

Photoelectron Spectroscopy of free Atoms

2p Photoelectron Spectra and Magnetic Dichroism of 3d Metals

Trends and Common Features in the Free Atom and Solid State 2p Photoelectron Spectra

A combined Laser and Synchrotron Radiation Experiment

Magnetized Free Atoms Versus Magnetized Thin Films

Philippe Wernet

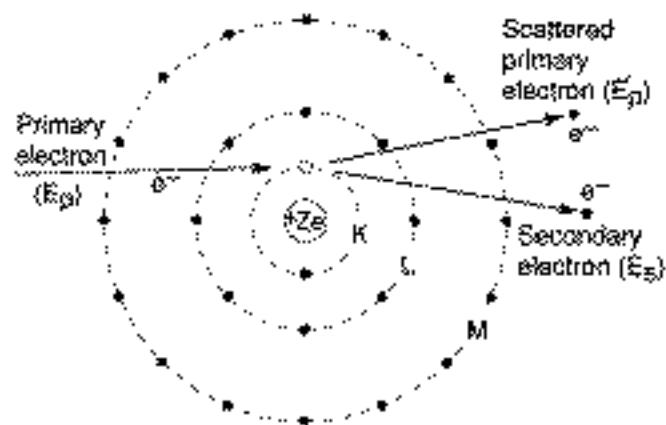
Stanford Synchrotron
Radiation Laboratory (SSRL)

Prof. Bernd Sonntag

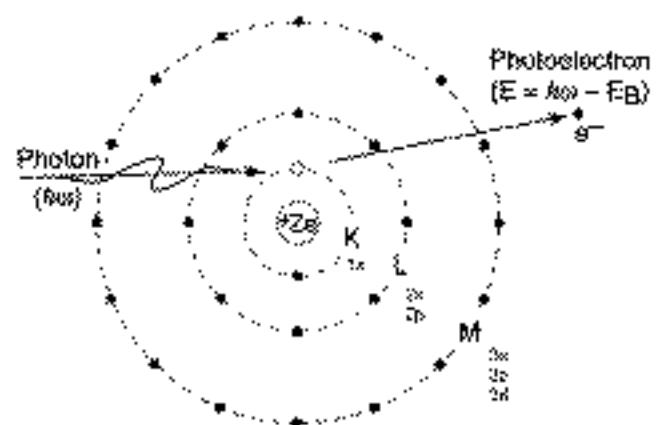
Universität Hamburg /
HASYLAB at DESY

Atom + Photon \rightarrow Ion + Electron

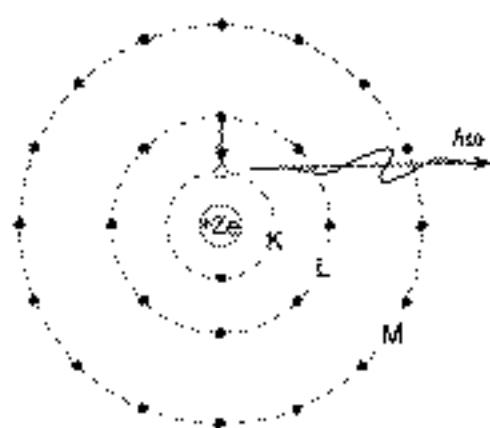
(a) Electron collision induced ionization



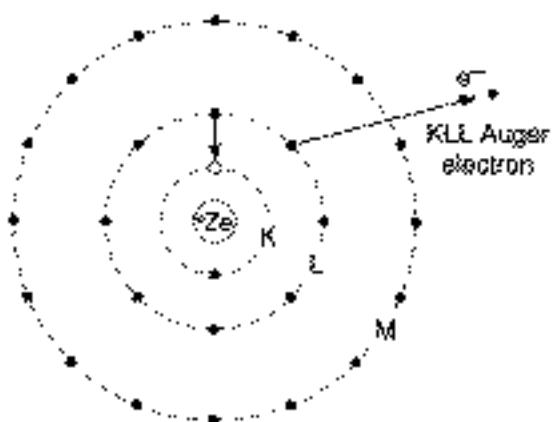
(b) Photoionization



(c) Fluorescent emission of characteristic radiation

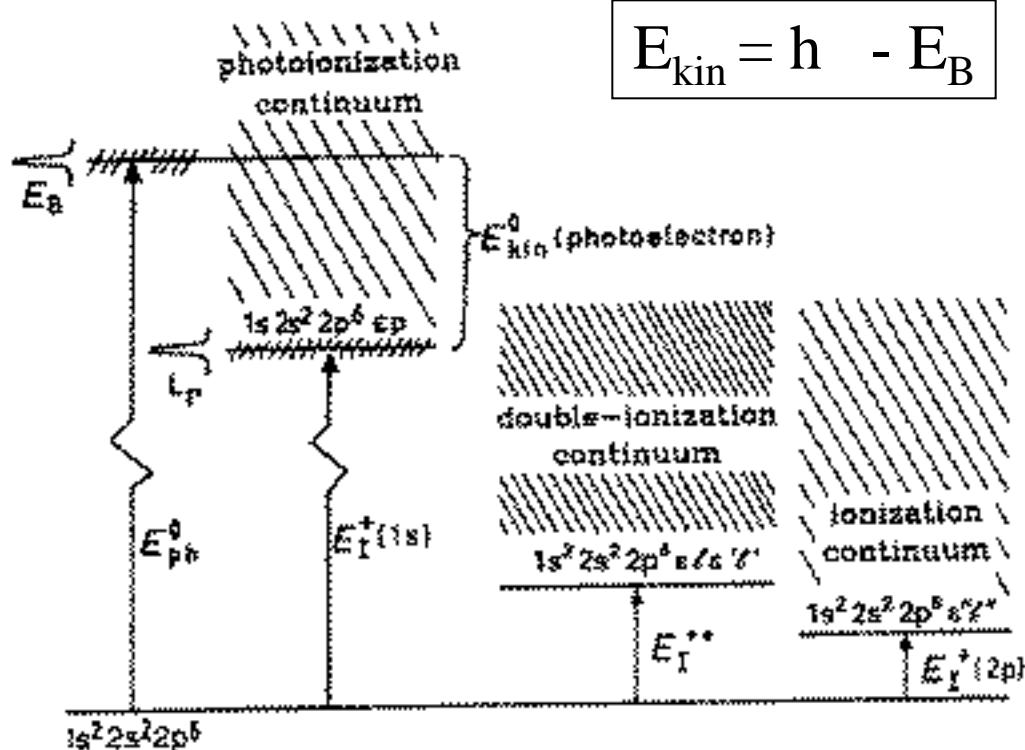


(d) Non-radiative Auger process

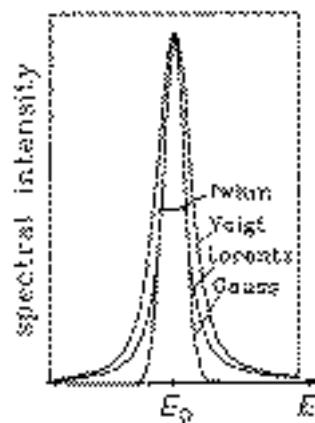


David Attwood, Soft X-Rays And Extreme Ultraviolet Radiation, Cambridge University Press

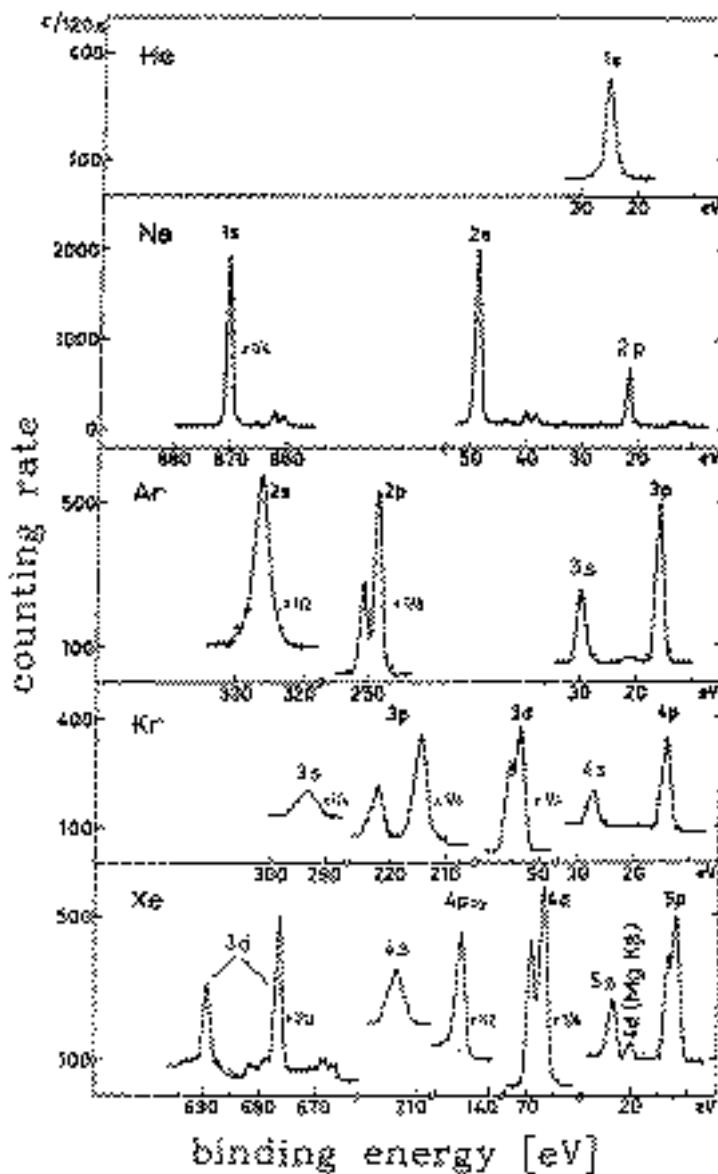
Photoionization of Ne $1s^2 2s^2 2p^6$



line shape



Some “Simple” Photoelectron Spectra



He $1s^2$

Ne $1s^2\ 2s^2\ 2p^6$

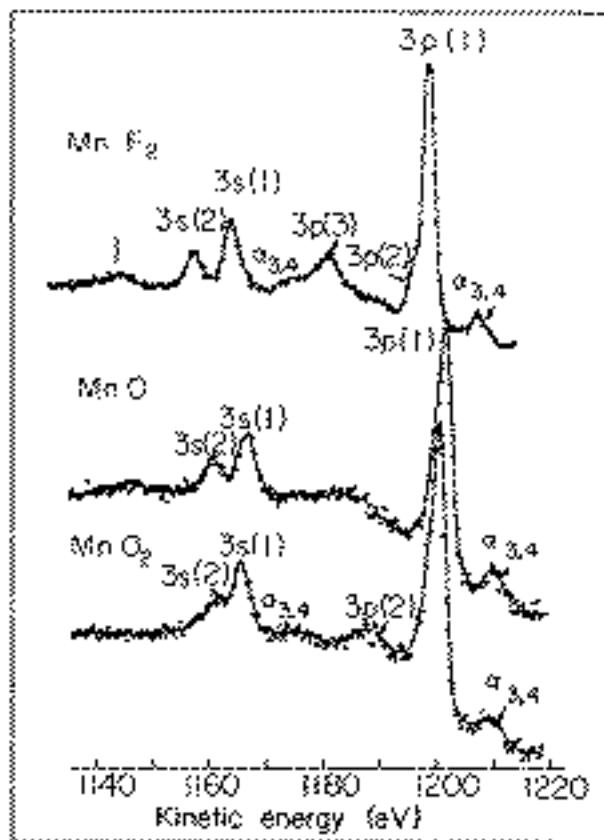
Ar $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Kr $1s^2\dots 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Xe $\dots 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$

Volker Schmidt, Electron Spectrometry of Atoms using
Synchrotron Radiation, Cambridge University Press

Multiplet Splitting – Open Shells



Free Mn atom ground state:
 $\text{Mn } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

Initial state (ionic crystals):
 $\text{Mn}^{2+} 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

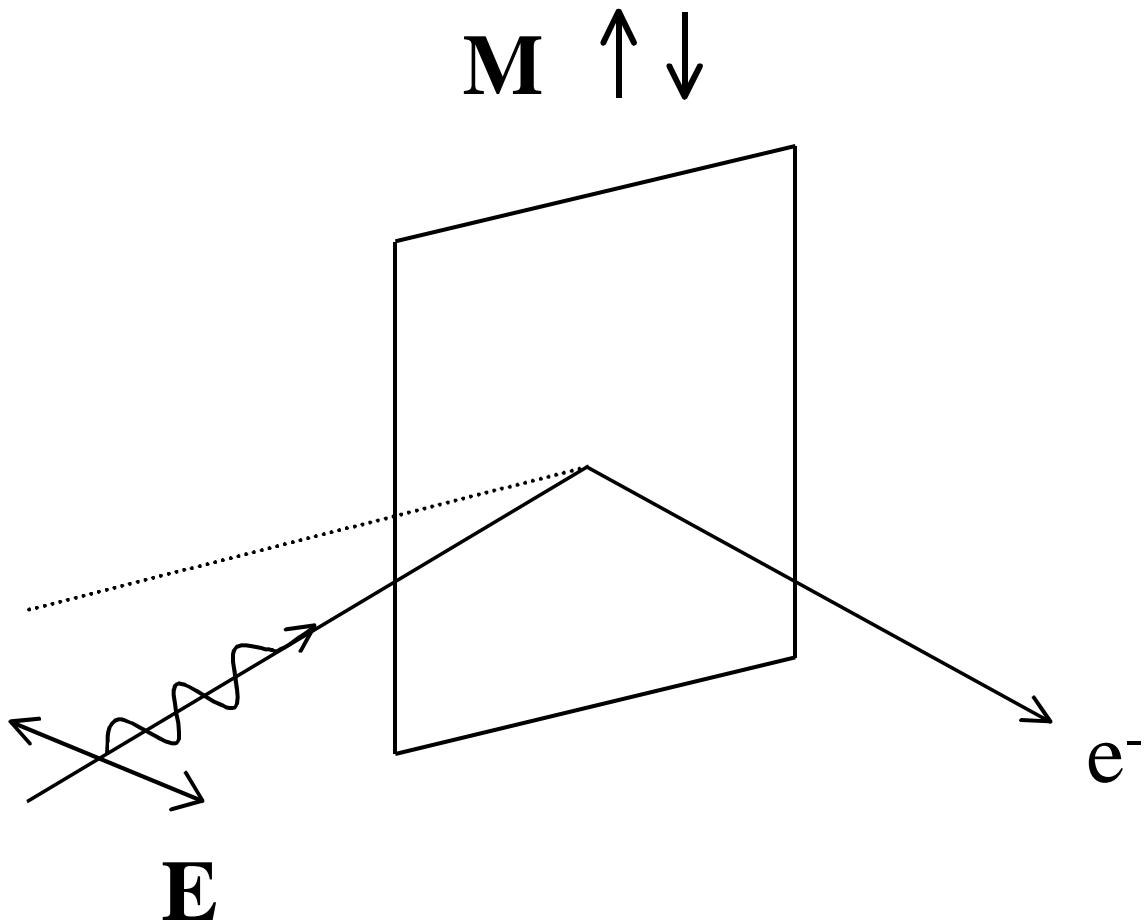
Final states:
 $\text{Mn}^{3+} 3s^1(^2\text{S}) \dots 3d^5 (^6\text{S})$
LS-coupling gives two
States: ${}^7\text{S}$ and ${}^5\text{S}$

C.S.Fadley, D.A. Shirley, A.J. Freeman, P.S. Bagus,
J.V. Mallow, PRL **23**, 1397 (1969).

C.S. Fadley, D.A. Shirley, PRA **2**, 1109 (1970).

Complex spectra due to multiplet splitting
and
Compare spectra of free and bound atoms

Dichroism in photoionization of magnetic solids and surface layers



$$\text{Dichroism} = I(\uparrow) - I(\downarrow)$$

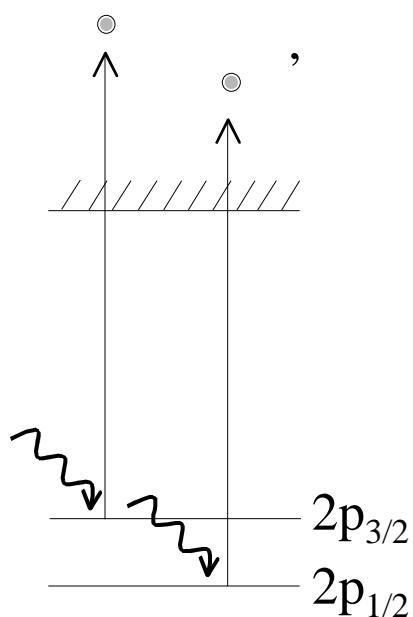
Linear Magnetic Dichroism
in the Angular Distribution (LMDAD)

Magnetic dichroism of an Fe(110) substrate and a Cr surface layer

Titel:
knabben1_mod.eps
Erstellt von:
Photoshop Version 2.5.1b15
Vorschau:
Diese EPS-Grafik wurde nicht gespeichert mit einer enthaltenen Vorschau.
Kommentar:
Diese EPS-Grafik wird an einen PostScript-Drucker gedruckt, aber nicht an andere Druckertypen.

Titel:
knabben2_mod.eps
Erstellt von:
Photoshop Version 2.5.1b15
Vorschau:
Diese EPS-Grafik wurde nicht gespeichert mit einer enthaltenen Vorschau.
Kommentar:
Diese EPS-Grafik wird an einen PostScript-Drucker gedruckt, aber nicht an andere Druckertypen.

[Knabben, Hillebrecht *et al.*, J. Electron Spectrosc. **86**, 201 (1997).]



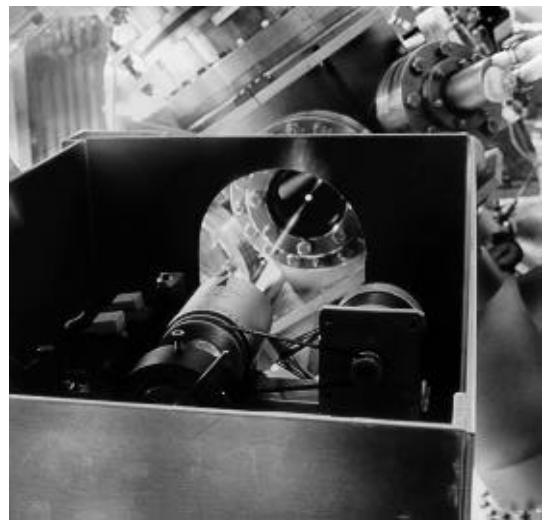
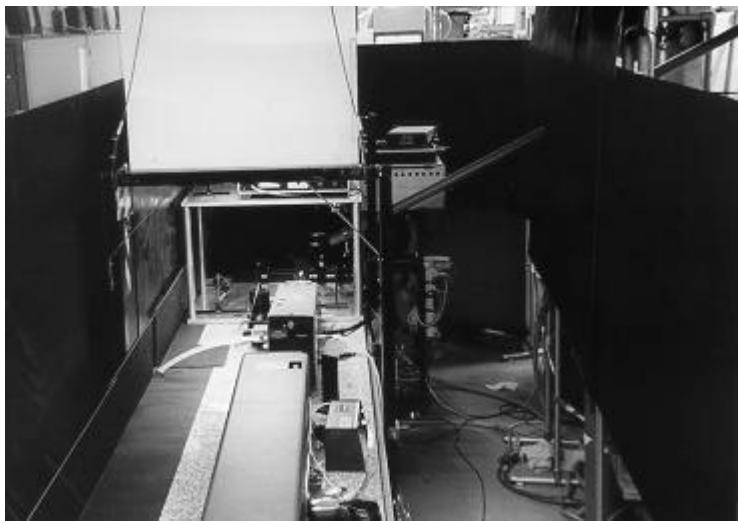
comparison of bound to free atoms



separation of interatomic and intraatomic effects

Experimental set-up

Title:
aufbauoleng.eps
Creator:
fig2dev Version 3.2 Patchlevel 3c
Preview:
This EPS picture was not saved
with a preview included in it.
Comment:
This EPS picture will print to a
PostScript printer, but not to
other types of printers.



Experimental set-up and geometry

Titel:
aufbaugeool.eps
Erstellt von:
fig2dev Version 3.2 Patchlevel 1
Vorschau:
Diese EPS-Grafik wurde nicht gespeichert
mit einer enthaltenen Vorschau.
Kommentar:
Diese EPS-Grafik wird an einen
PostScript-Drucker gedruckt, aber nicht
an andere Druckertypen.

Angular Distribution of Photoelectrons from free Atoms

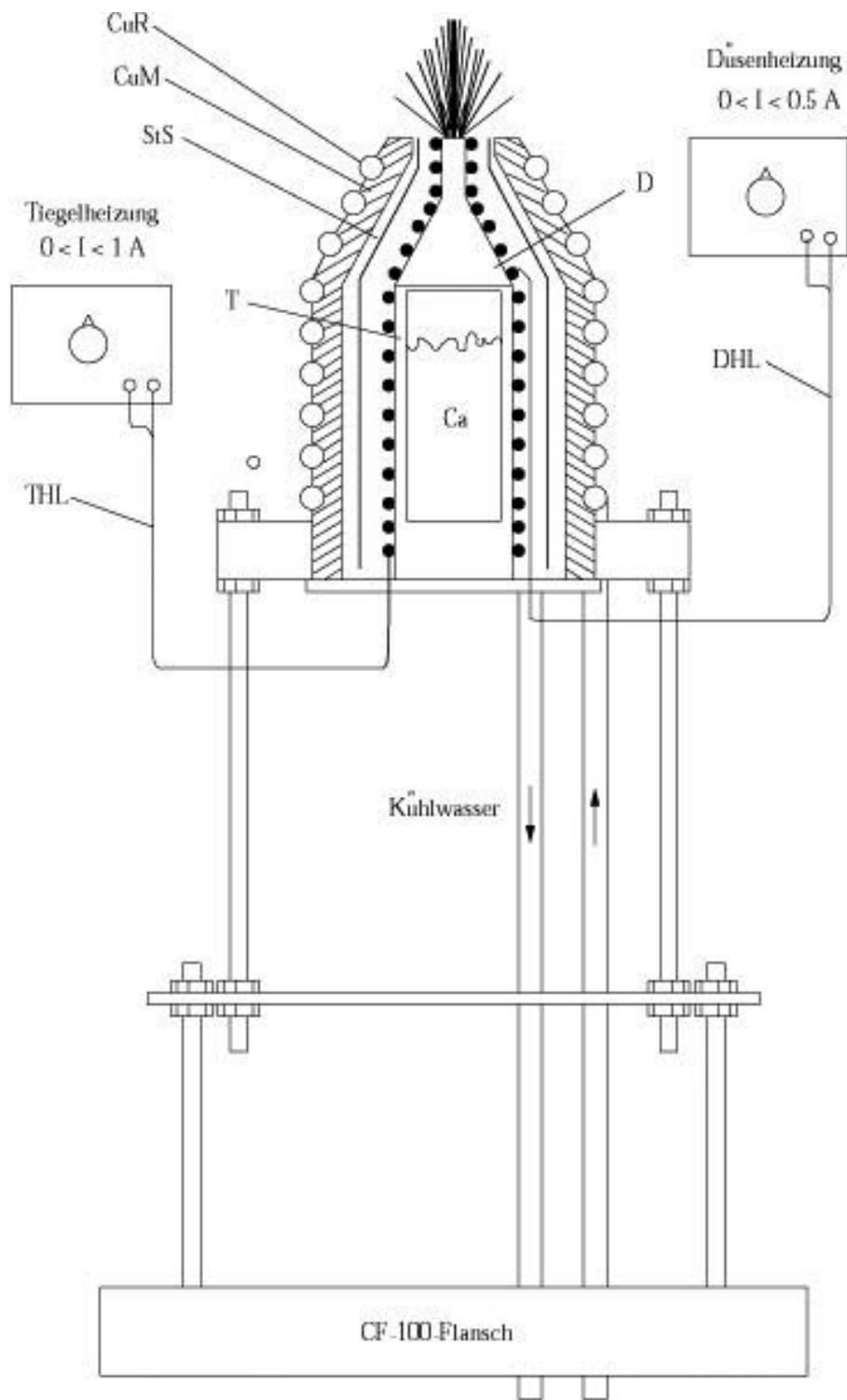
$$I\alpha \frac{d\sigma(i)}{d} = \frac{\sigma(i)}{4\pi} [1 + \beta(i)P_2(\cos\theta)]$$

linearly polarized ionizing light
unpolarized free atoms

$$P_2(\cos 54.7^\circ) = 0$$

$= 54.7$ deg is the so-called “magic angle”

High Temperature Metal Atom Beam Source



High Resolution Electron Energy Analyzer

Title:

scienta3.eps

Creator:

fig2dev Version 3.2 Patchlevel 3c

Preview:

This EPS picture was not saved
with a preview included in it.

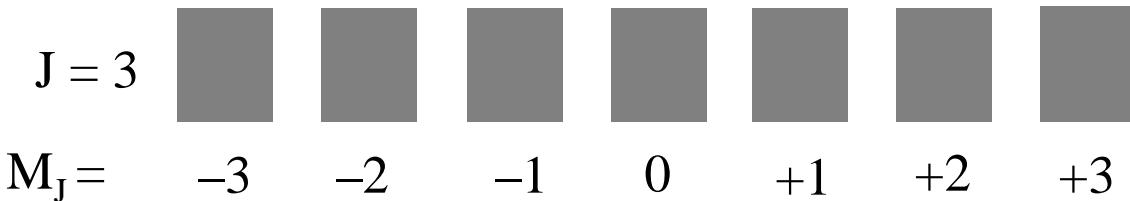
Comment:

This EPS picture will print to a
PostScript printer, but not to
other types of printers.

Preparation of free oriented Cr atoms

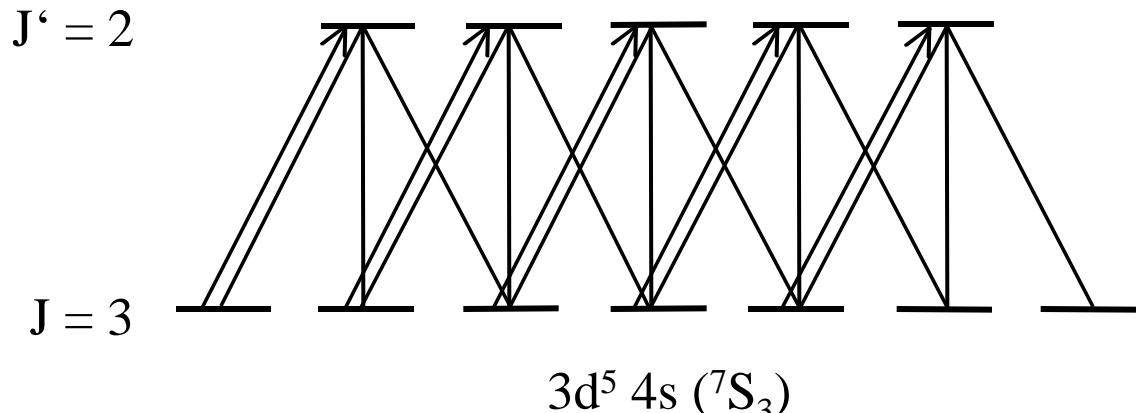
$\text{Cr } 2\text{p}^6 \dots 3\text{d}^5 4\text{s } (^7\text{S}_3)$

ground state - not oriented

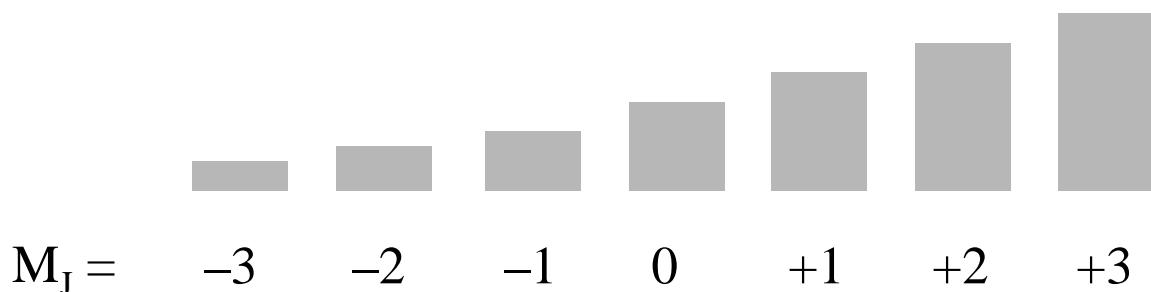


optical pumping with circularly polarized
laser radiation ($\lambda = 429 \text{ nm}$)

$3\text{d}^5 4\text{p } (^7\text{P}_2)$



ground state - oriented



LMDAD in 2p-photoionization of free oriented Cr atoms

Titel:

Erstellt von:

Spectra

Vorschau:

Diese EPS-Grafik wurde nicht gespeichert
mit einer enthaltenen Vorschau.

Kommentar:

Diese EPS-Grafik wird an einen
PostScript-Drucker gedruckt, aber nicht
an andere Druckertypen.

$$\text{LMDAD} = I(\cdot, \cdot) - I(\cdot \cdot)$$

LMDAD - patterns : + / - and - / +

LMDAD in 2p-photoionization of a thin Cr layer

Titel:

Erstellt von:

Spectra

Vorschau:

Diese EPS-Grafik wurde nicht gespeichert
mit einer enthaltenen Vorschau.

Kommentar:

Diese EPS-Grafik wird an einen
PostScript-Drucker gedruckt, aber nicht
an andere Druckertypen.

$$\text{LMDAD} = I(\uparrow) - I(\downarrow)$$

LMDAD - patterns : + / - and - / +

Comparison of LMDAD of free and bound Cr atoms

Titel:

Erstellt von:

Spectra

Vorschau:

Diese EPS-Grafik wurde nicht gespeichert
mit einer enthaltenen Vorschau.

Kommentar:

Diese EPS-Grafik wird an einen
PostScript-Drucker gedruckt, aber nicht
an andere Druckertypen.



proof of atomic nature of dichroism
in inner-shell photoionization of 3d-
metal thin films

shape of dichroism curve

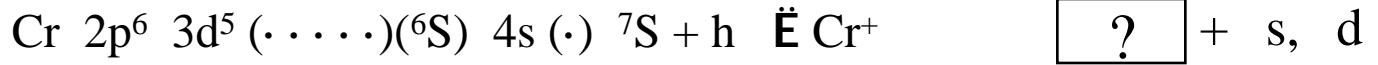
major influences

- ÿ intraatomic interactions
- ÿ atomic multiplet splitting
+satellite emission in final
ionic state
- ÿ Coulomb interactions of 2p
core hole and 3d valence
electrons

minor influences

- ÿ interatomic interactions
- ÿ secondary electrons
- ÿ Doniach-Sunjic line shape
- ÿ photoelectron diffraction

Approximations for an atomic model

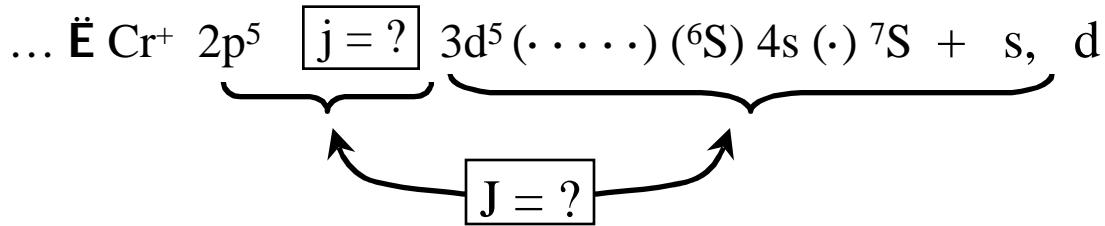


⇒ characterization of final ionic state

s one configuration approximation



s frozen valence shells



s angular momentum coupling

- spin-orbit interaction in 2p hole $j = 1/2, 3/2$

- valence electrons ${}^7S: L = 0, S = 3$

- 2p-3d Coulomb interaction $\vec{j} + \vec{s} = \vec{J}$

apple $J = j + S, \dots, |j - S|$ (JK-coupling for $L = 0$)

$J = 7/2, 5/2$	for $j = 1/2$
----------------	---------------

| $J = 9/2, 7/2, 5/2, 3/2$ | for $j = 3/2$ |

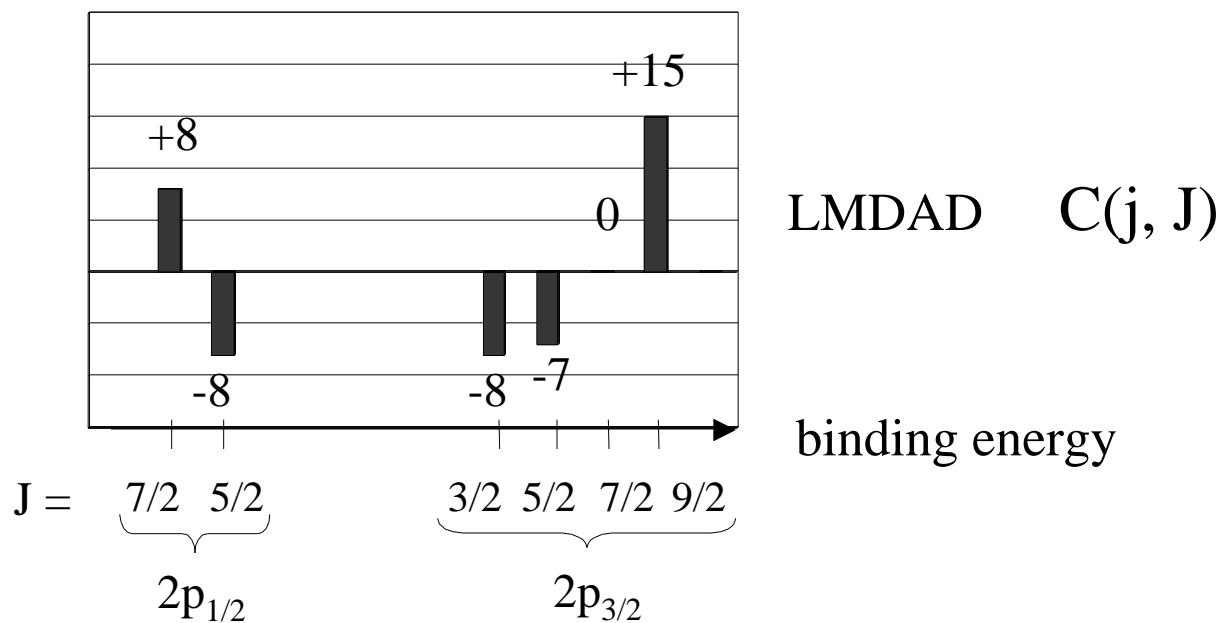
Dichroism within the approximations

difference of two photoelectron spectra for opposite orientations

$$\text{LMDAD} = A_{10} \cdot C(j, J) \cdot D_s D_d \sin(\theta_s - \theta_d)$$

atomic orientation angular momentum coupling dynamics of process
 from $\langle \alpha l | d | 2p \rangle = D_l \exp(i \ddot{A}_l)$
 independent of j and J

apple the shape of the LMDAD-curve is given by $C(j, J)$

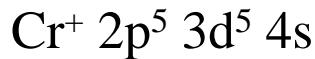


apple LMDAD - patterns: + / - and - / +

apple sum rule $\sum_j C(j, J) = 0$

Different theoretical approaches: LMDAD

one configuration:



Titel:

Erstellt von:

Spectra

Vorschau:

Diese EPS-Grafik wurde nicht gespeichert mit einer enthaltenen Vorschau.

Kommentar:

Diese EPS-Grafik wird an einen PostScript-Drucker gedruckt, aber nicht an andere Druckertypen.

$2\text{p}_{1/2}$ or $2\text{p}_{3/2}$

$3\text{d}^5 (\cdot \dots \cdot) (^6\text{S}) 4\text{s} (\cdot)$

$2\text{p}_{3/2} 3\text{d}^5 (\cdot \dots \cdot) (^6\text{S}) 4\text{s}$

$2\text{p}_{3/2} 3\text{d}^5 (\cdot \dots ,) (^4\text{L}) 4\text{s}$

$2\text{p}_{1/2} 3\text{d}^5 (\cdot \dots \cdot) (^6\text{S}) 4\text{s}$

and

$2\text{p}_{3/2} 3\text{d}^5 (\cdot \dots ,) (^2\text{L}) 4\text{s}$

patterns  angular momentum coupling in ion (multiplet)
sum rules  satellites

Extension of the atomic model

$$\langle \text{Ion} : J | = a \langle 2p_{1/2} 3d^5(^6S) 4s : J | + b \langle 2p_{3/2} 3d^5(^2D) 4s : J | + \dots$$

↳ one configuration approximation

↳ spin-flip allowed

↳ intermediate coupling



numerical determination of dipole matrix elements
(of LMDAD) within a Hartree-Fock (HF) -
calculation

[Michael Martins (FU Berlin)]

Conclusions

- | Cr 2p photoelectron spectra of oriented and aligned free atoms and a thin magnetized layer
 - (| Mn 2p photoelectron spectra of free atoms and a MnO single crystal)
- ÿ importance of 2p-3d Coulomb interactions in 2p photoionization of *bound* 3d-metal atoms
- | atomic multiplet splitting and valence shell recoupling in 2p⁵3d⁵(4s) configurations
- ÿ Cr and Mn can serve as a basis for the discussion of 2p photoelectron and 2p dichroism spectra of 3d transition metal atoms in general
- (| Combination of LMDAD and LD: complete characterization of dynamics of process, extraction of dipole matrix elements, of dipole amplitudes and phases)