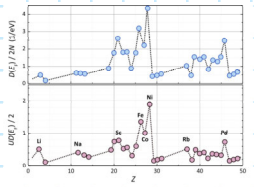
Lecture 24

Wednesday, January 19, 2022 1:13 PM

Review

$$\frac{1}{2} U \cdot D(E_F) > 1$$

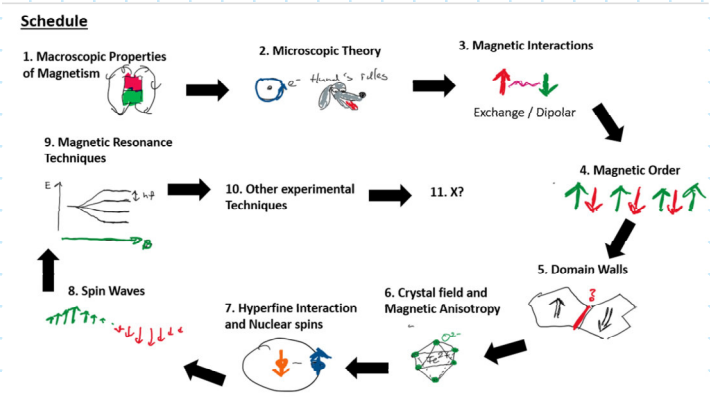


$$\chi = I \cdot \chi_p$$

χ_p : Pauli – susceptibility

$$I = \frac{1}{1 - \frac{1}{2} U \cdot D(E_F)}$$

$\rightarrow \infty$

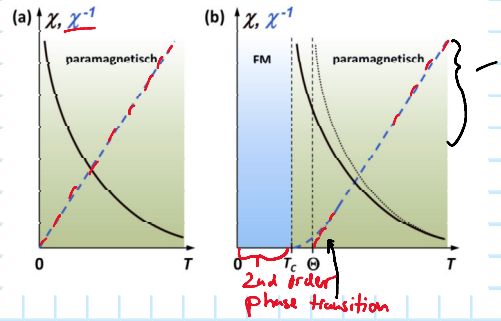


4. Magnetic Order

$$T_c = \gamma \cdot C$$

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

Curie – Weiss – law



– works well for $T \gg T_c$

works not so well for $T \geq T_c$ due to magnetic interaction in the paramagnetic region

Works not so well for $T \geq T_C$ due to magnetic interaction in the paramagnetic region

- Intiaction of a „paramagnetic" Curie-temperature (Weiss-Constant) $\Theta = T_C +$ a bit of interaction

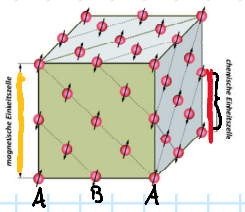
Material	T_C (K)	Θ (K)	C (K)	M_s (kA/m)	p
Fe	1044	1100	2.22	1 750	2.22
Co	1360	1415	2.24	1 450	1.72
Ni	629	649	0.588	510	0.60
Gd	289	302	5.00	2 060	7.63
Dy	85	157	—	3 050	10.4
EuO	69.4	78	4.68	1 880	7.0
CrO_2	396	—	—	325	2.0
MnAs	630	318	—	501	3.4

B_A
1030 T
6.85 T

- MFT works also not so well $T \ll T_C$ (Spin-Waves introduce a T-dependence in FM region)

2. Antiferromagnet

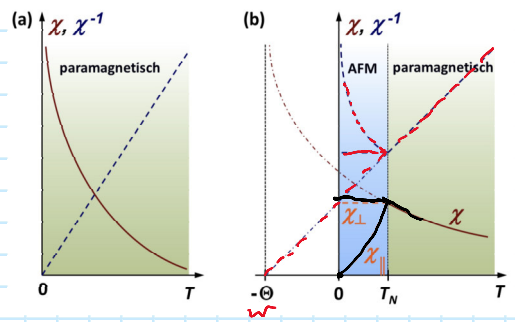
MnO:

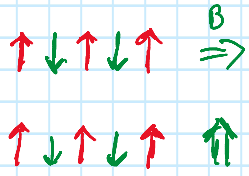


X-ray: chemical unit cell
neutron scattering: magnetic unit cell

$$T_N = |\gamma_{AB} - \gamma_{AA}| \cdot C$$

$$\chi = \frac{2C}{T + \Theta} \qquad \Theta = |\gamma_{AB} + \gamma_{AA}| \cdot C$$





$\Rightarrow \chi_\perp = \frac{1}{|\gamma_{AB}|}$

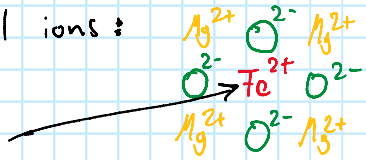
$\chi_\parallel = 0 \quad @\ T = 0$

$\chi_\parallel = \frac{1}{|\gamma_{AA}|} \quad @\ T_C$

5. Crystal field and magnetic anisotropy

5.1. Crystal field

Transition metal ions:



e⁻ in 3d of Fe are exposed to an inhomogeneous electric field induced by neighboring ions

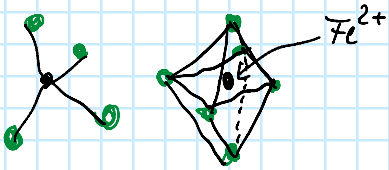
e in 3d of Fe are exposed to an inhomogeneous electric field induced by neighboring ions

=> Crystal field

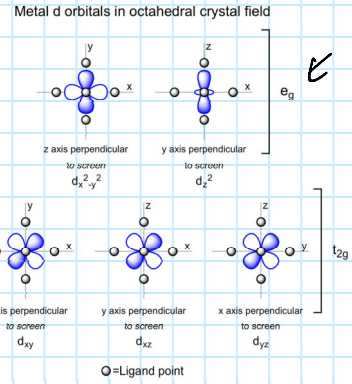
- breach spherical symmetry
- ≈ 1 eV for 3d
- stronger than spin-orbit interaction $\lambda \cdot \vec{S} \cdot \vec{L}$

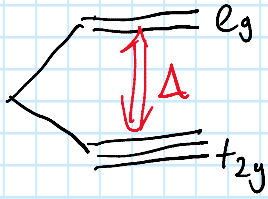
↳ Violation for 3rd Hunds' rule (J is not a good quantum number anymore)

Tetrahedral



- Imagine you are a d-shell electron
  → where would you like to sit?





distance Δ between the levels now will decide the spin state

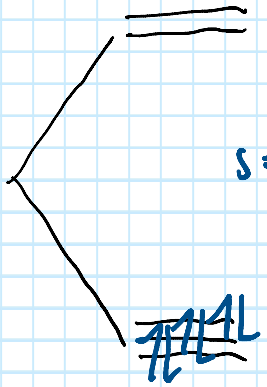
https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Modules_and_Websites_(Inorganic_Chemistry)/Crystal_Field_Theory/Crystal_Field_Theory

again for Fe^{2+} (d^6)

S = 2

$\Delta \ll 1$ eV

(low spin state)



S = 0

$\Delta \gg 1$ eV

(high spin state)

Orbital quenching

$g_L \sqrt{L(L+1)}$ $g_S \sqrt{S(S+1)}$

$g_L(L(L+1))^{1/2}$ $g_S(S(S+1))^{1/2}$

ion	shell	S	L	J	term	p_1	p_{exp}	p_2
Ti^{3+}, V^{4+}	$3d^1$	$\frac{1}{2}$	2	$\frac{3}{2}$	$^2D_{3/2}$	1.55	1.70	1.73
V^{3+}	$3d^2$	1	3	2	$^3F_2$	1.63	2.61	2.83
Cr^{3+}, V^{2+}	$3d^3$	$\frac{3}{2}$	3	$\frac{3}{2}$	$^4F_{3/2}$	0.77	3.85	3.87
Mn^{3+}, Cr^{2+}	$3d^4$	2	2	0	$^5D_0$	0	4.82	4.90
Fe^{3+}, Mn^{2+}	$3d^5$	$\frac{5}{2}$	0	$\frac{5}{2}$	$^6S_{5/2}$	5.92	5.82	5.92
Fe^{2+}	$3d^6$	2	2	4	$^5D_4$	6.70	5.36	4.90
Co^{2+}	$3d^7$	$\frac{3}{2}$	3	$\frac{9}{2}$	$^4F_{9/2}$	6.63	4.90	3.87
Ni^{2+}	$3d^8$	1	3	4	$^3F_4$	5.59	3.12	2.83
Cu^{2+}	$3d^9$	$\frac{1}{2}$	2	$\frac{5}{2}$	$^2D_{5/2}$	3.55	1.83	1.73
Zn^{2+}	$3d^{10}$	0	0	0	$^1S_0$	0	0	0

- For 3d elements the predicted value of the total magnetic moment leads to poor results

⇒ crystal field > spin-orbit (3rd Hund's rule)

- instead, often $L = 0$, $J = S$

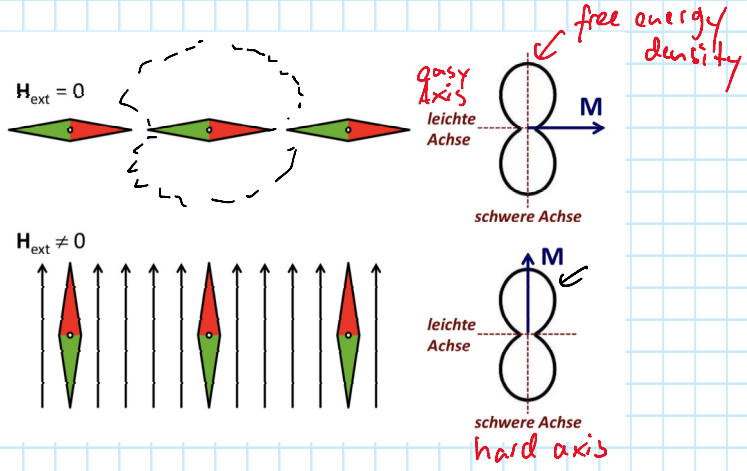
⇒ orbital moment is quenched

Semiclassical: orbital angular momentum precesses in the crystal field with unchanged magnitude, but components which average to zero

- Often orbital angular moment is not fully quenched → spin-orbit is not fully negligible

5.2. Magnetic Anisotropy

- In general: Different spatial directions do not have the same magnetic properties



- Three main sources for magnetic sources

$$E_{ani} = E_{MC} + E_{Shape} + E_{ind}$$

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E_{MC}: Magnetocrystalline

E_{ind}: Induced

Magnetocrystalline Anisotropy

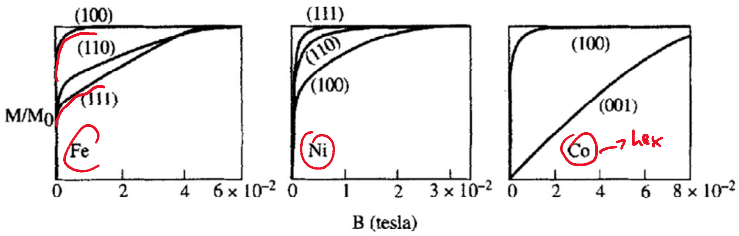


Fig. 6.22 Magnetization in Fe, Co and Ni for applied fields in different directions showing anisotropy. After Honda and Kaya 1926, Kaya 1928.

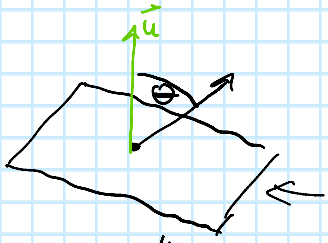
Phenomenological description:

magnetic free energy (density) $f_{ani} = \frac{E_{ani}}{V}$

as a function of $\vec{m} = \frac{\vec{M}}{|\vec{M}|} = \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix} = \begin{pmatrix} \sin\Theta \cdot \cos\varphi \\ \cos\Theta \cdot \sin\varphi \\ \cos\Theta \end{pmatrix}$

Uniaxial anisotry

$f_{uni} \approx K_{u1} \cdot \cos^2\Theta$



general:

$$f_{uni} = K_{u1} |\vec{m} \cdot \vec{u}|^2 + K_{u2} |\vec{m} \cdot \vec{u}|^4 + \dots$$