

Lecture: Solid State Chemistry

(Further spectroscopical methods, 8.6.06)

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Orders of magnitude in energy → spectroscopic techniques

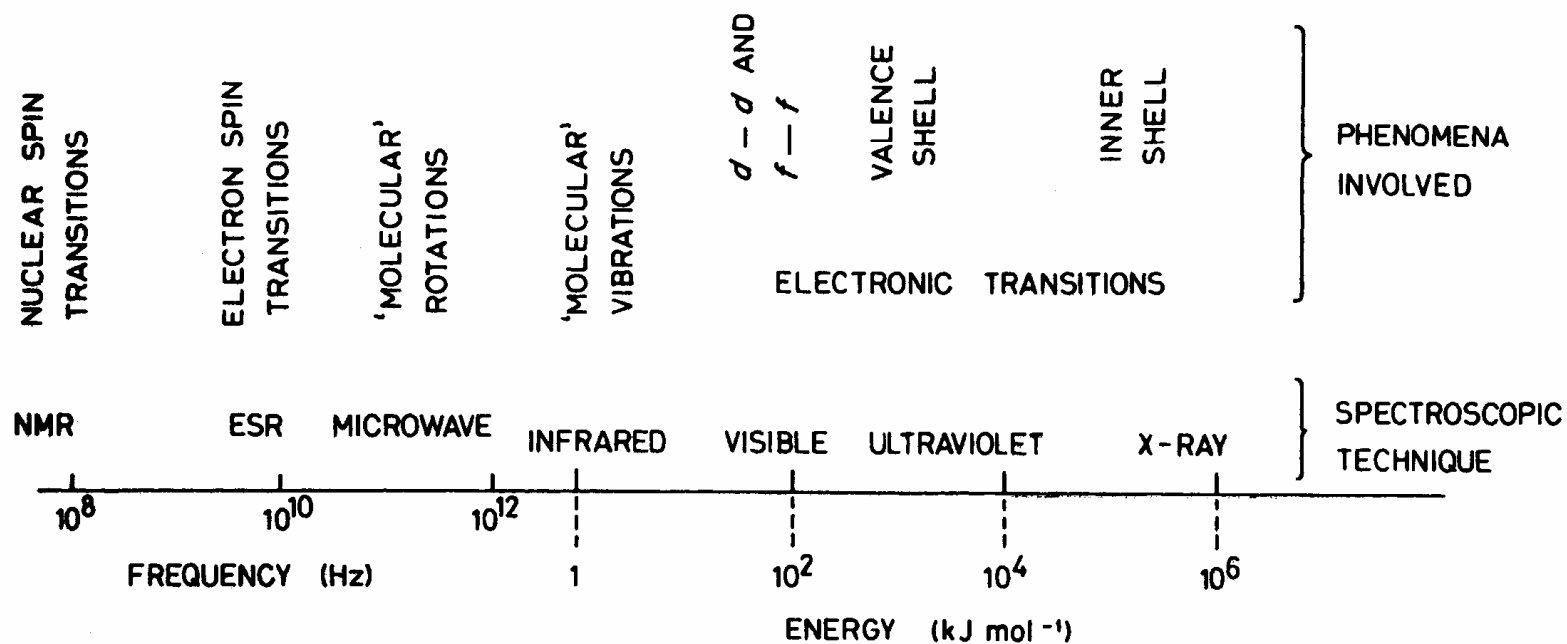
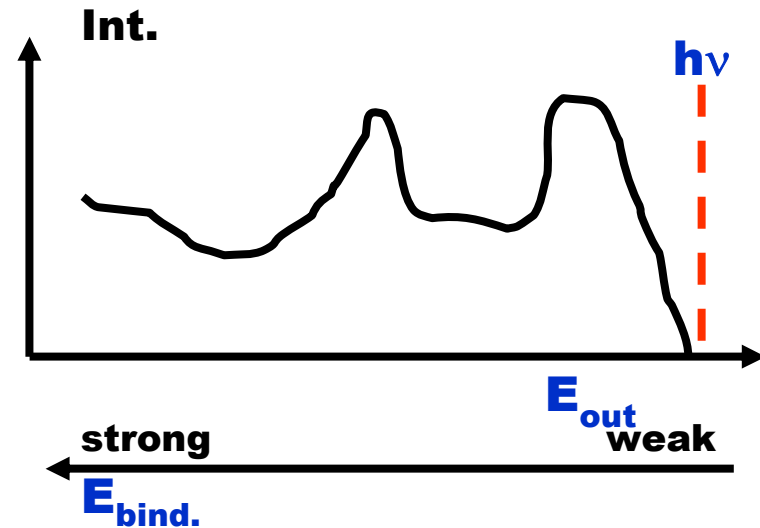
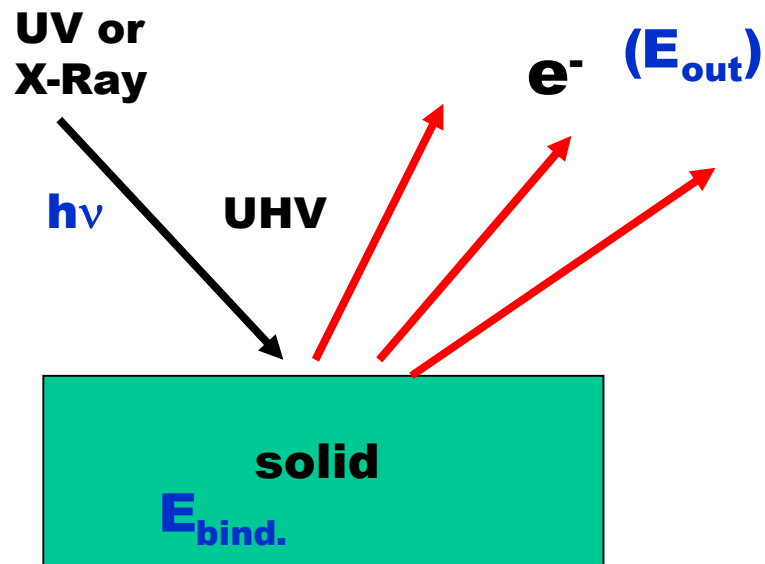


Fig. 4.6 Principal regions of the electromagnetic spectrum and the associated spectroscopic techniques

ESCA: Photoemission or Photoelectron spectroscopy

ESCA = Electron Spectroscopy for Chemical Analysis

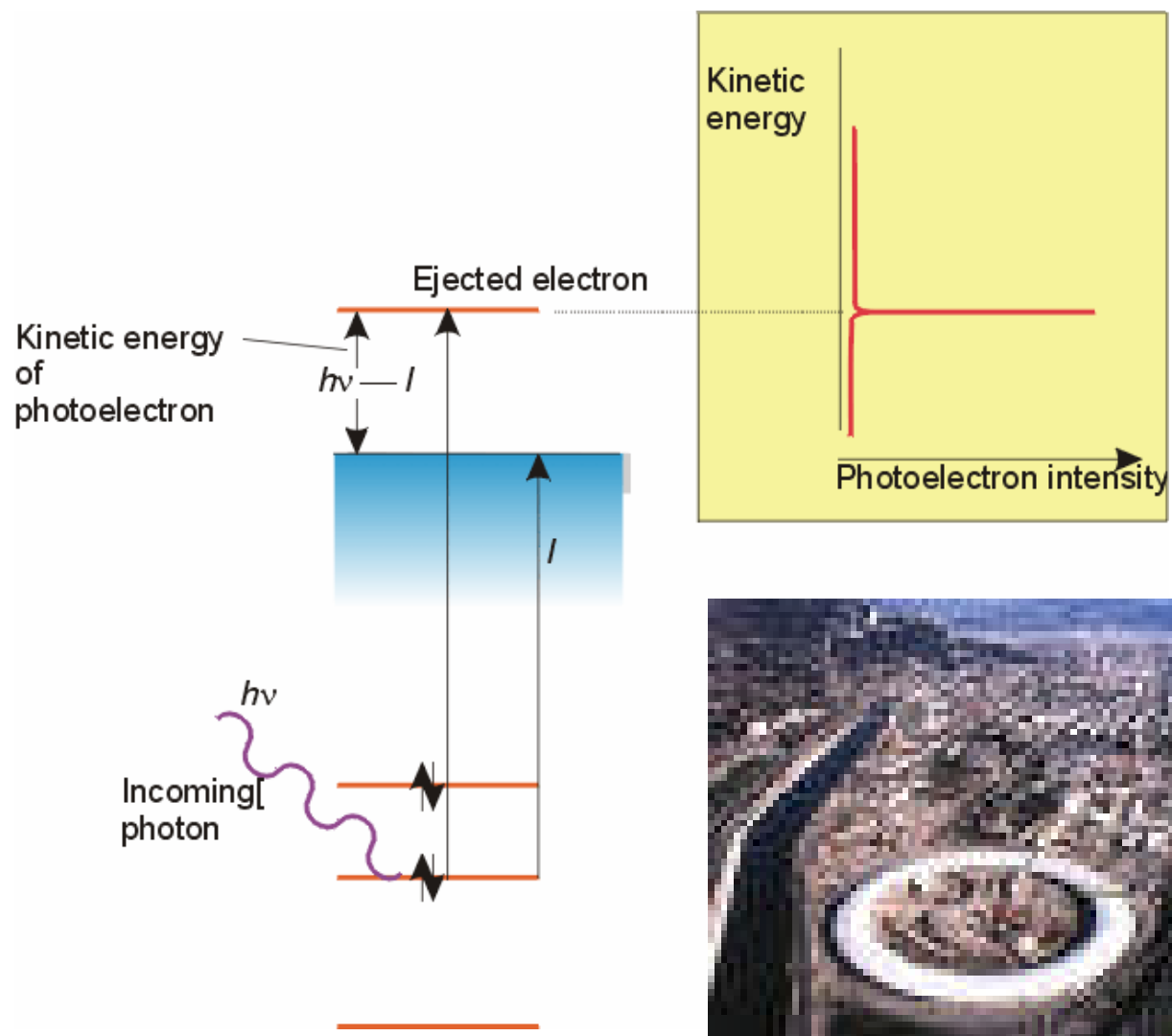
Basic equation: $E_{\text{out}} = h\nu - E_{\text{bind.}}$



- the higher the binding energy ($E_{\text{bind.}}$) the lower the E_{out} !

- ESCA is in particular a surface sensitive method (UHV !)

ESCA: Photoemission or Photoelectron spectroscopy



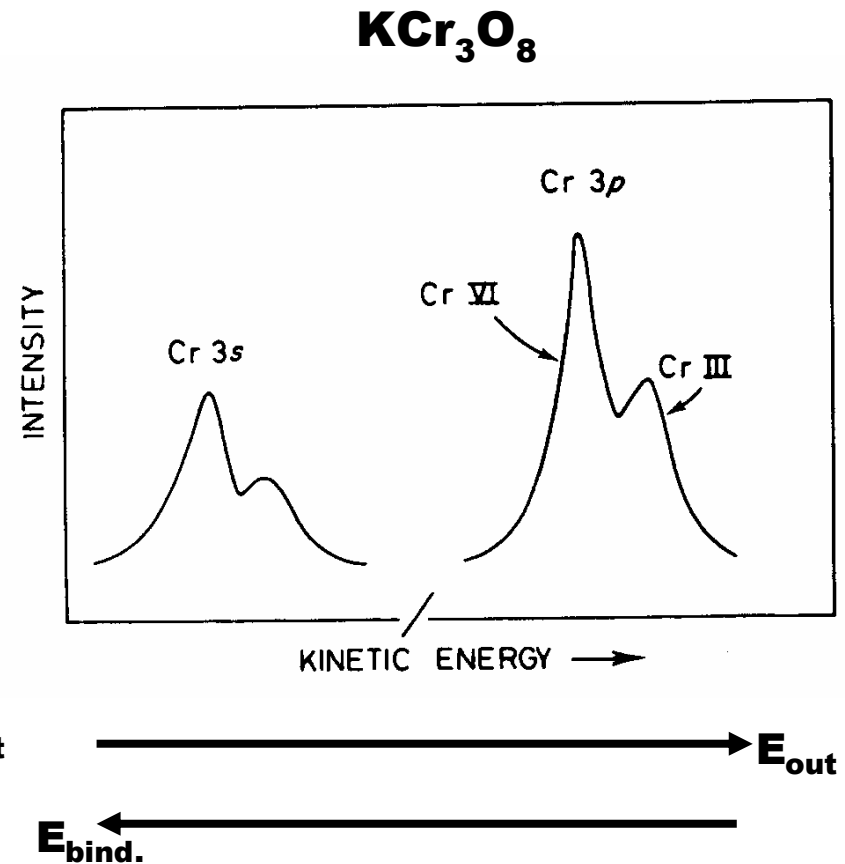
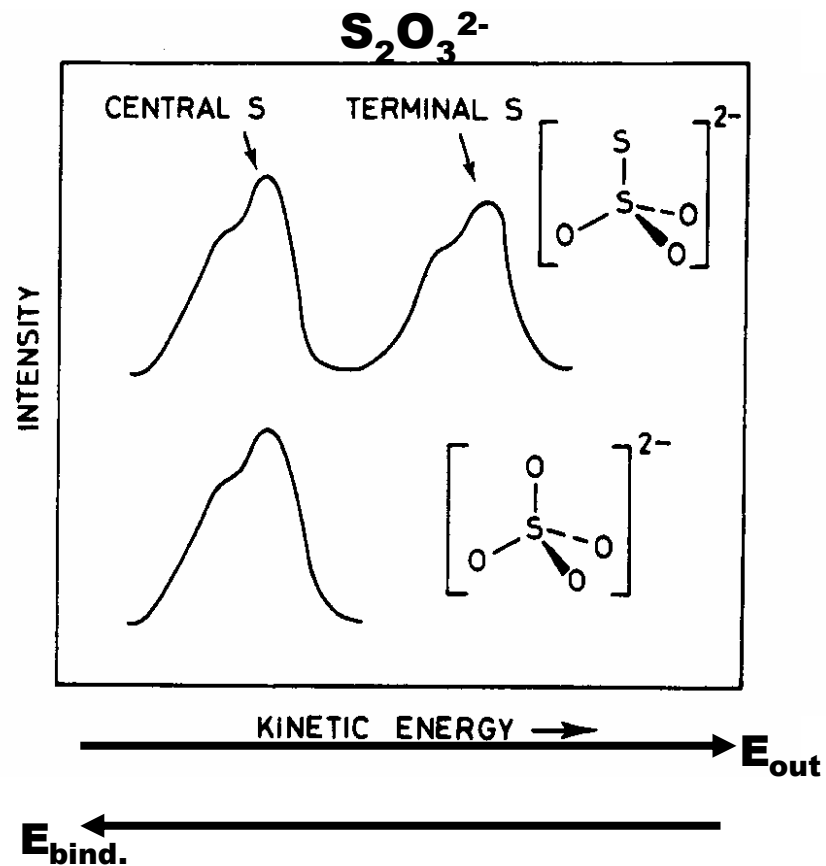
ESCA: Photoemission or Photoelectron Spectroscopy

Exciting Radiation	Outcoming Radiation
UV (~ 20 eV) → <u>UPS</u>	electrons from occupied <u>valence</u> states
X-Ray (~ 10 keV) → <u>XPS</u>	electrons from (occupied) <u>core</u> states

- **commercial laboratory based spectrometers (UHV-technique) are available but relatively expensive and of limited versatility !**
- **more promising for the future is the use of synchrotron radiation:
→ continuous spectrum of exciting radiation (UV → X-Ray)**
- **intensity of synchrotron radiation is orders of magnitudes higher !
(e.g. angle resolved detection of outcoming radiation is possible
- detection of „orbital shapes“)**
- **polarization of synchrotron radiation allows spin polarized experiments**

ESCA: Photoemission or Photoelectron spectroscopy

- analysis of the energy levels of electrons in molecules („chemical shift“)
- band structure of solids



Synchrotron Storage Ring

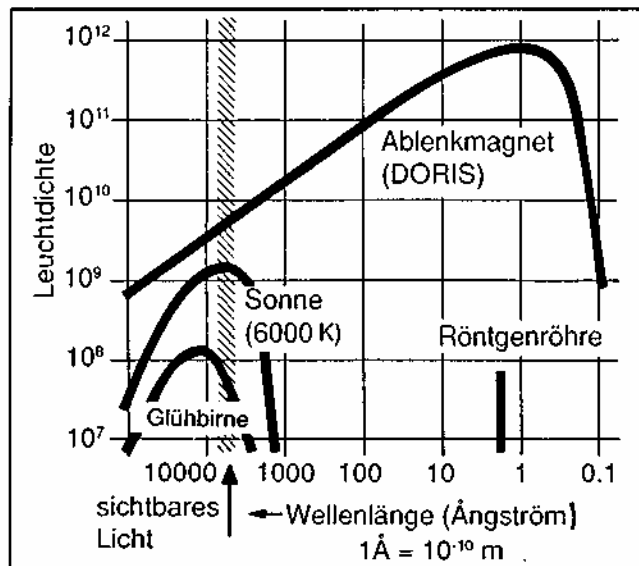
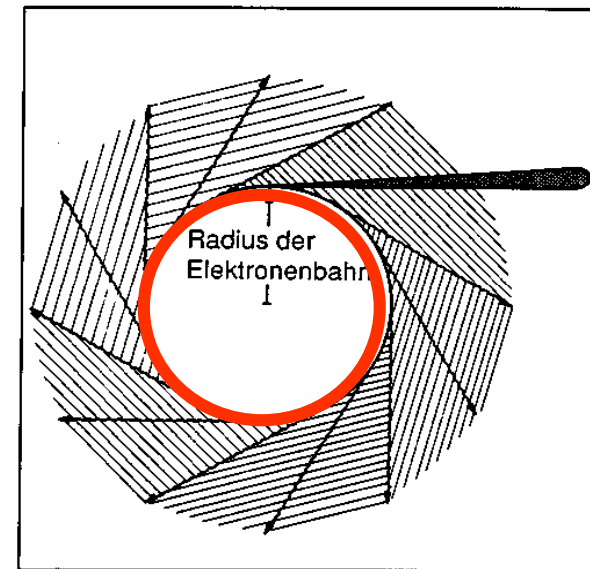


Abb. 5: Die Leuchtdichte von DORIS im Vergleich zu einigen bekannten Strahlungsquellen. (Die Leuchtdichte ist die Zahl der Photonen, die pro Sekunde und Wellenlängenintervall in eine bestimmte Richtung abgestrahlt wird.)



EXAFS and XANES

Spectroscopical methods associated with specific physical effects at/near characteristic X-ray absorption edges:

EXAFS: Extended X-Ray Absorption Fine Structure

XANES: X-Ray Absorption Near Edge Structure

- tunable synchrotron radiation in the X-Ray region necessary

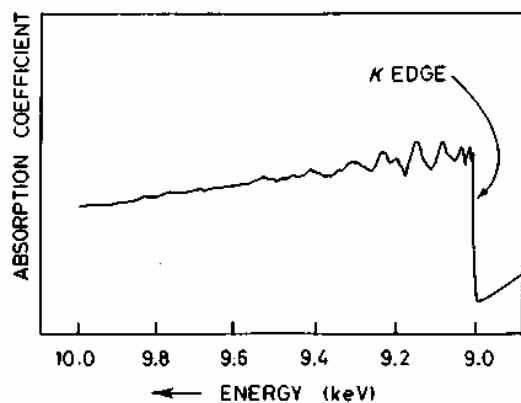


Fig. 4.19 EXAFS spectrum of Cu. (From E. A. Stern, *Sci. Amer.*, 234, 96, 1976)

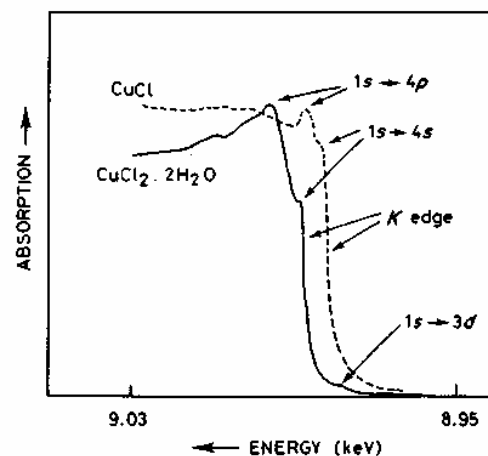
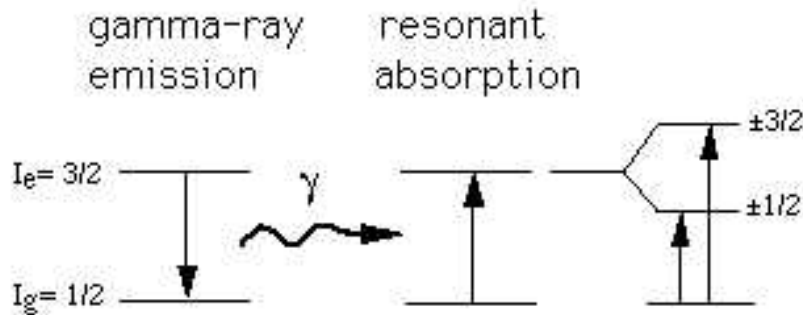


Fig. 4.18 AEFS spectra of CuCl and CuCl₂ · 2H₂O. (From Chan, Hu and Gamble, *J. Mol. Str.*, 45, 239, 1978)

Moessbauer Spectroscopy

→ the nucleus of the specific isotope of an atom embedded in a solid (e.g. ^{57}Fe) is excited by γ -rays emitted by an instable isotope of a neighbor element (e.g. ^{57}Co)



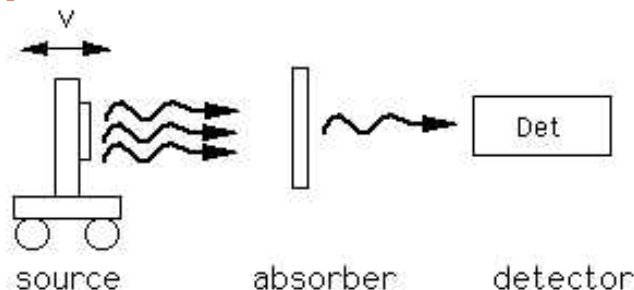
„Chemical shift“
and „Hyperfine splitting“

source:
e.g. ^{57}Co
(tunable)

absorber:
e.g. ^{57}Fe

frequently applied for
→ ^{57}Fe , ^{119}Sn , ^{127}J ...

Doppler effect



→ chemical surrounding (symmetry, coordination number, oxidation state, magnetism) of atoms with these nuclei in a solid can be probed in a highly sensitive way ($\sim 10^{-8}$ eV)

Moessbauer Spectroscopy

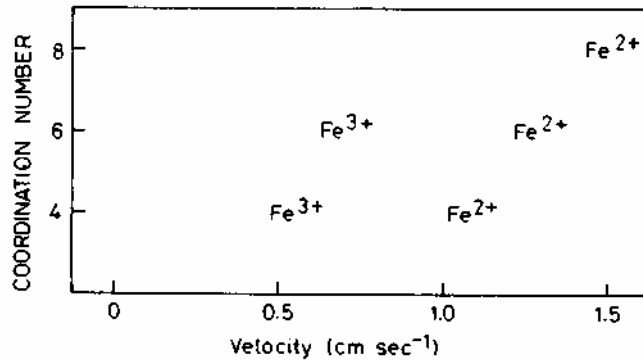


Fig. 4.27 Chemical shifts in iron-containing compounds. (From Bancroft, *Mössbauer Spectroscopy*, McGraw-Hill, 1973)

Two major informations from Moessbauer spectra:

a) „Chemical Shift“
(not to be confused with the same term in NMR and ESCA)

→ **oxidation state**

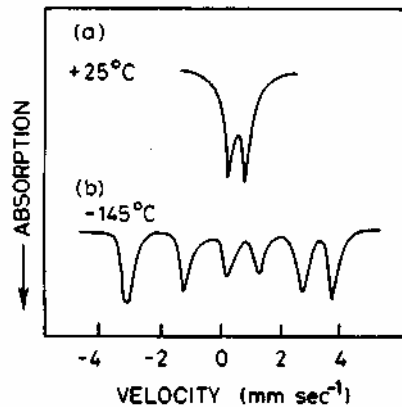


Fig. 4.28 Mössbauer spectrum of KFeS_2 (a) above and (b) below the Néel temperature. (From Greenwood, *Chem. Brit.*, 3, 56, 1967)

b) Hyperfine Splitting

→ **magnetic interactions**