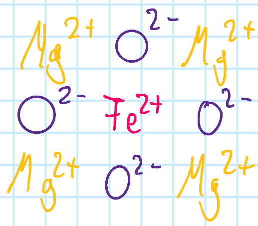
# Lecture 26 - WiSe2022/2023

Thursday, January 5, 2023 7:01 PM

## 5. Crystal field and magnetic anisotropy

### 5.1. Crystal field

- Transition metal ion in a crystal

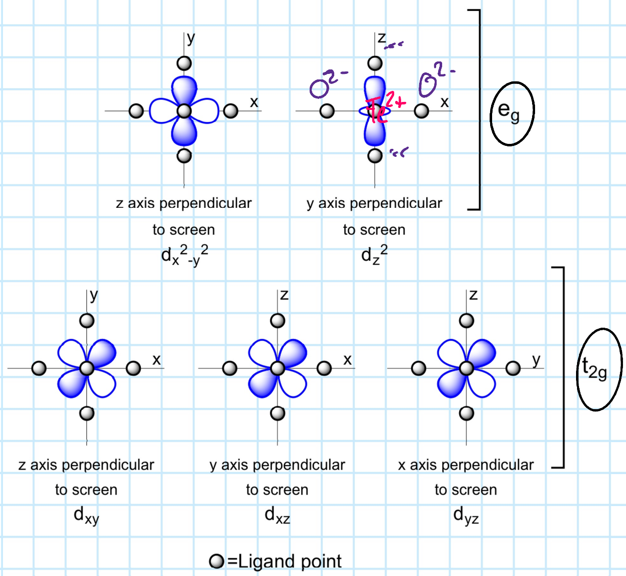


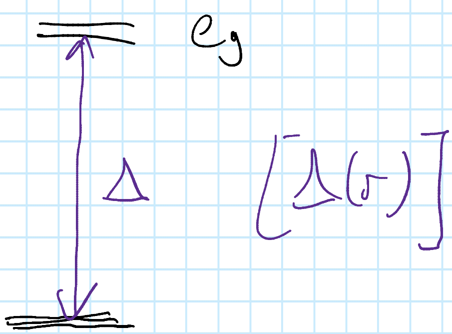

- $e^-$ in 3d of Fe are exposed to an inhomogeneous electric field induced by neighboring ions

⇒ Crystal field
- breaks spherical symmetry
- $\simeq 1eV$ for 3d
- stronger than the spin-orbit interaction $\lambda \cdot \vec{S} \cdot \vec{L}$

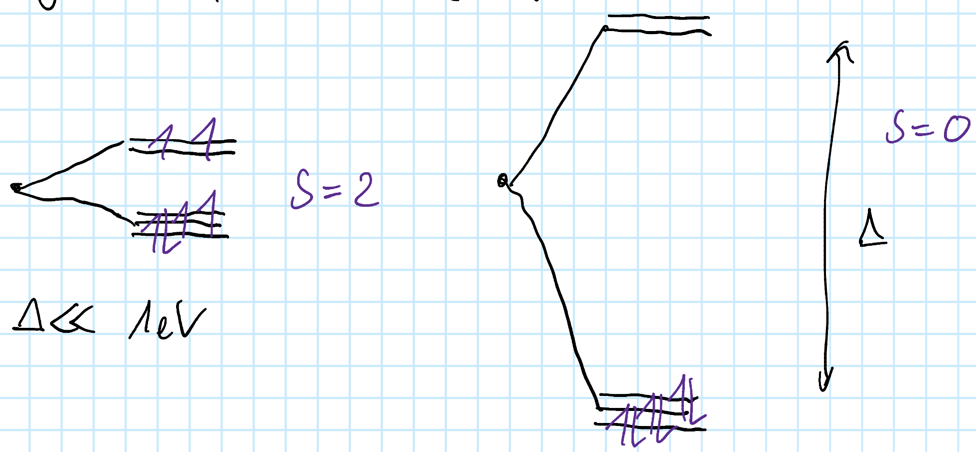
↳ Violation for 3rd Hunds rule ($J$ is <u>not</u> a good quantum number anymore)

Metal d orbitals in octahedral crystal field



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




$\Delta \ll 1eV$

(high-spin state) (low-spin state)

| 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 |

## 5.2 Orbital Quenching

- For the 3d elements the prediction of the total magnetic moment $g_J \cdot [J(J+1)]^{1/2}$ is often wrong

$\Rightarrow$ crystal field > spin-orbit (3rd Hund's rule)

- instead, often $L=0$, $J=S \Rightarrow \mu_{eff} = 2\mu_B \sqrt{S(S+1)}$

$\hookrightarrow$ Orbital moment is quenched

- semiclassical: orbital moment precesses in

• Semiclassical: orbital moment precesses in the crystal field with unchanged magnitude, but components that average to zero

↿ ↿ ↿ ↿ ↿ $Mn^{2+}$

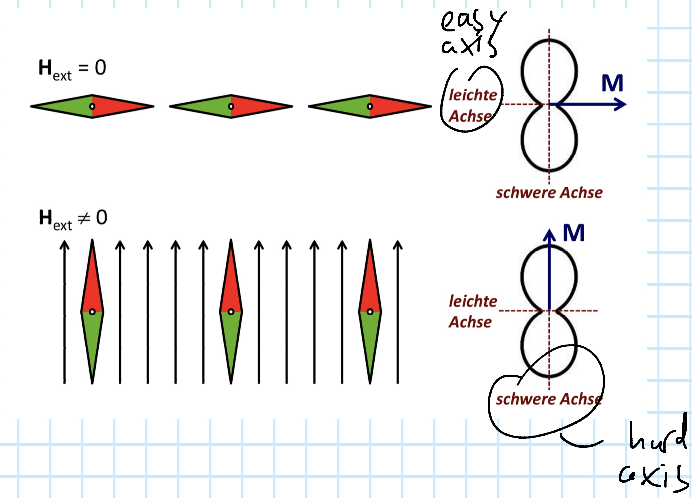
$m_l$ +2 +1 0 −1 −2

$L = 0$

• Often the orbital angular momentum is not completely quenched → spin orbit interaction is not completely neglegible

## 5.3. Magnetic Anisotropy

• In general: Different spatial directions do <u>not</u> have the same magnetic properties




• useful: data storage

• Three main reason for magnetic anisotropy

$$E_{ani} = E_{MC} + E_{shape} + E_{ind} + \dots$$

$E_{MC}$: Magnetocrystalline; $E_{ind}$: induced

# Magnetocrystalline Anisotropy

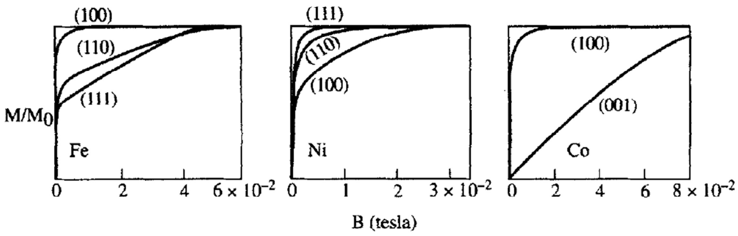



**Fig. 6.22** Magnetization in Fe, Co and Ni for applied fields in different directions showing anisotropy. After Honda and Kaya 1926, Kaya 1928.