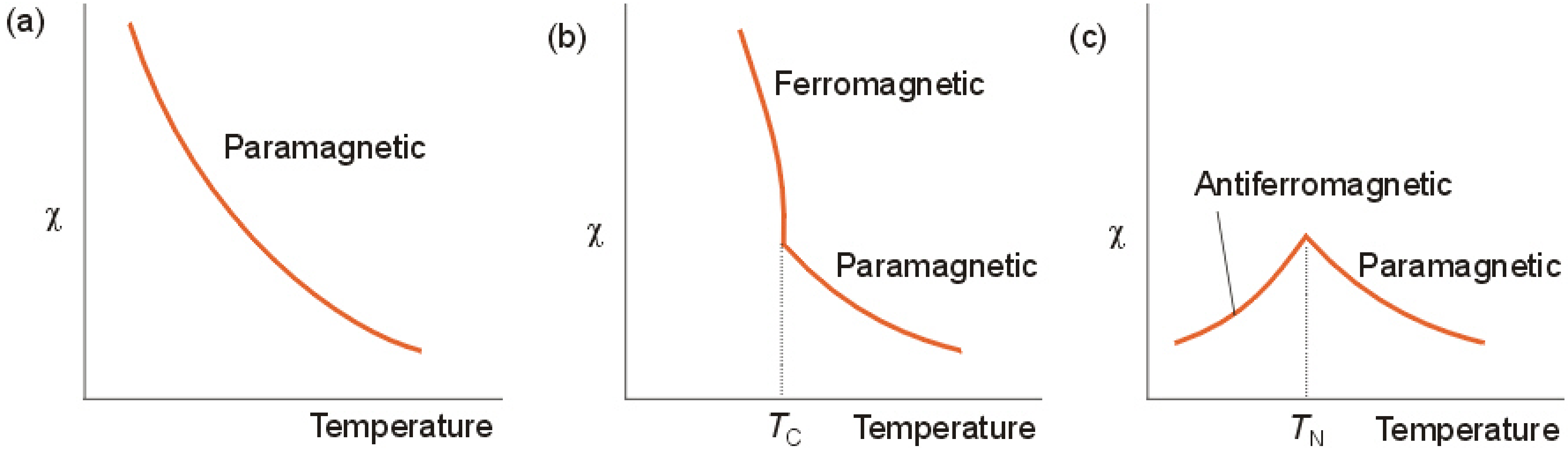
- Magnetoplumbite etc.: $PbFe_{12}O_{19}$: Fe_3O_4-layers separated by Pb^{2+}

- $Nd_2Fe_{14}B$ (complicated layered structure)

Magnetism in solids

- Magnetic domain: magnetic moments are coupled in a volume element consisting of a great number of unit cells.

- Below a critical temperature the “magnetization“ (M) (→ magnetic suszeptibility (χ)) for ferromagnets and antiferromagnets show a complex dependence of the temperature (T) and of the strength of an applied external field. Above the critical temperature paramagnetic behaviour occurs.

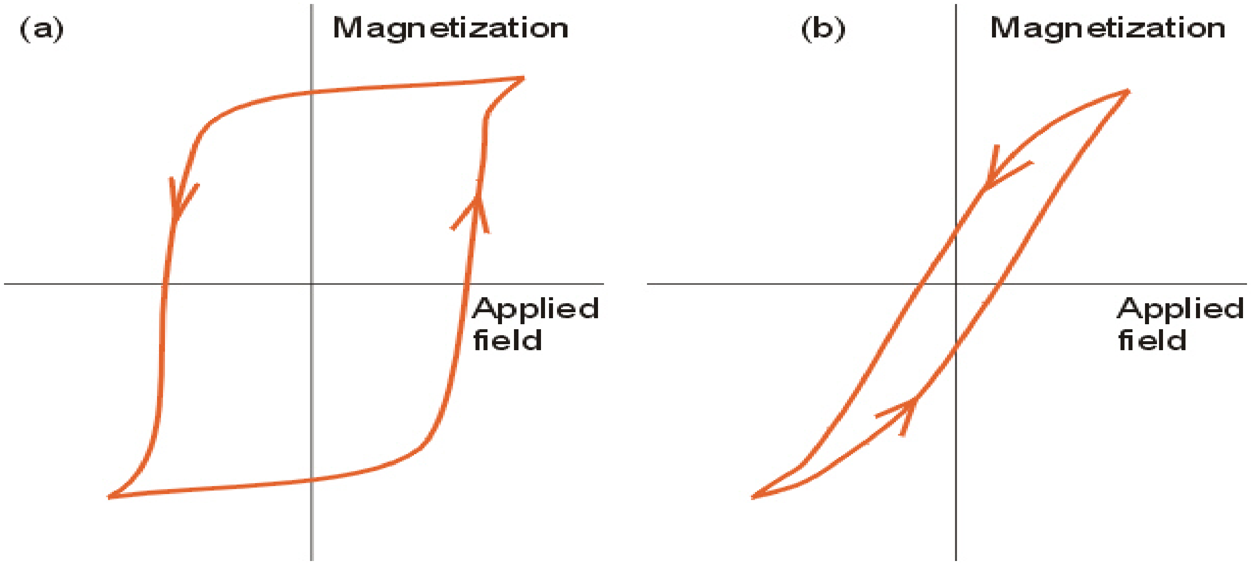


Curie temperature

Néel temperature

Magnetism in solids

- Upon cyclic application of an external magnetic field the magnetization changes in characteristic way for different magnetic materials and shows in particular a hysteresis loop



hard magnet

soft magnet

- different fields of applications for hard and soft magnetic materials
- area under the hysteresis loop is proportional to energy loss