

Soft-landing of Radioactive Probes on Clean Metal Surfaces and at Interfaces

IS 425

ASPIC Group

Hahn-Meitner-Institut, Berlin

Free University Berlin

**ISOLDE Workshop and Users
meeting 2007/2008**

17-19.December.2007



SF4



- **Hahn-Meitner Institute**

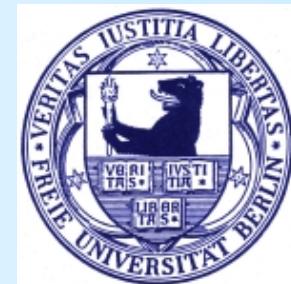
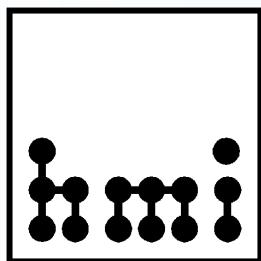
H. H. Bertschat[†], H. Granzer, H. Haas,
Y. Manzhur, K. Potzger, S. Seeger,
A. Weber, W.-D. Zeitz

- **Freie Universität Berlin**

W. D. Brewer, P. Imielski,
M. J. Prandolini, J. Schubert

- **The ISOLDE Collaboration**

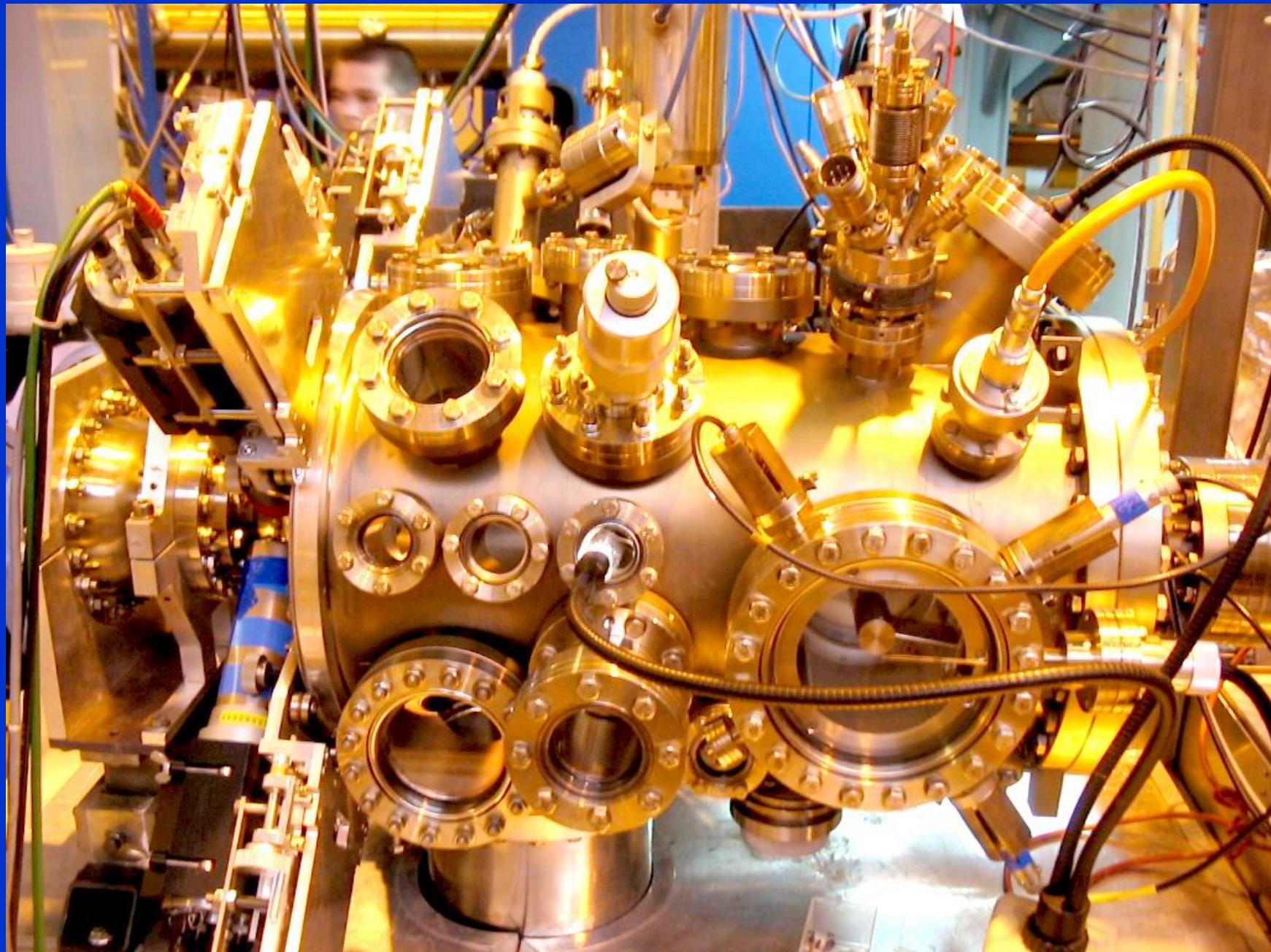
D. Forkel-Wirth, M. Dietrich,
T. Agne, K. Johnston, and many more



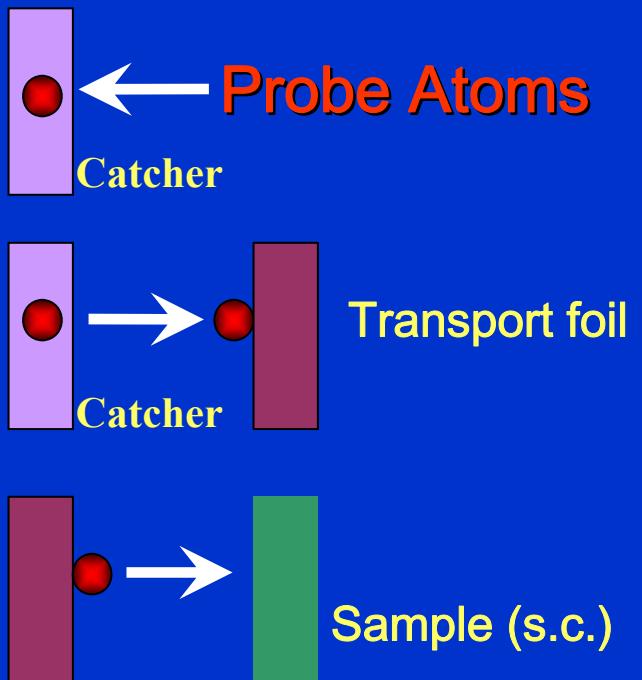
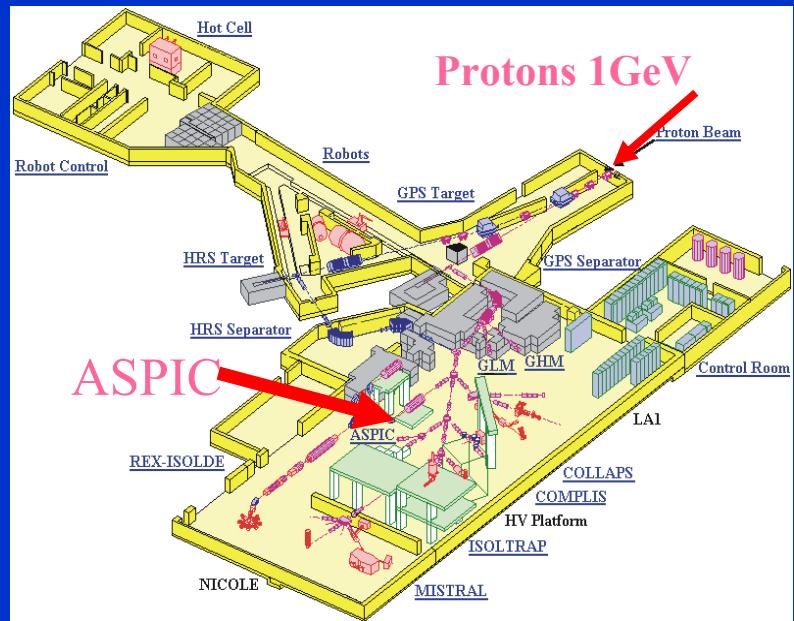
Picture of the Sample Holder



$$B_{\text{ext}} \sim 0.01 \text{ T}$$

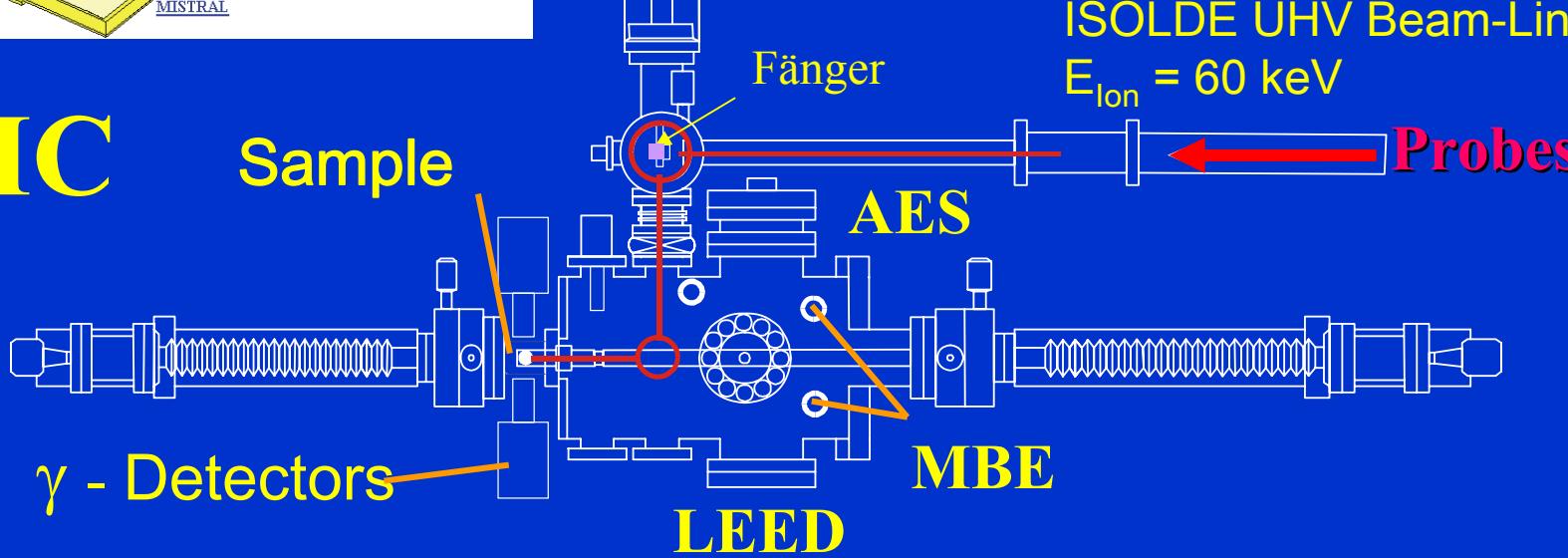


Soft-landing of Probe Atoms



ASPIIC

Sample



Adsorption Sites of Probe Atoms

^{111}Cd Isotopes on s.c. Ni(001)

Site in Top Layer

NN = 8

Kink Site

NN = 6

Site on Surface

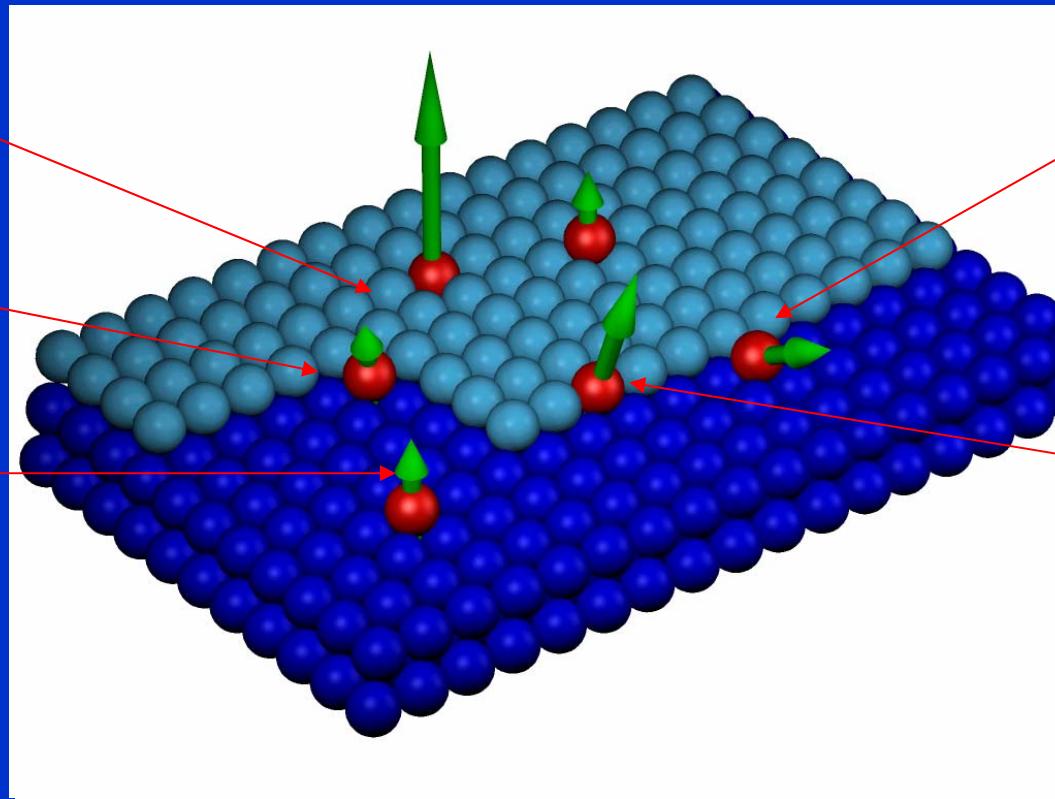
NN = 4

Site at Edge

NN = 5

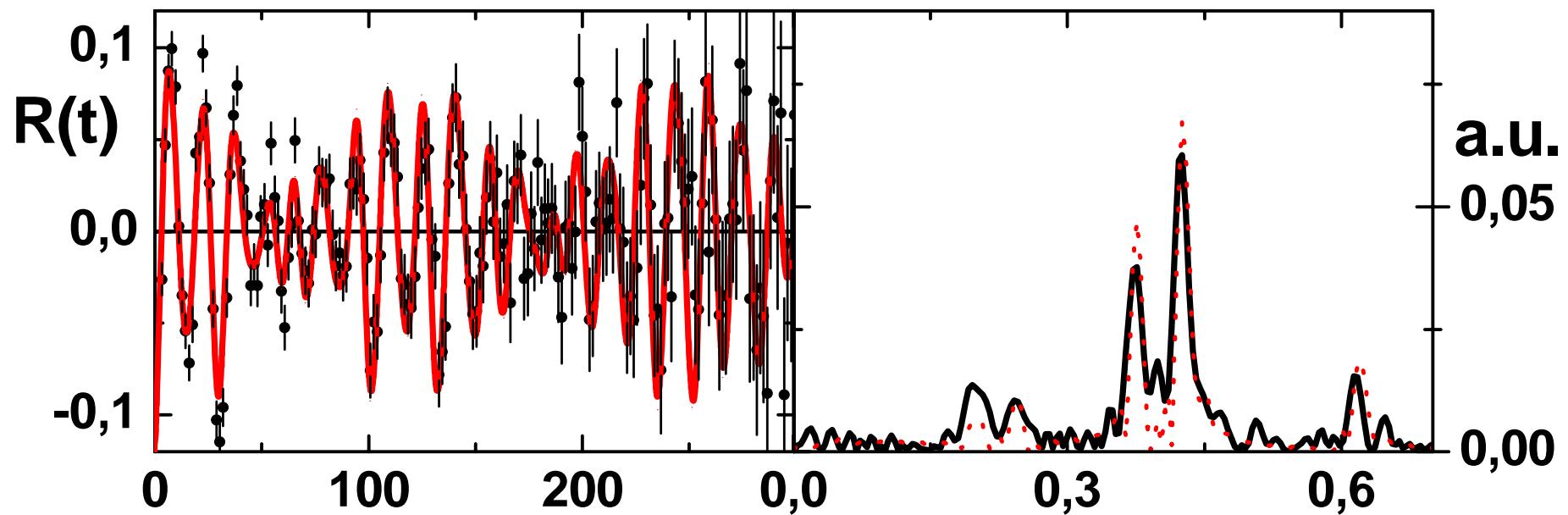
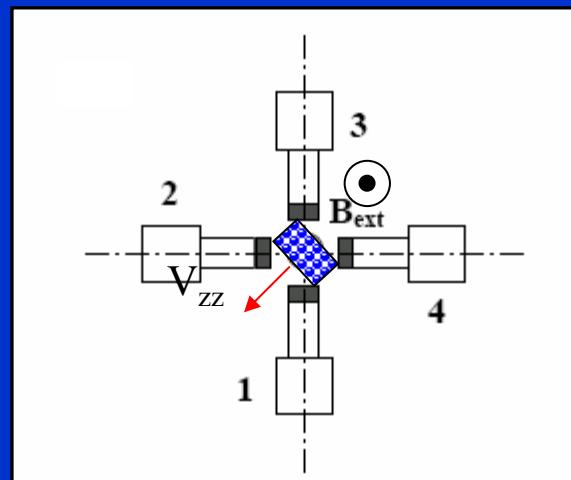
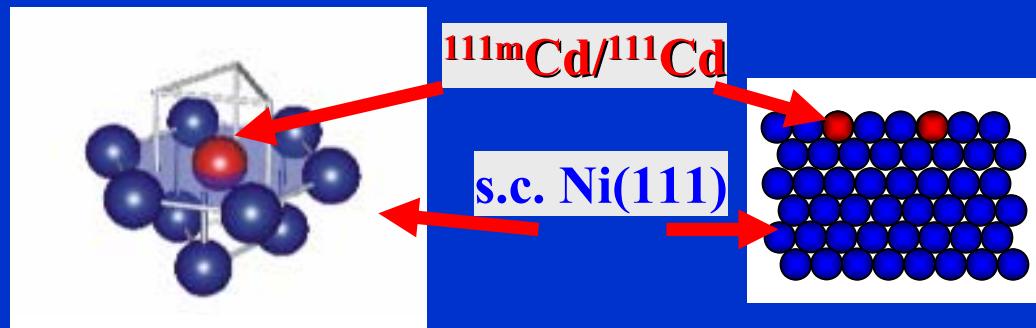
Site in the Edge

NN = 7



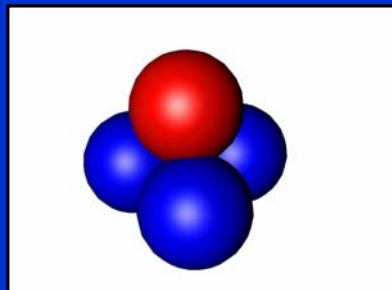
The electric field gradient serves as “fingerprint”
for atomic sites

NN = 9



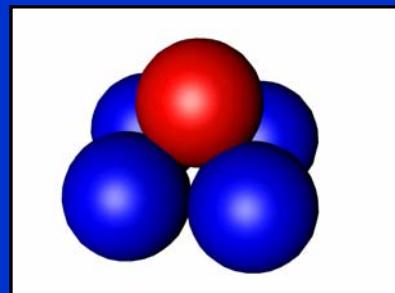
Magnetic Hyperfine Fields of Cadmium on Selected Sites on Ferromagnetic Nickel

$\text{NN} = 3: (+) \ 16.0 \ (3) \text{ T}$



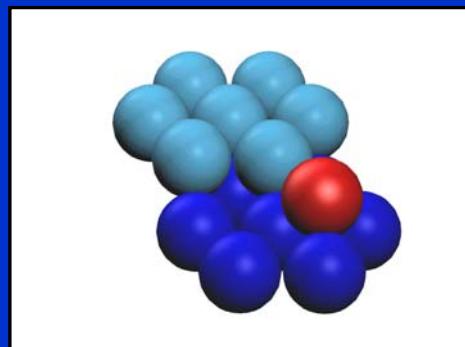
Ni(111)

$\text{NN} = 4: (+) 7.3 \ (2) \text{ T}$



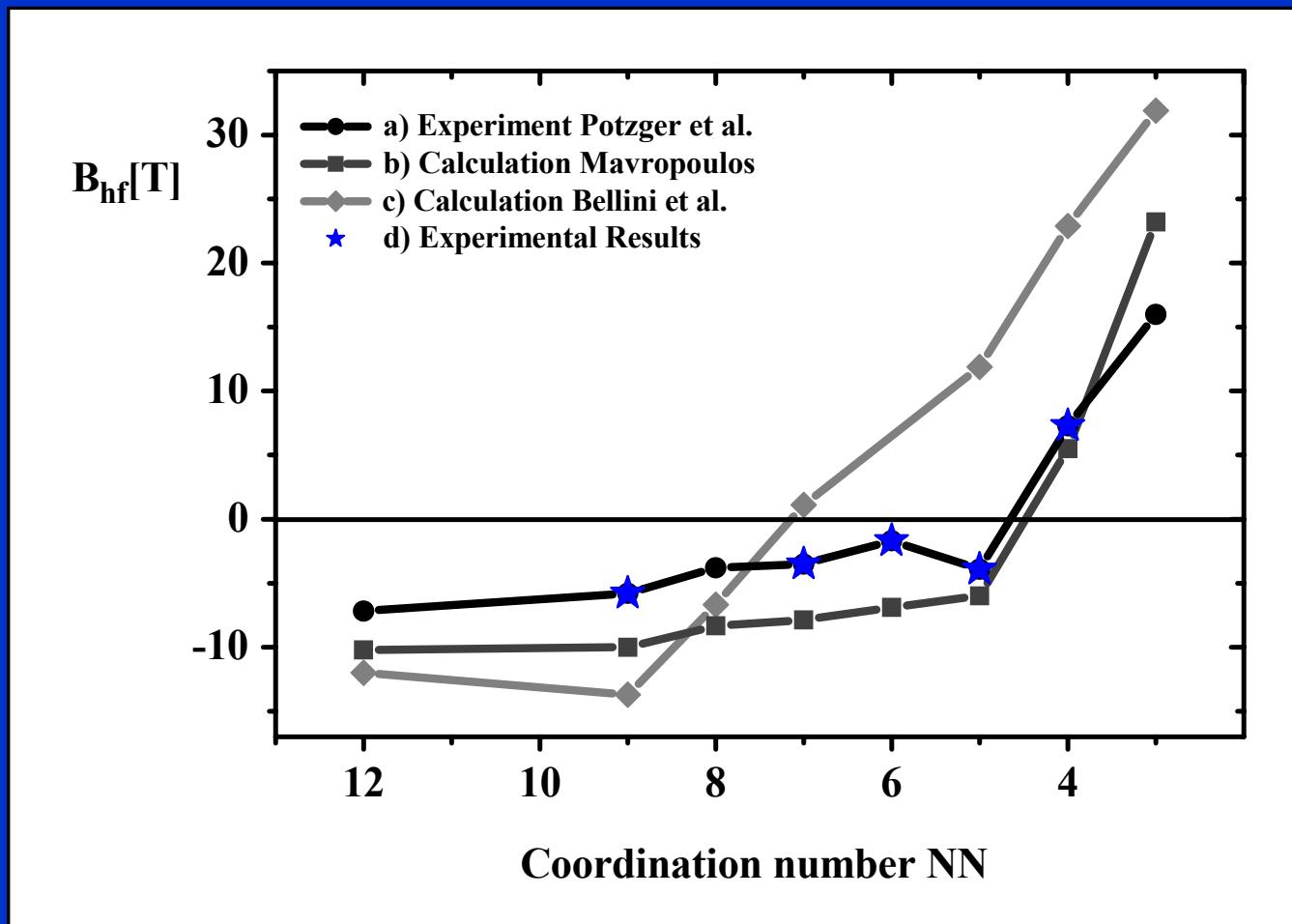
Ni(001)

$\text{NN} = 4: (+) 8.1 \ (5) \text{ T}$



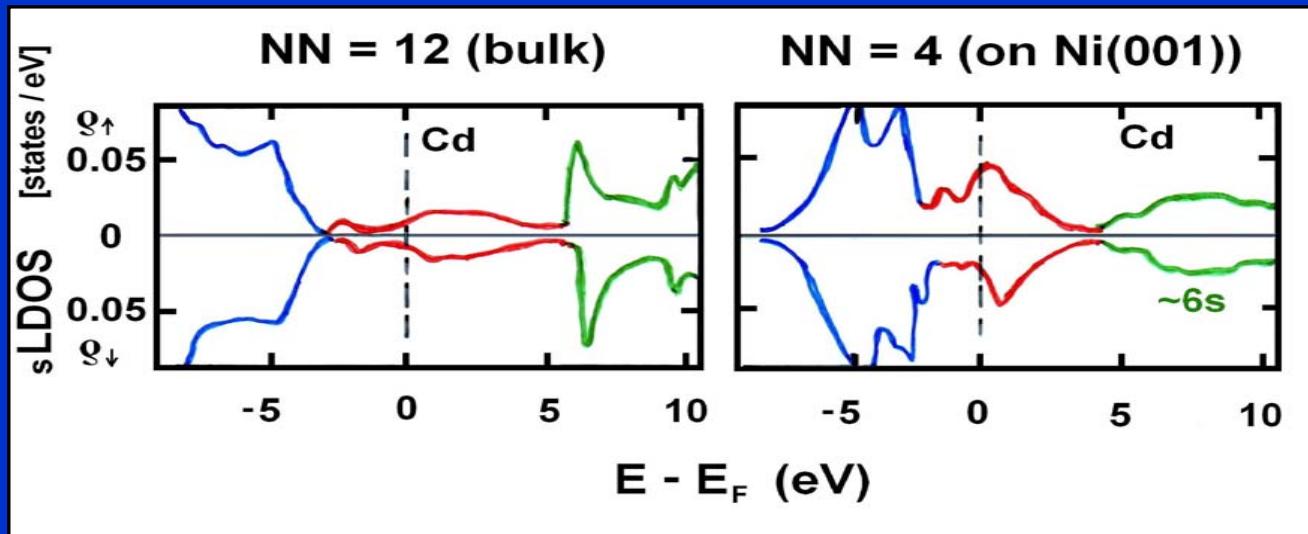
Ni(111)

Results and Comparison with Theoretical Calculations



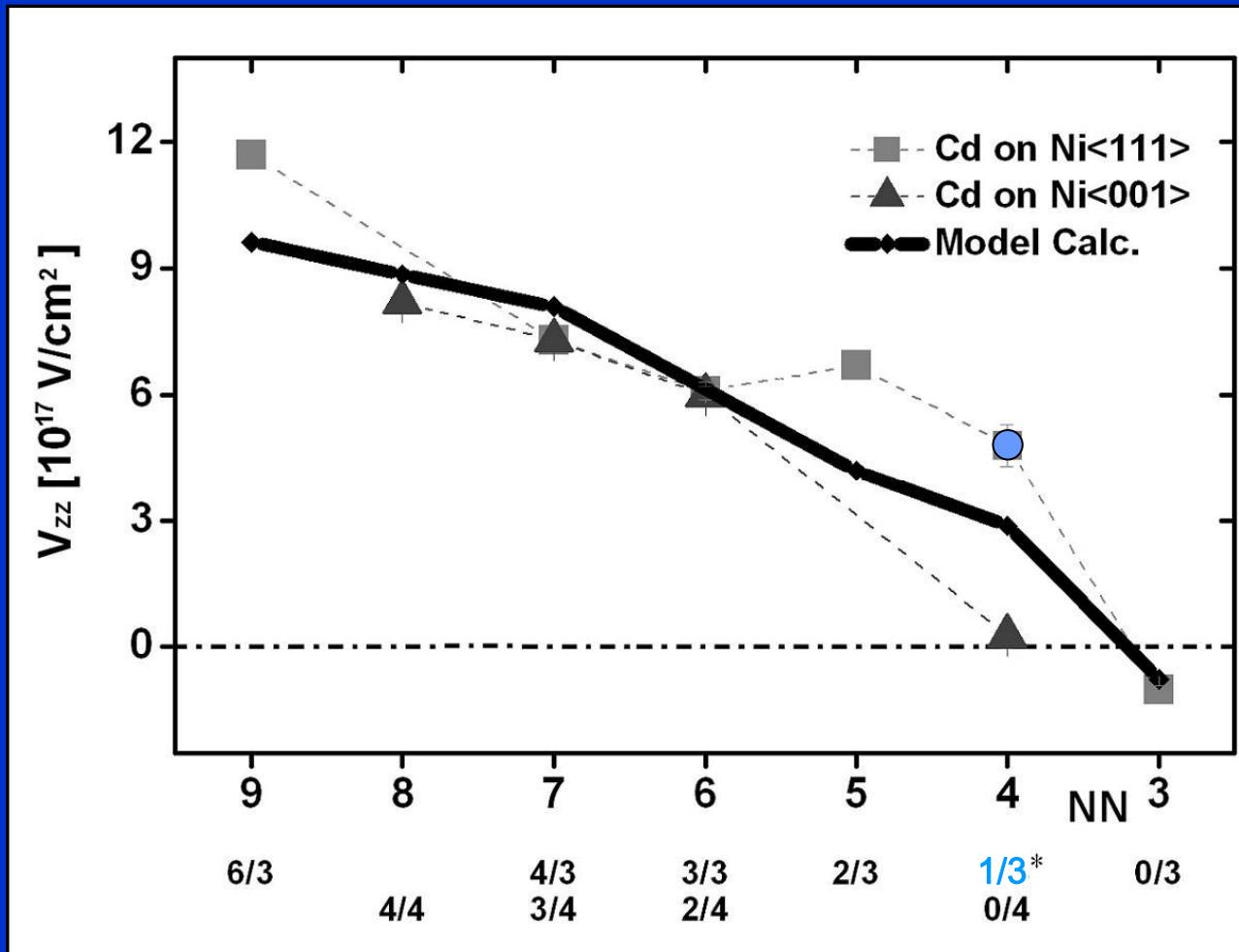
- V. Bellini, S. Cottenier, M. Çakmak, F. Manghi, and M. Rots, Phys. Rev. B **70** (2004) 155419
Ph. Mavropoulos, J. Phys.: Condens. Matter **15**, (2003) 8115
K. Potzger, A. Weber, H. H. Bertschat, and W.-D. Zeitz, Phys. Rev. Lett. **88** **24** (2002): 247201.

Level Densities of s-Electrons at Isolated Cadmium Atoms in and on Nickel



Ph. Mavropoulos, J. Phys.: Condens. Matter **15** (2003) 8115
Kanamori et. al. Hyp. Int. **9** (1981) 363

Electric Field Gradients at Cadmium Atoms on Different Sites on Nickel Surfaces



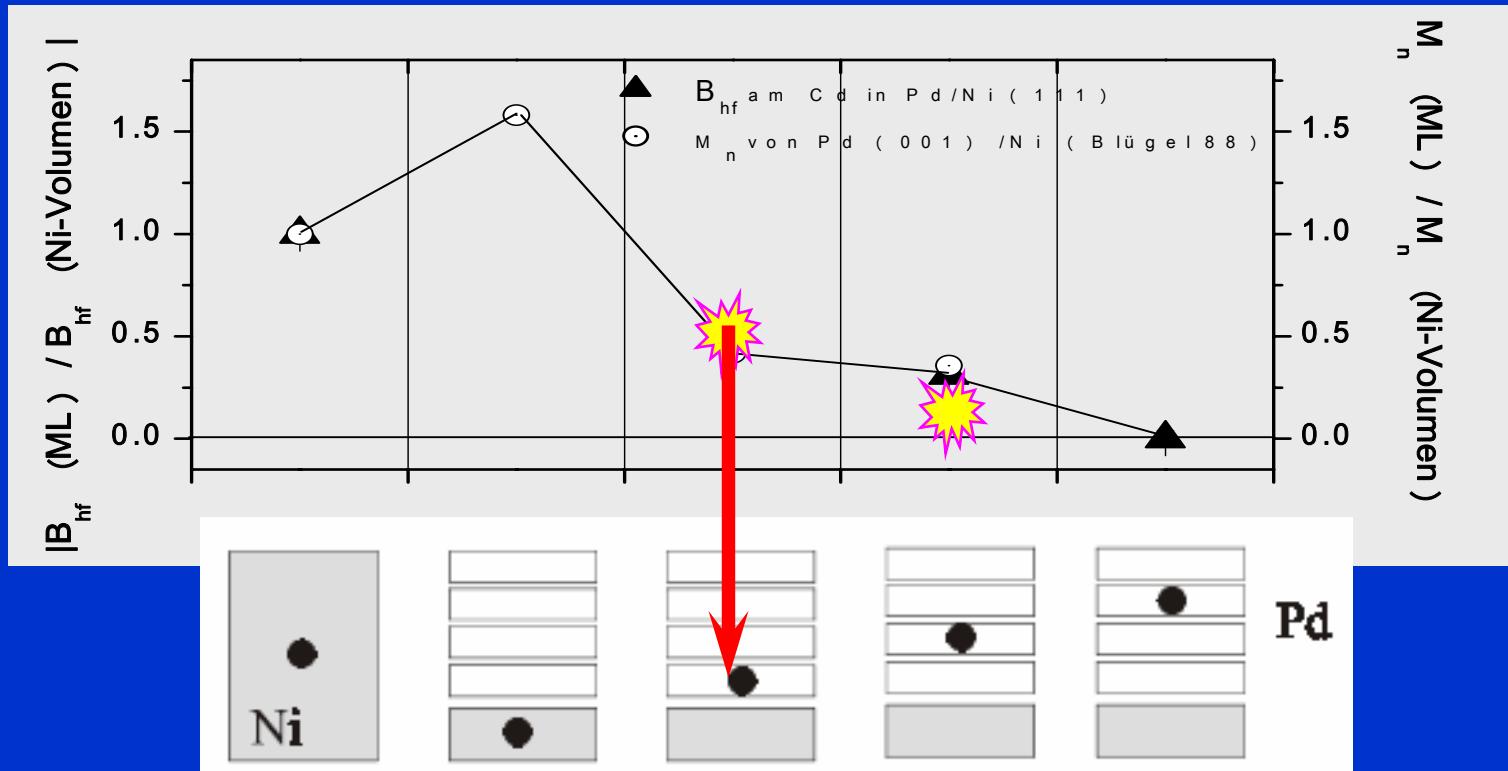
Potzger, K. PhD thesis of Freie Universität Berlin, 2001.

Cottenier, S., Bellini, V., Cakmak, M., Manghi, F., and Rots, M.. Phys. Rev. B 70 (2004): 155418.

Prandolini M. et al., Appl. Phys Lett. 85 (2006) 76



B_{hf} at Cd in Pd monolayers near the Ni/Pd interface in comparison to the predicted magnetic moments in Pd



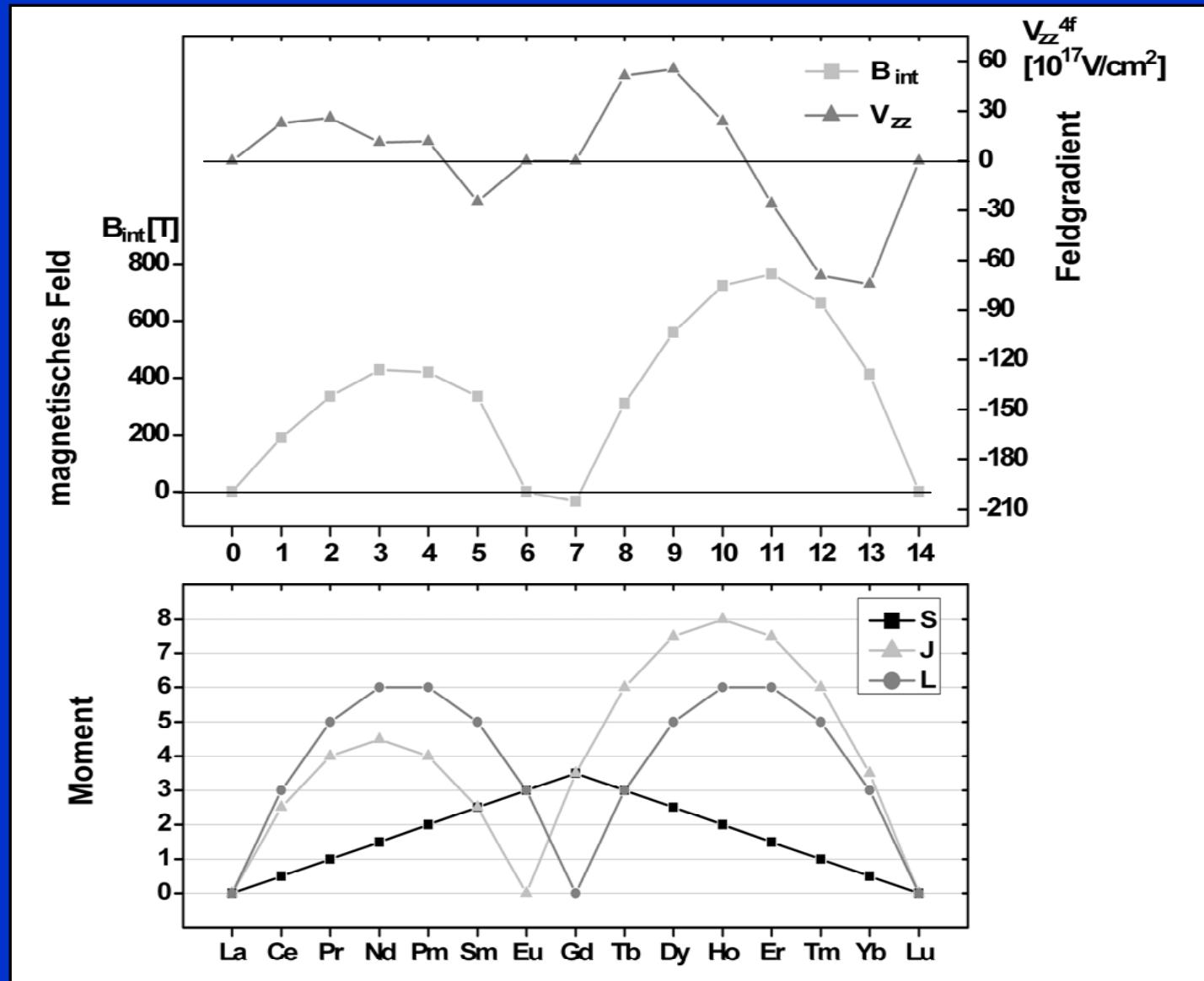
The dots represent the respective positions of the Cd guest atoms.

Properties of Rare Earth Elements

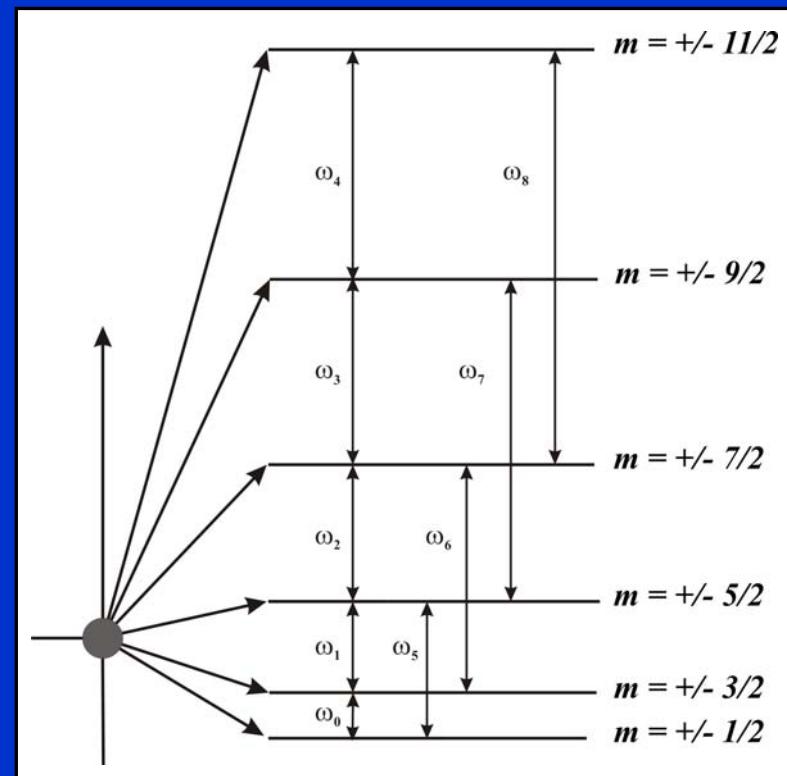
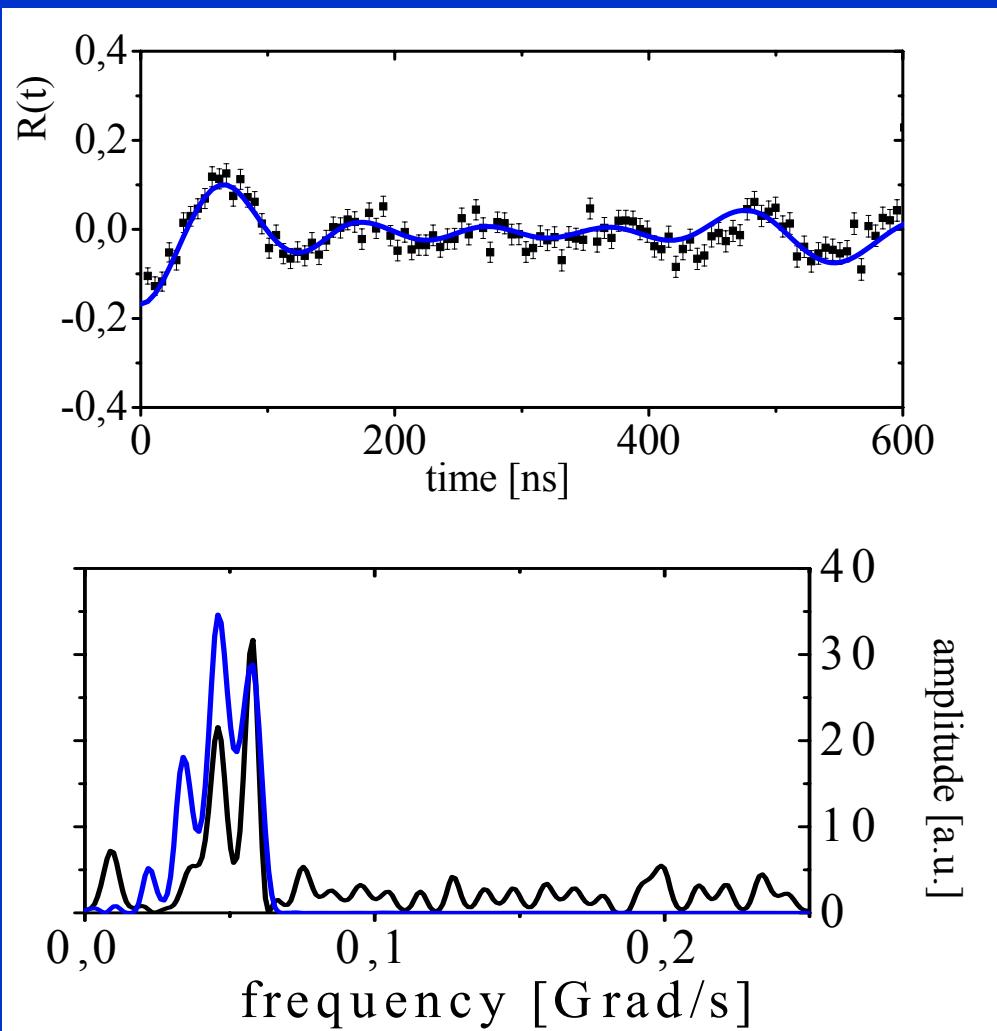
Field
gradients,

Magnetic
Hyperfine
Fields,

and
Moments
in free
rare earth
elements



^{149}Eu in ZnO – quadrupolar interaction



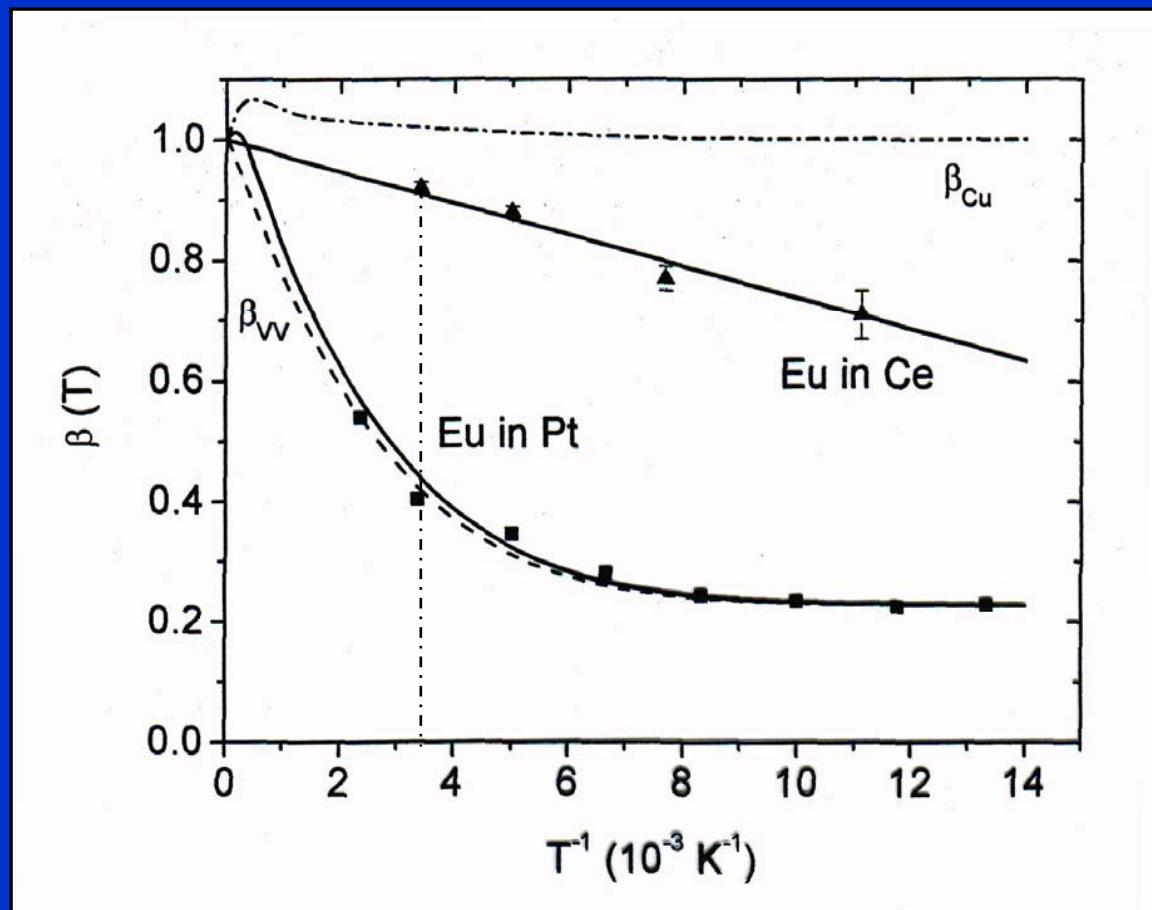
Seven different frequencies

$$\omega_0 = 0.0115 \text{ Grad/s}$$

Eu in Cerium and Platinum

The paramagnetic enhancement factor $\beta(T)$ may be used to determine the valence. This factor is defined as the ratio of the measured hyperfine field to an externally applied field B_{ext} .

$$\beta(T) = B_{\text{total}}/B_{\text{ext}}$$

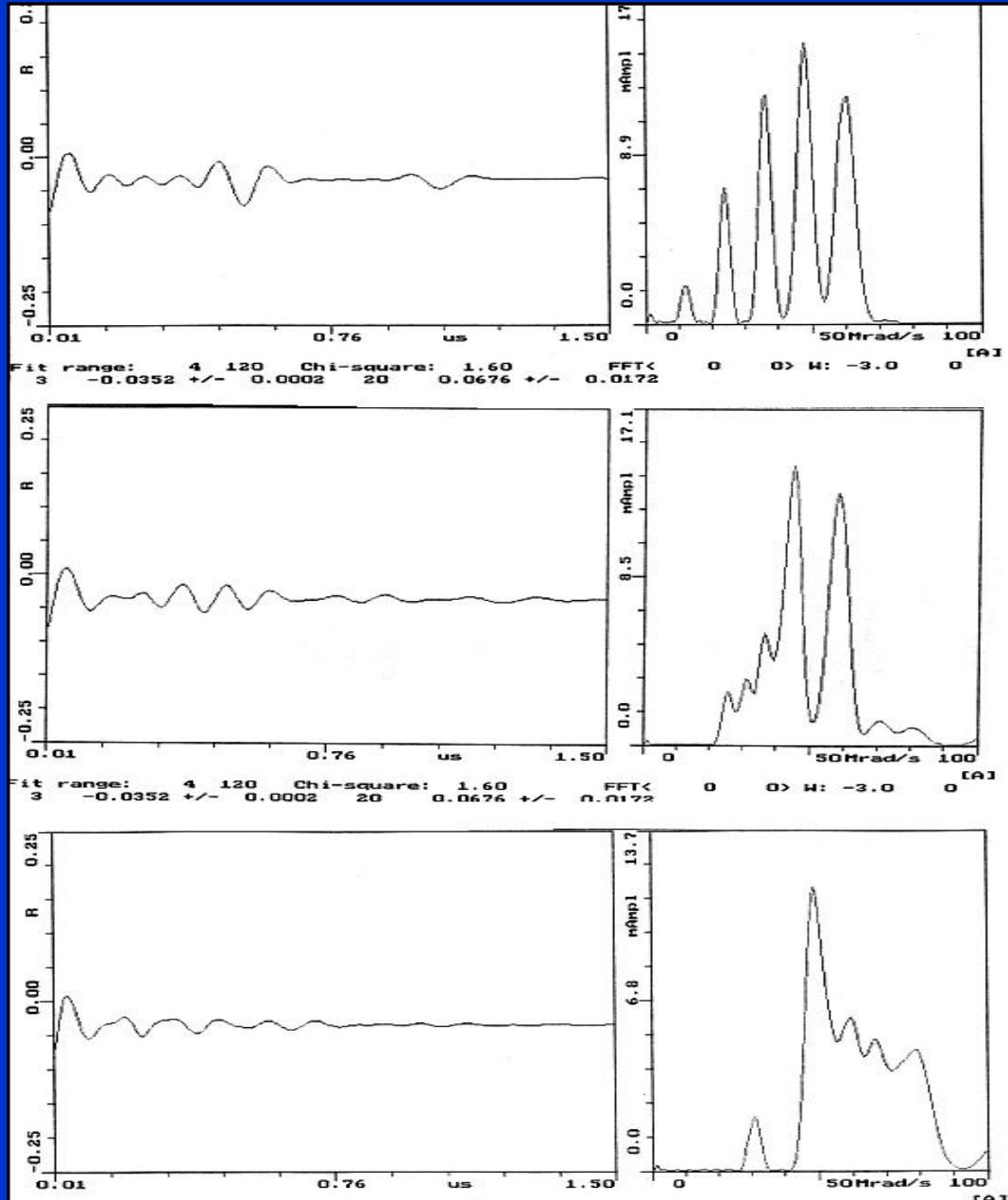


Simulations: combined interaction

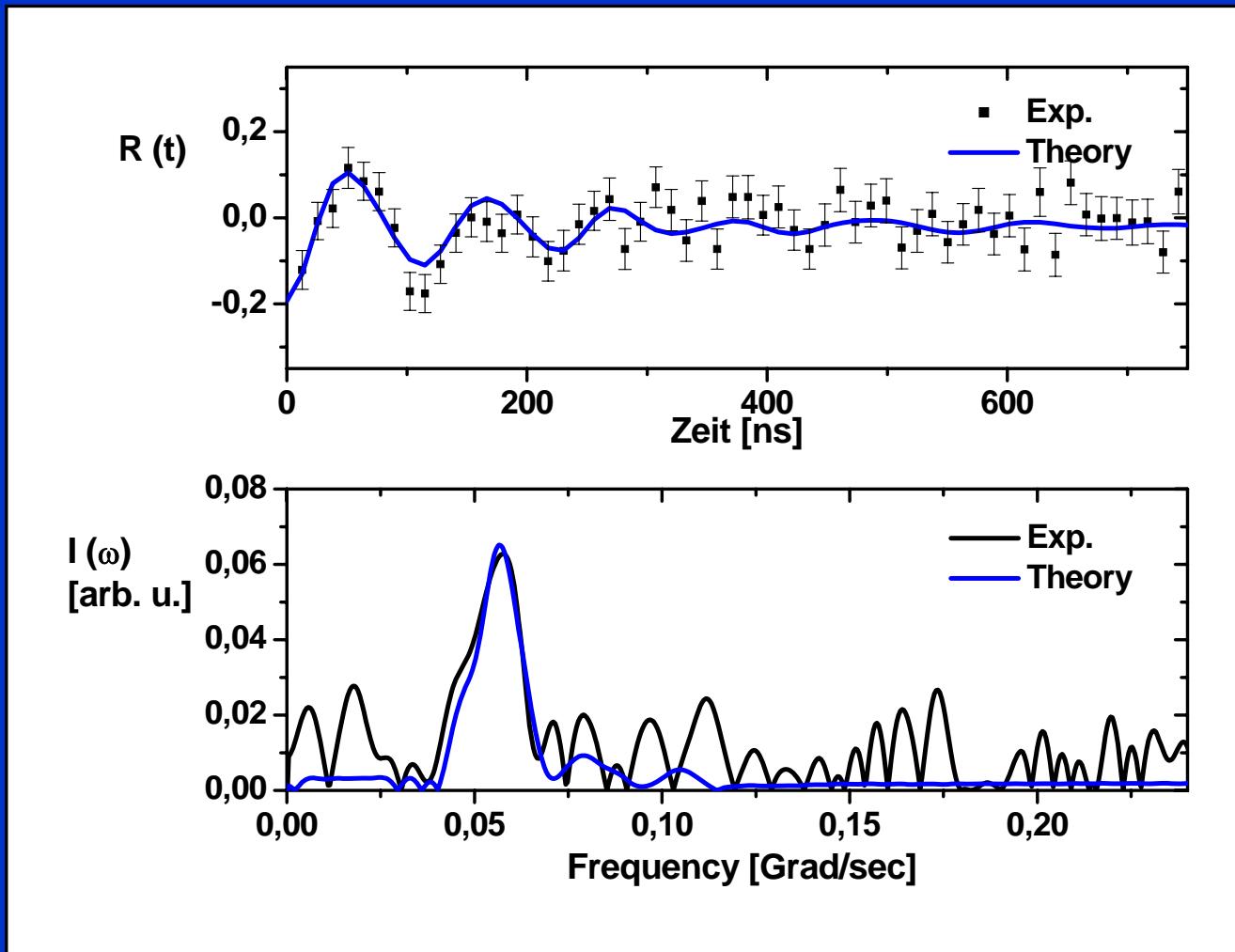
There is a difference in $\beta(T)$ for Eu^{2+} and Eu^{3+} at the room temperature:

$$\beta(\text{Eu}^{3+}, \text{RT}) = 0.4$$

$$\beta(\text{Eu}^{2+}, \text{RT}) = 0.9$$



^{149}Eu in ZnO, with external field



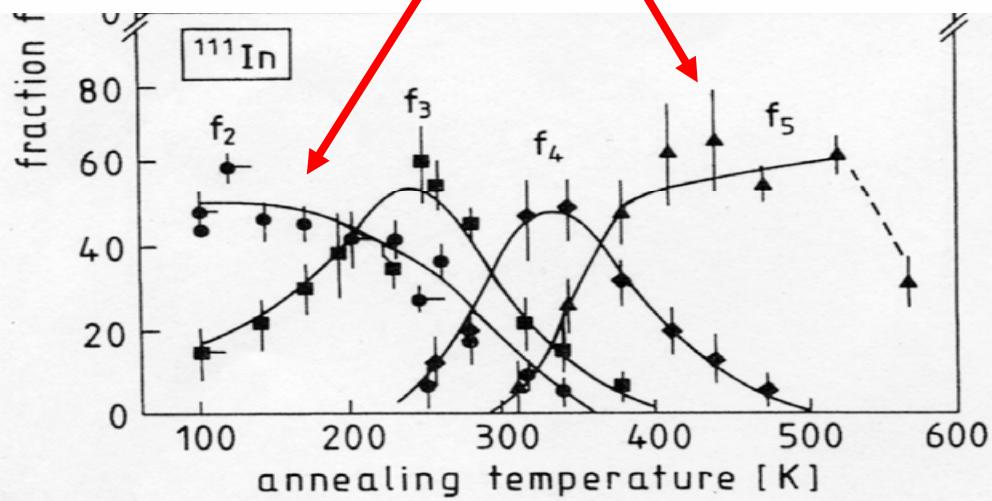
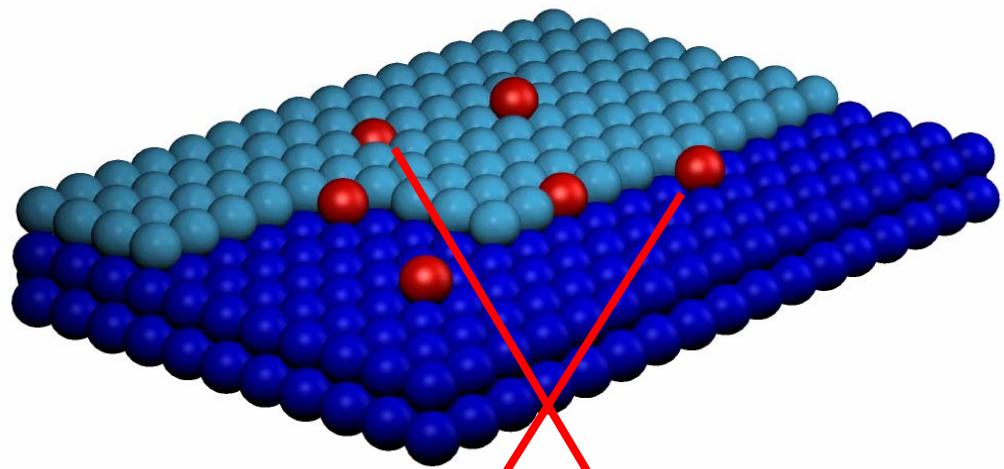
Fit agrees with the assumption of Eu^{2+}



Conclusion

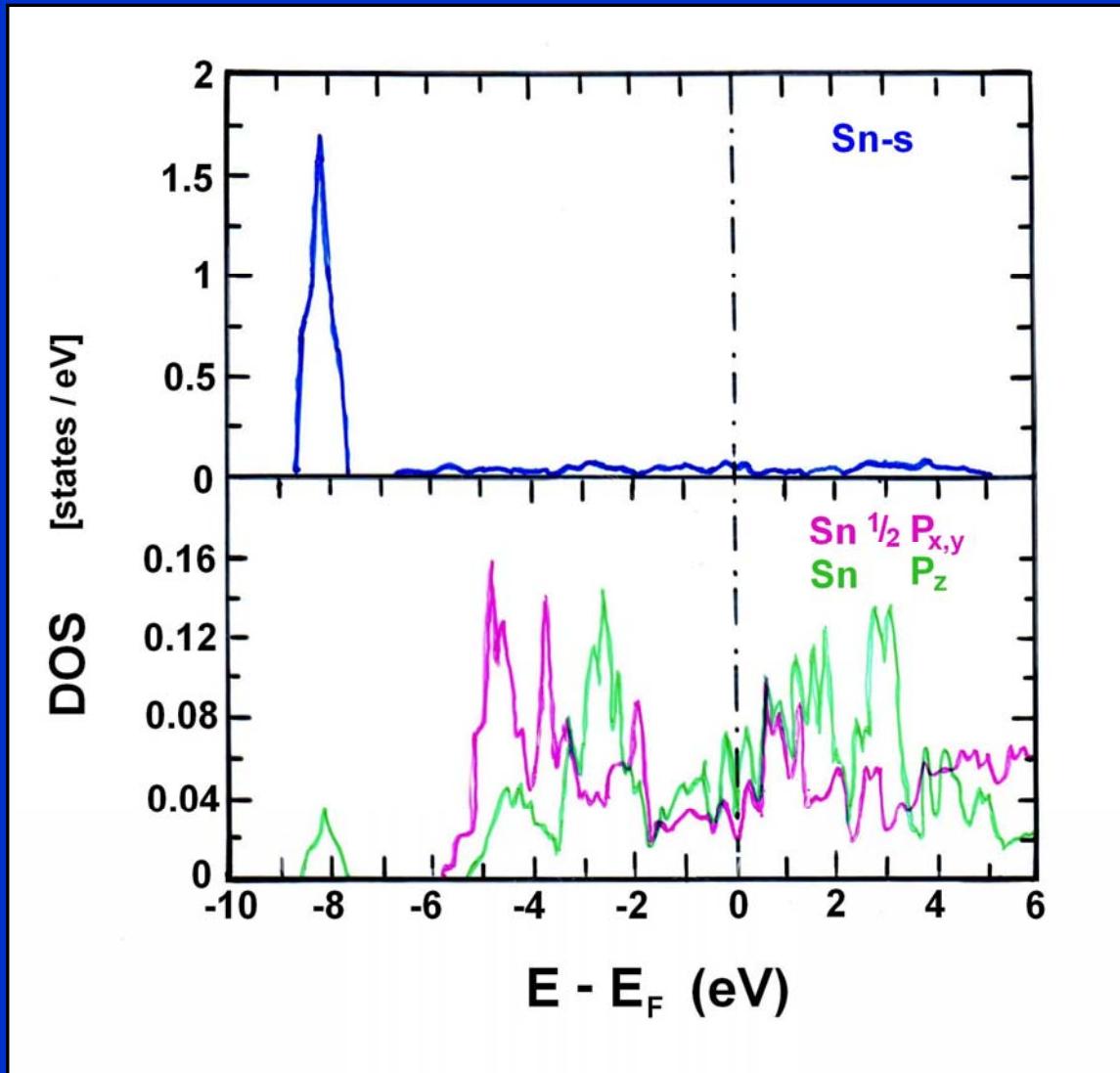
- The magnetic hyperfine fields and electric field gradients of Cadmium on different sites on Nickel surfaces have been measured.
- The magnetic hyperfine fields derive from a polarisation in the s-conduction band.
- The electric field gradients are a reflection of the population in the sublevels (p_x , p_y , p_z) of the p-band.
- Magnetic and quadrupolar interactions utilising the $11/2^-$ levels in ^{147}Eu und ^{149}Eu have been measured.
- The combined interaction at isolated Eu-atoms in ZnO is in agreement with divalent Europium.

Preparation of Sites of Probe Atoms

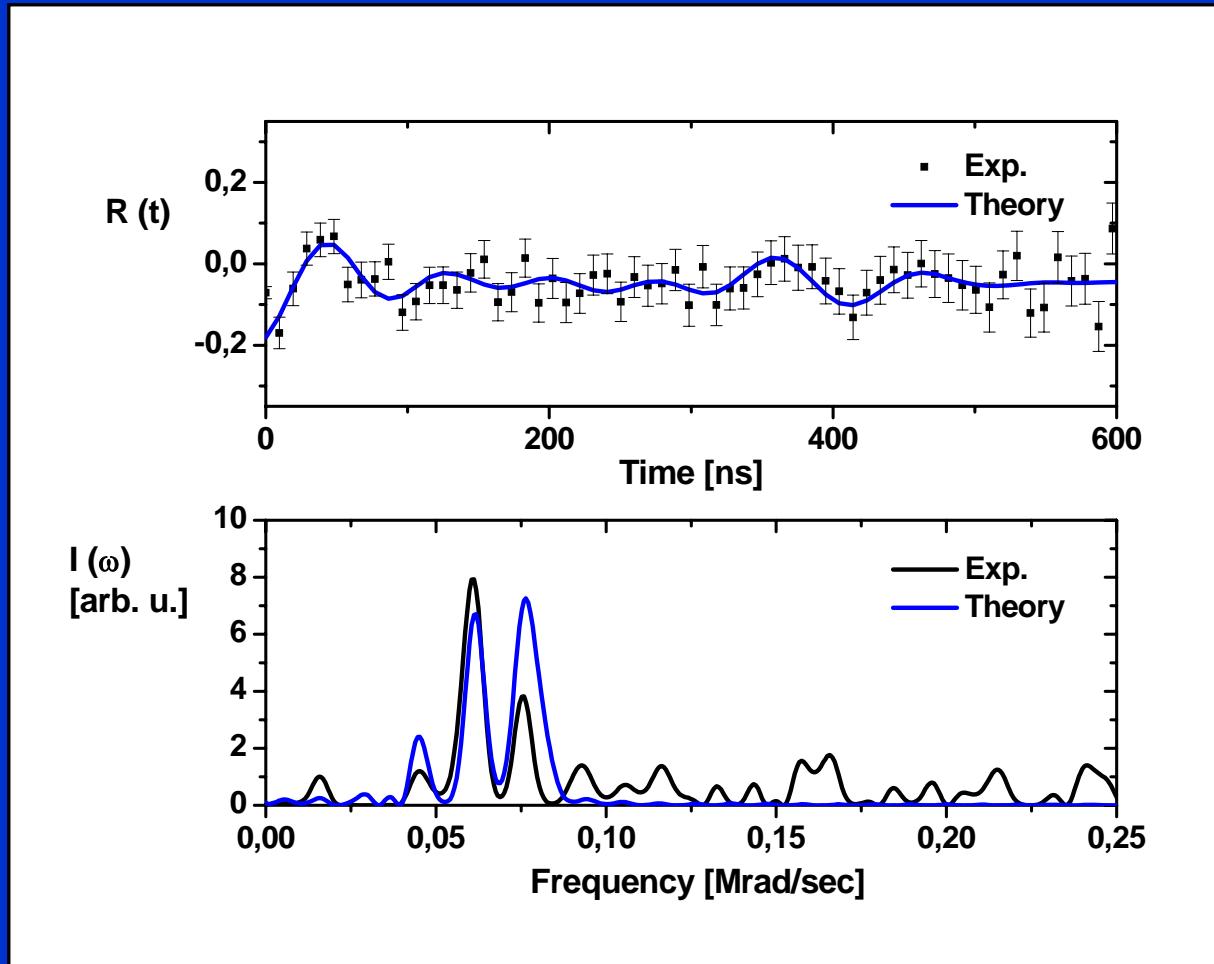


$^{111}\text{In}/^{111}\text{Cd}$ on Pd(111)
E. Hunger Ph.D. thesis (1989)

Level Densities of Tin on Nickel



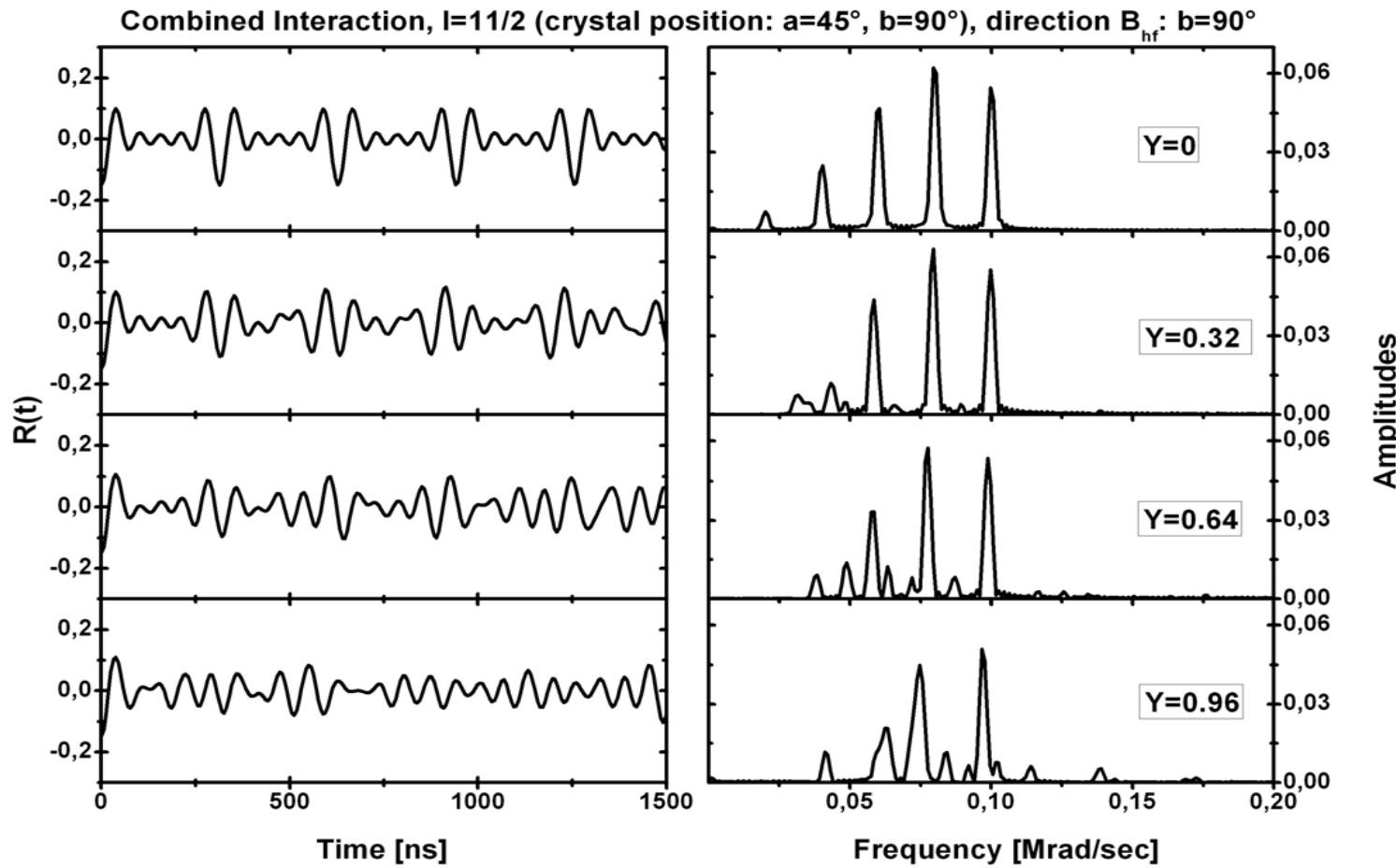
^{147}Eu probe atoms on Pd(111) surface



^{147}Eu in Pd(111) layer
Temperature: 300 K



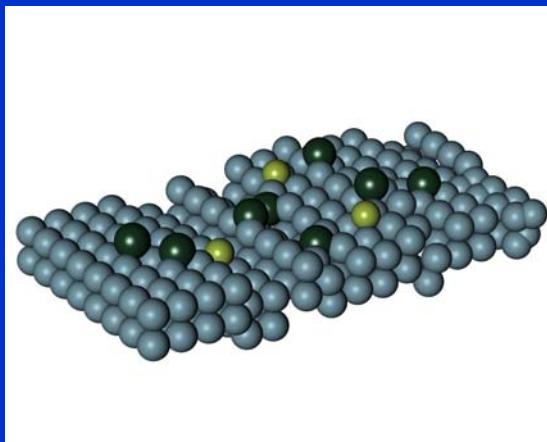
Simulations: combined interaction



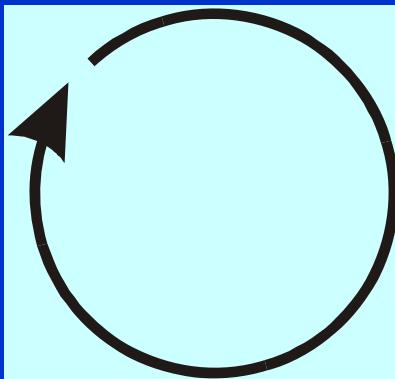
The parameter $Y = \omega_L/\omega_Q$ is the ratio of magnetic to quadrupolar interaction frequencies.



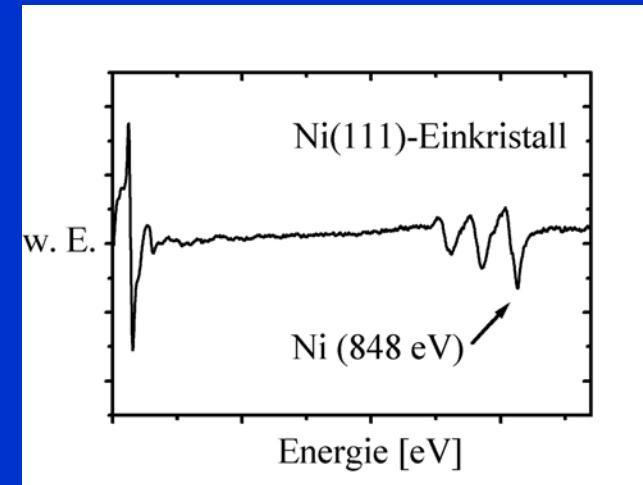
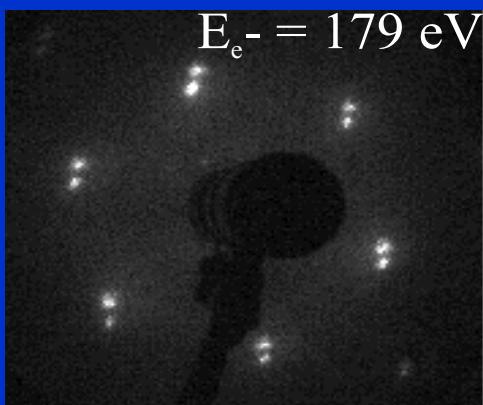
Preparation of Samples



Sputter

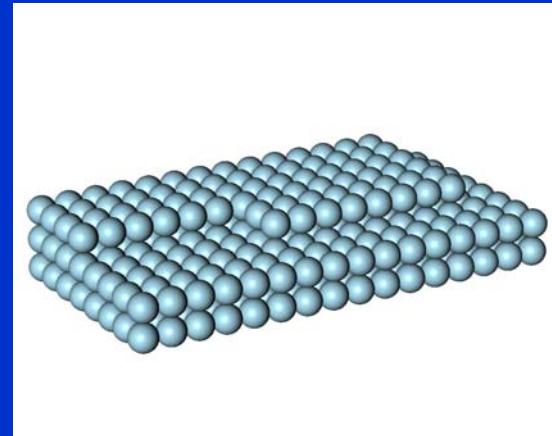


Control: LEED



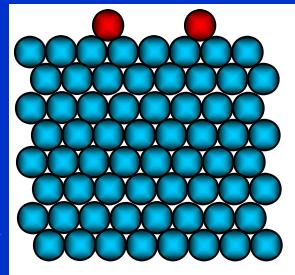
Control: AES

Annealing



Pictographs of the Ni/Pd experiments:

$^{77}\text{Br}/^{77}\text{Se}$

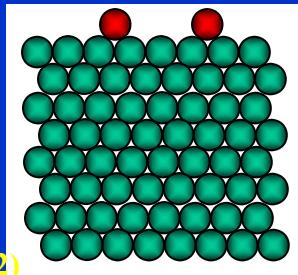


s.c. Ni

Surface
Magnetism

PRL 77, 4261 (1996)

PRL 88, 247201 (2002)



s.c. Pd

Theory: Mavropoulos et al., PRL 81, 1505 (1998)

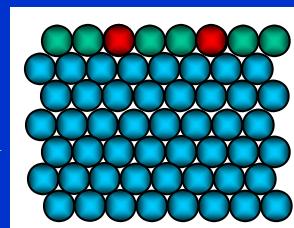
J. Phys.: Condensed Matter 15, 8115 (2003)

Magnetic Polarization of Palladium

$^{100}\text{Pd}/^{100}\text{Rh}$

Pd

s.c. Ni



$^{111\text{m}}\text{Cd}/^{111}\text{Cd}$

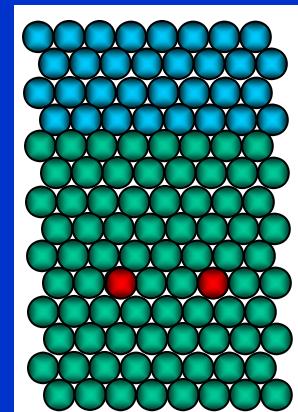
Ni

s.c. Pd

Ultra-thin Palladium on Ni

PRL 80, 2721 (1998)

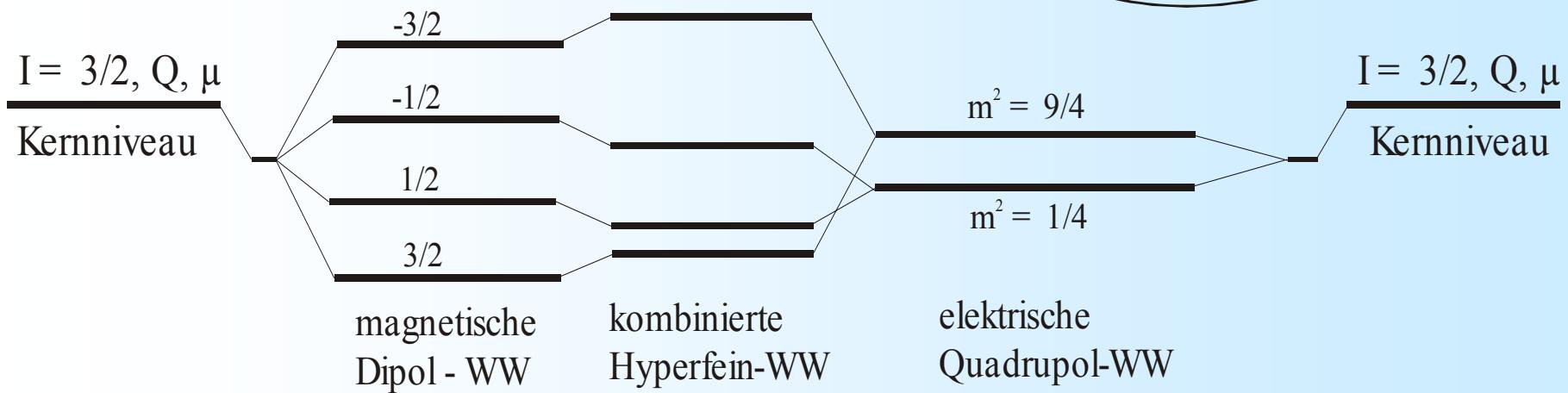
(Surface Science Lett. 442 L 1001 (1999))



Ultra-thin Nickel on Pd

PRL 78, 342 (1997)

Hyperfine interaction



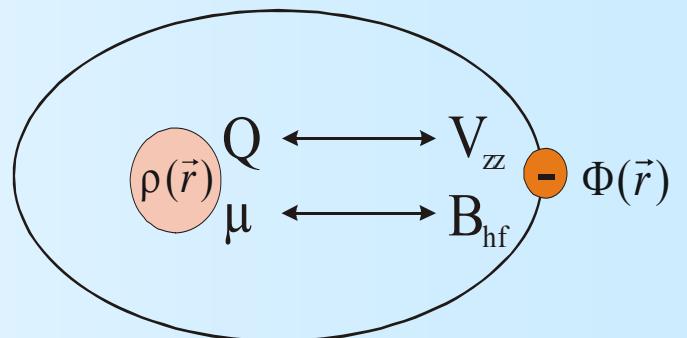
$$\Delta E = -g\mu_N \cdot \mathbf{B}_{hf}$$

$$\omega_L = -g\mu_N / \hbar \cdot \mathbf{B}_{hf}$$

$$\Delta E = (V_{zz}, B_{hf}, \dots)$$

$$\omega_c = f(\omega_Q, \omega_L)$$

Das Atom



$$m^2 = 9/4$$

$$I = 3/2, Q, \mu$$

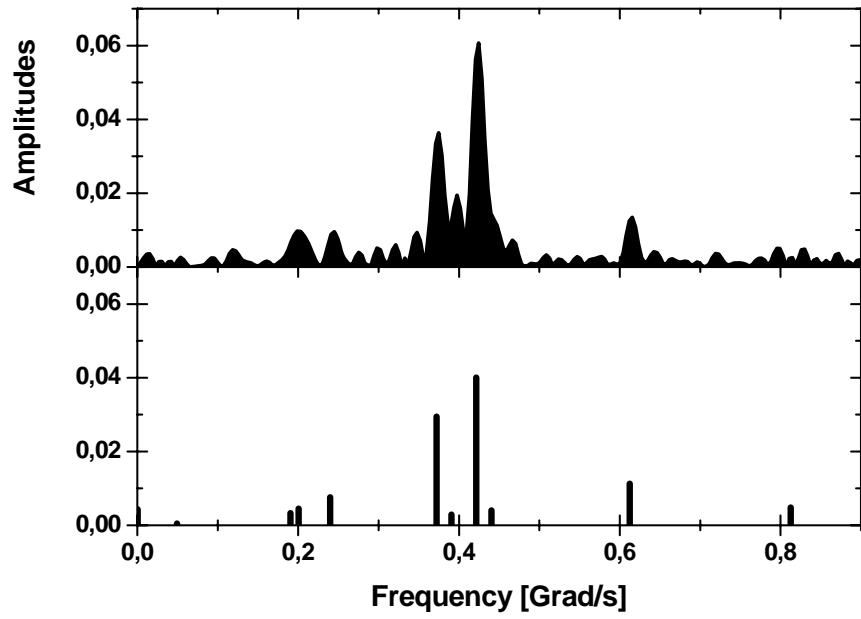
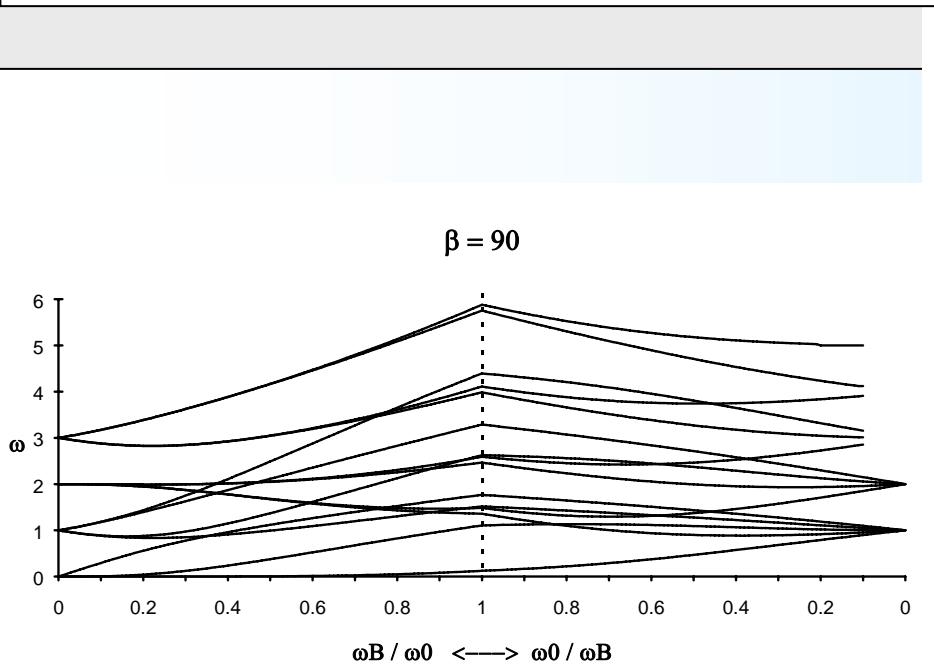
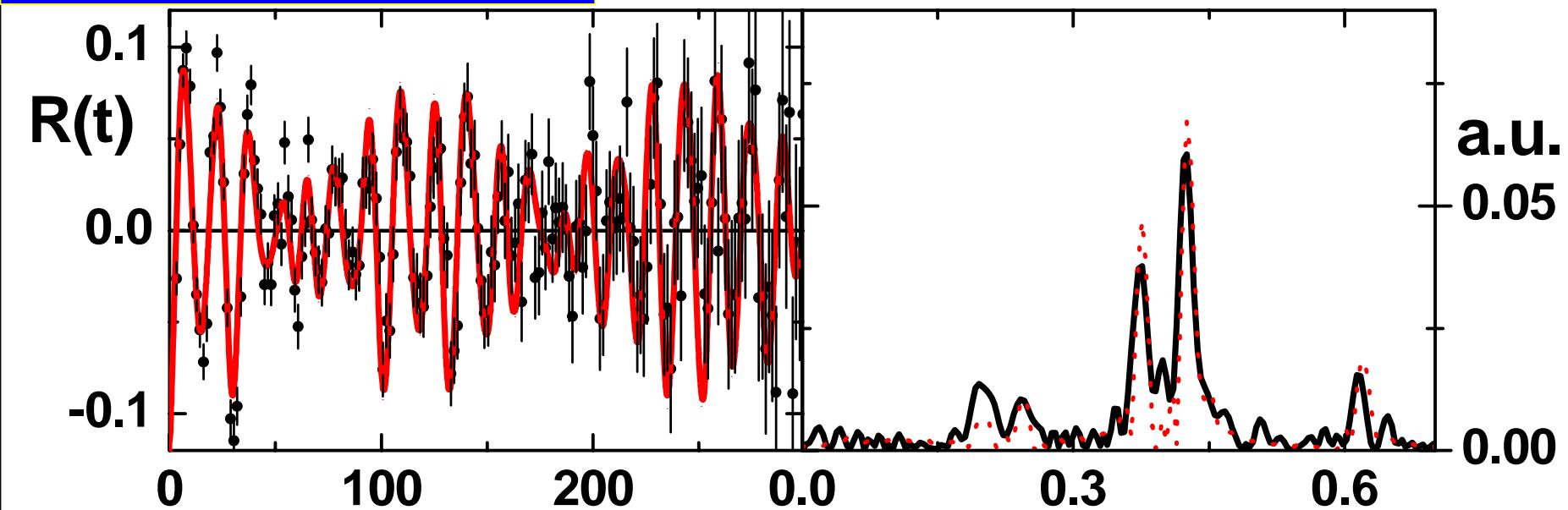
$$m^2 = 1/4$$

Kernniveau
Kernniveau

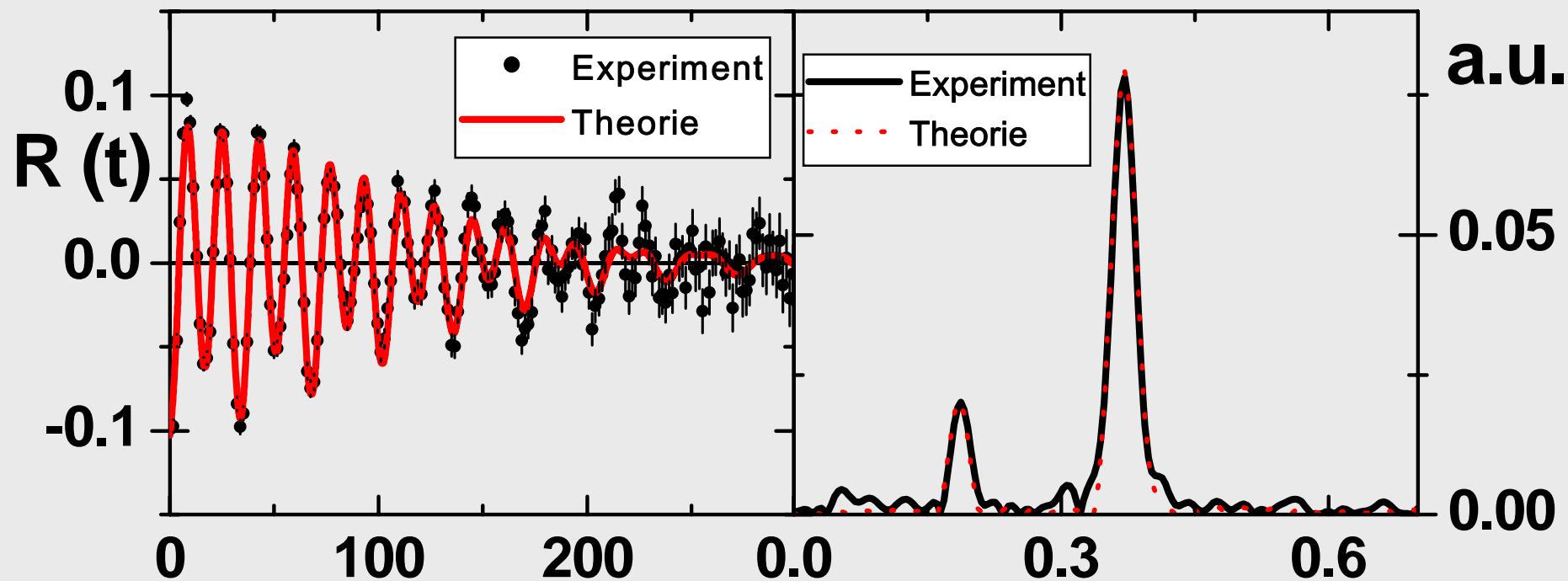
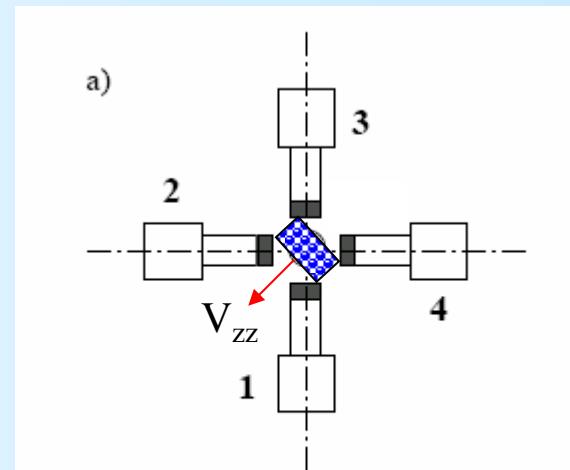
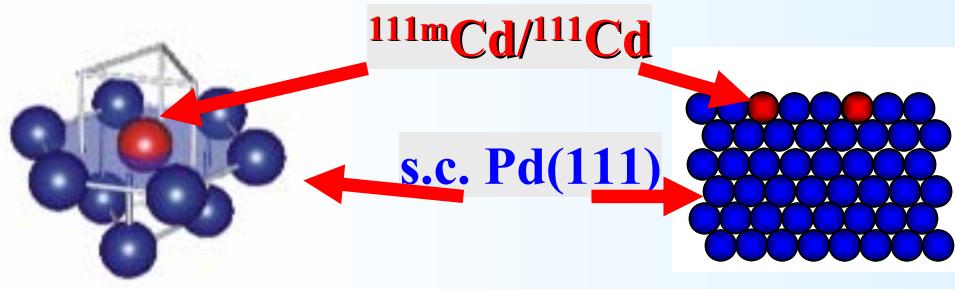
$$\Delta E = \frac{3}{4} \frac{|m_i^2 - m_j^2|}{I(2I-1)} eQ \cdot \mathbf{V}_{zz}$$

$$\omega_Q = \frac{eQ}{4I(2I-1)\hbar} \cdot \mathbf{V}_{zz}$$

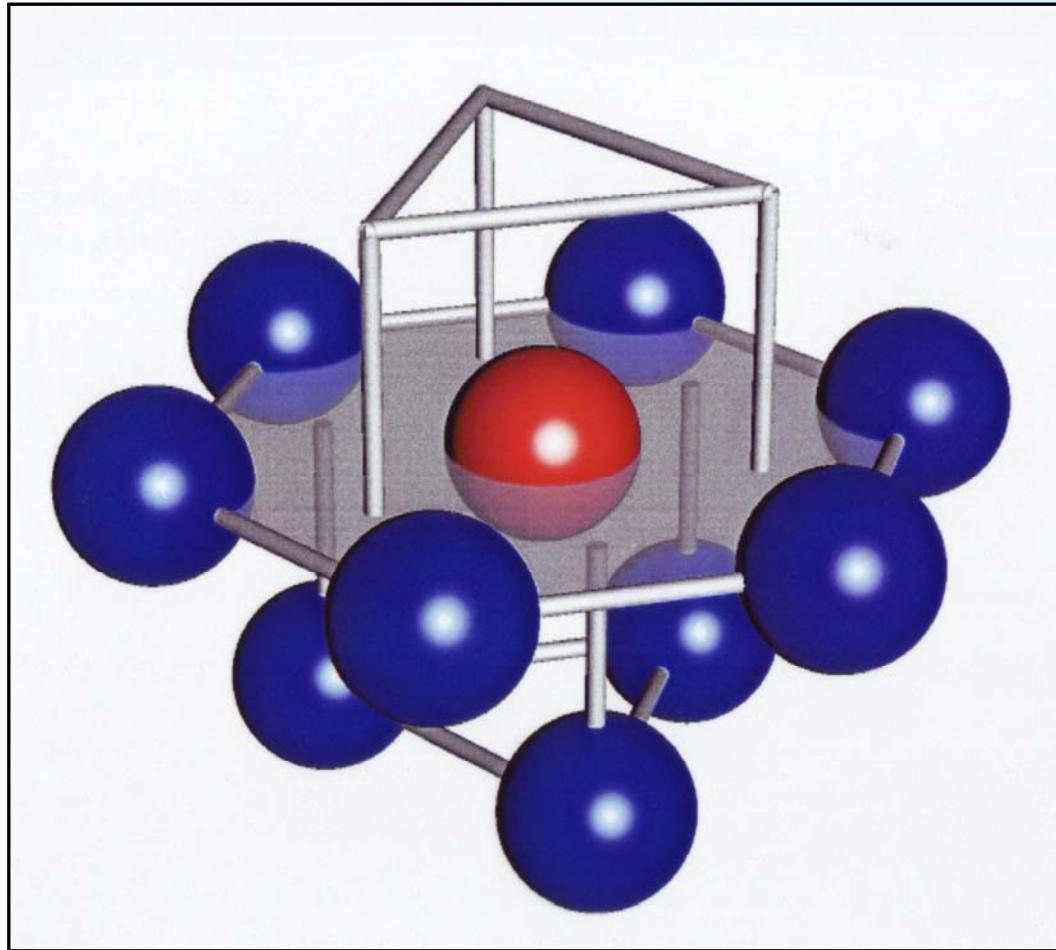
NN=9 $^{111}\text{In}/^{111}\text{Cd}$ auf Ni(111)



NN = 9



Coordination Number of a Guest-Atom on the Ni(111) Surface



Lander Molecule on the Cu(111) Surface*

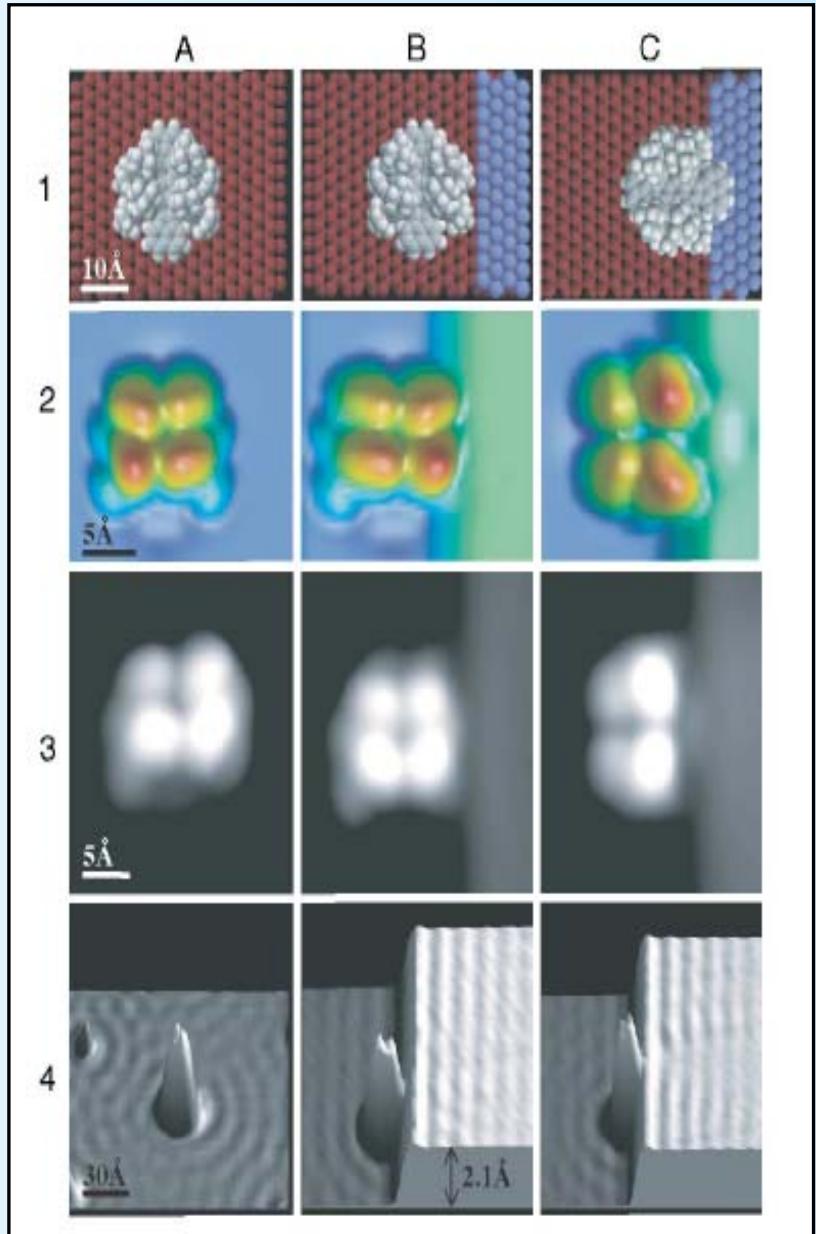
(A) Molecule on a free surface,
(B) isolating side at (100) step,
(C) conducting “wire” at step

LT – STM

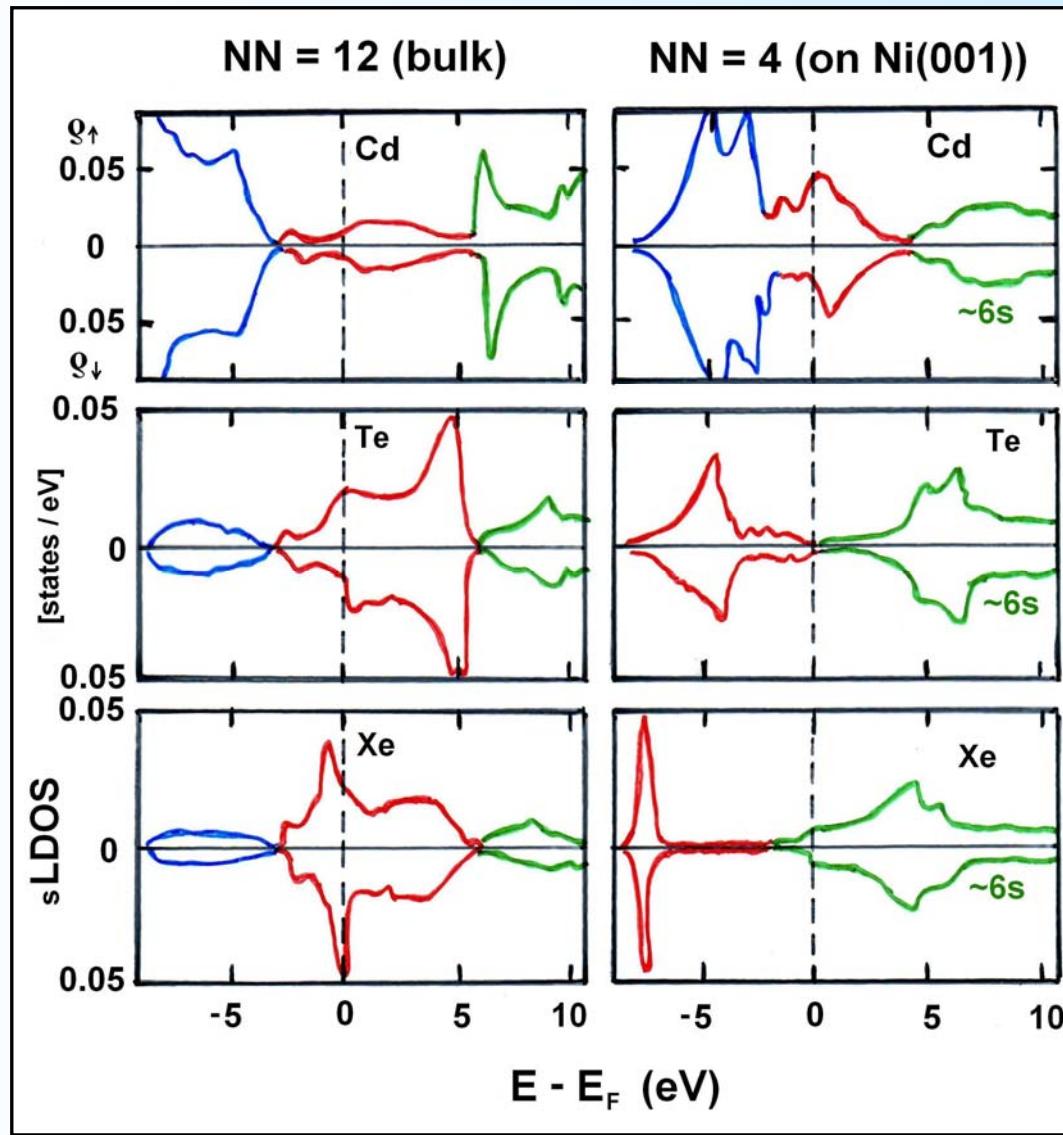
T = 8K; V = -0.1V; I = 0.2 nA



* Ref: F. Moresco et al., Phys. Rev. Lett. 91
(2003) 036601



Spin resolved level densities of s-electrons *

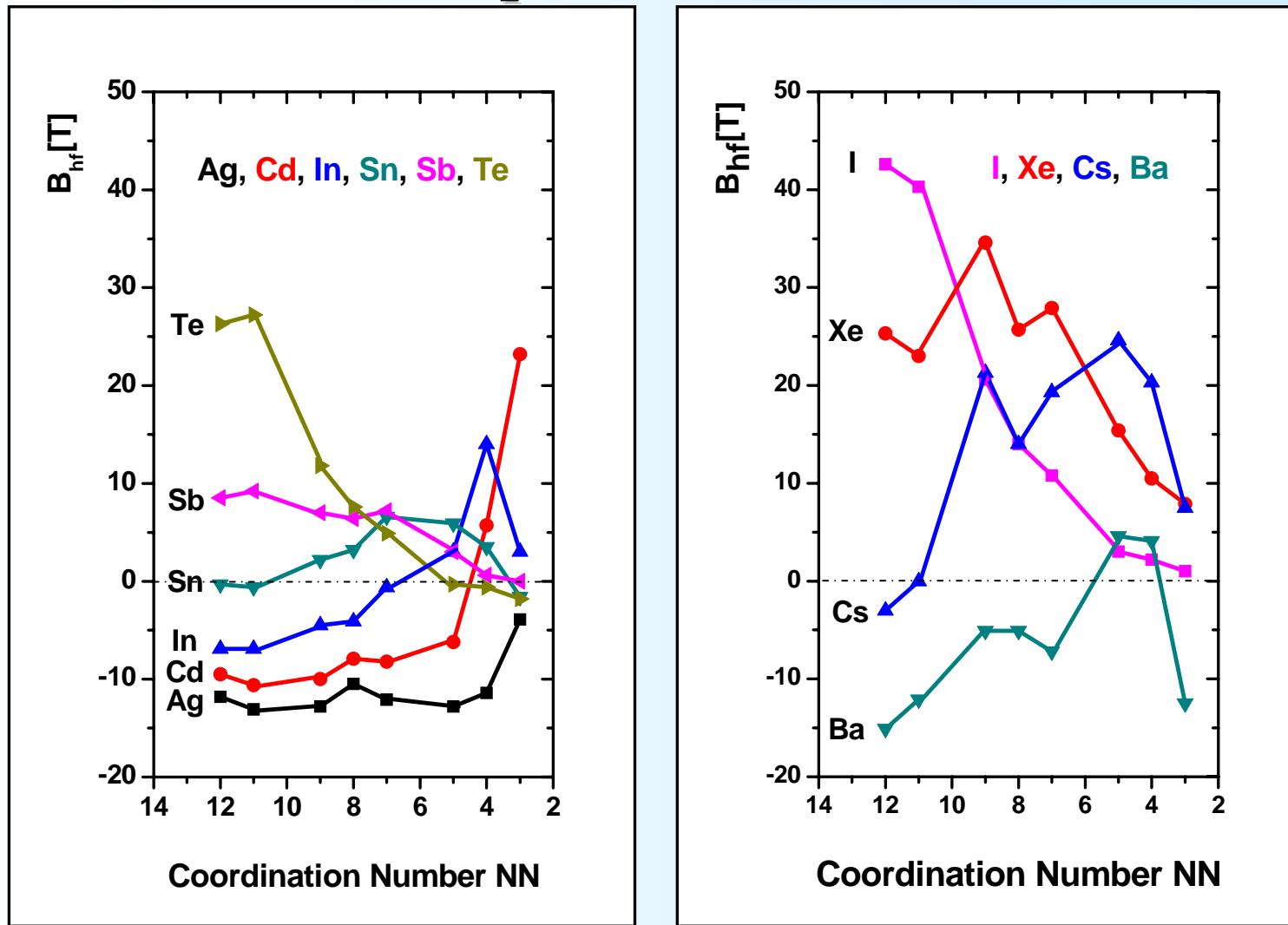


* Ref: Ph. Mavropoulos, J. Phys.: Condens. Matter 15 (2003) 8115

** see also: Kanamori et.al. Hyp. Int. 9 (1981) 363



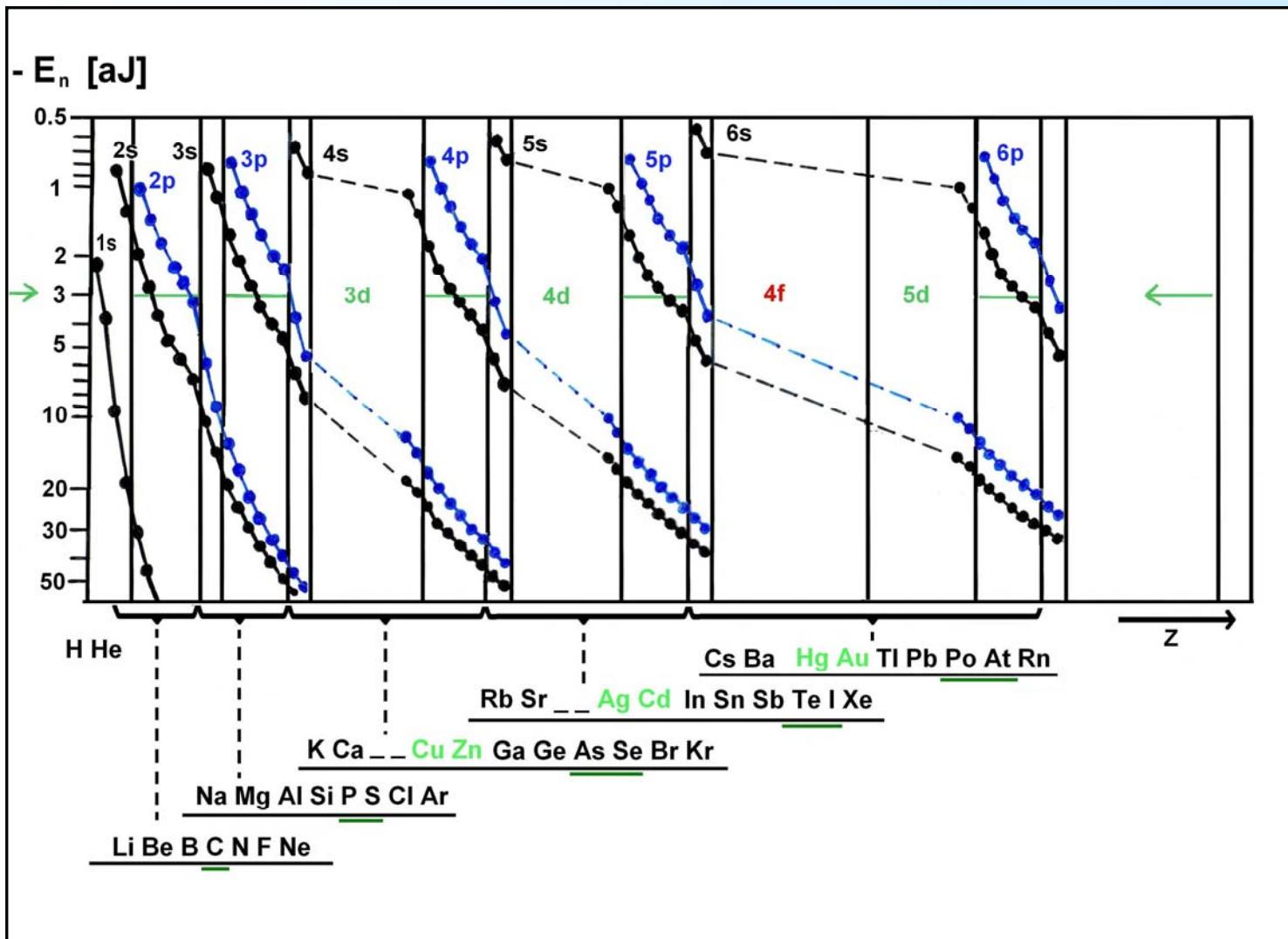
Predicted Magnetic Hyperfine Fields of 5sp-Elements on Ni*



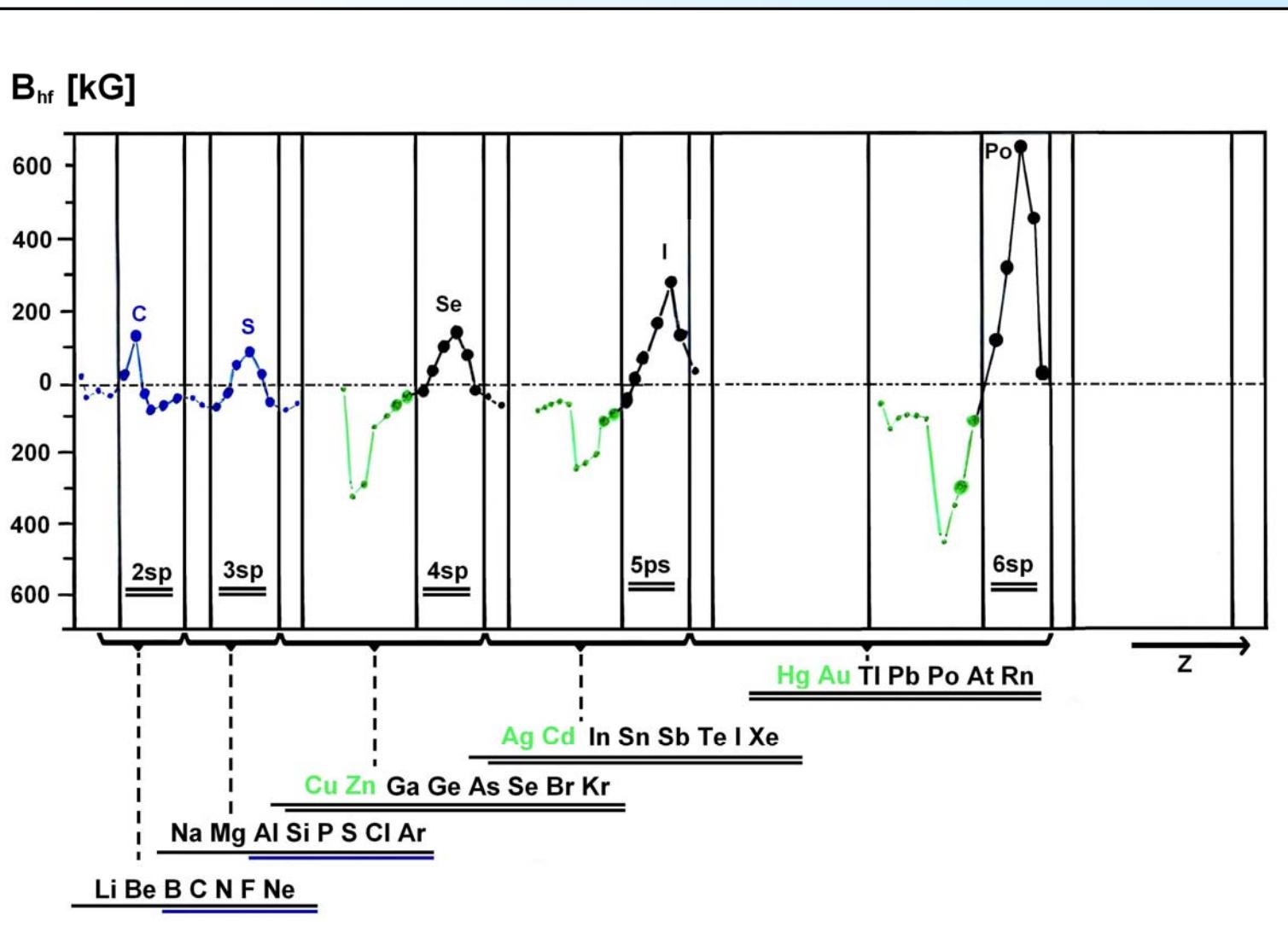
* Ph. Mavropoulos, J. Phys.: Condens. Matter 15 (2003) 8115



Atomic Energy Levels



Magnetic Hyperfine Fields in Nickel Bulk



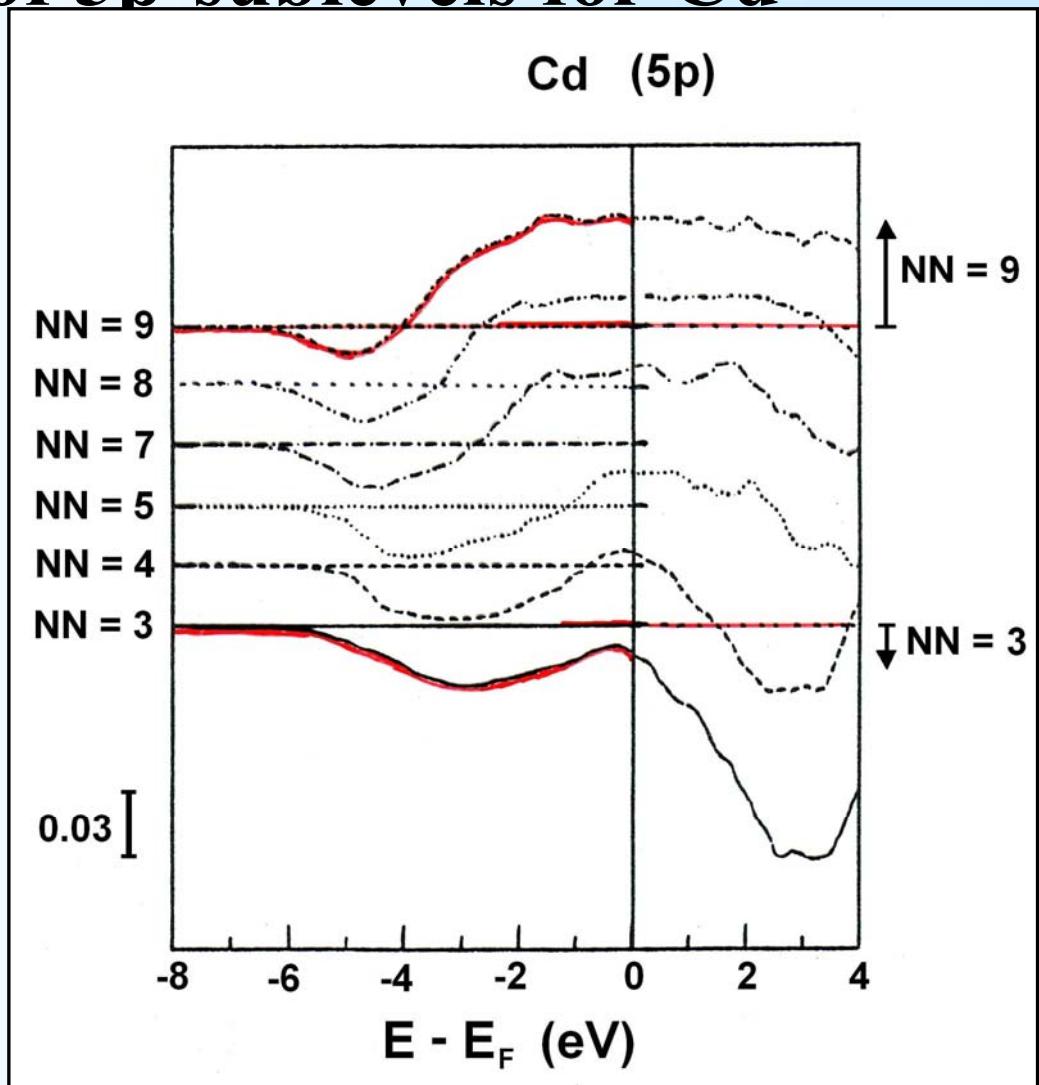
Ref: Rao, Hyp. Int. 24-26 (1985) 1119



Coordination number dependence of occupation of 5p-sublevels for Cd

$$\Delta n_P = \frac{1}{2} (n_{P_x} + n_{P_y}) - n_{P_z}$$

$$n_{pi} = \int_{E_F}^{E} \rho_{pi} dE$$



Ref: S. Cottenier et al., Phys. Rev. B 70, 155418 (2004)



Electric field gradient: EFG

(“fingerprint“ for the specific site)

$$H_{\text{EFG}} = P[3I_z^2 - I^2 + \eta(I_+^2 + I_-^2)/2]$$

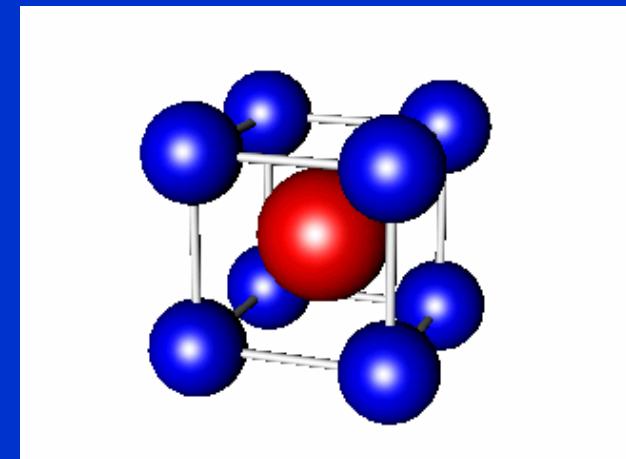
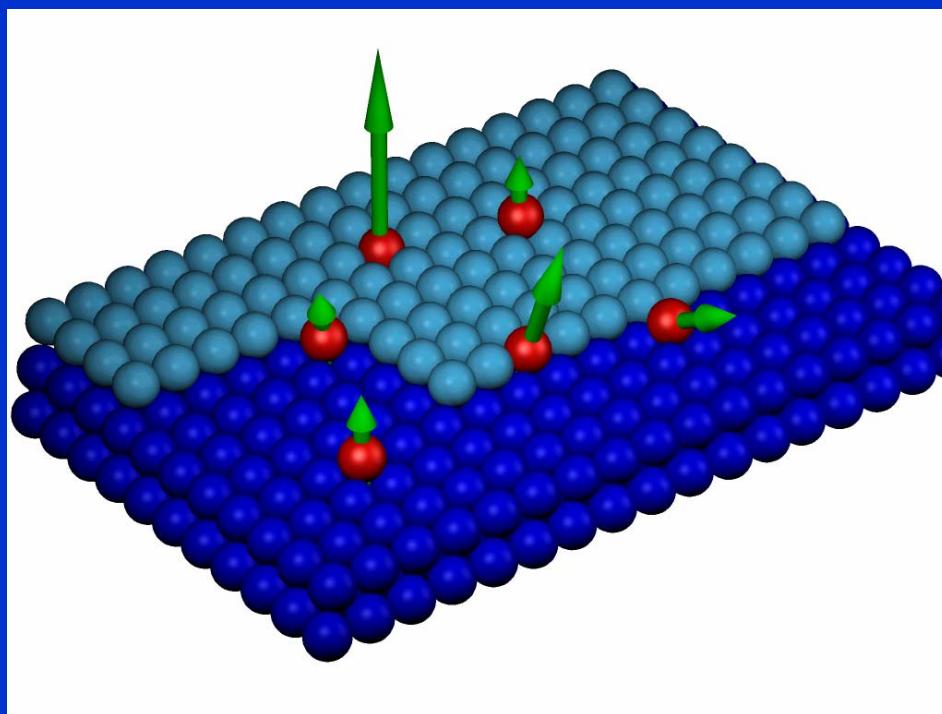
$$P \propto Q_N [V_{zz}]$$

$$\eta = (V_{yy} - V_{xx})/V_{zz}$$

Asymmetry parameter

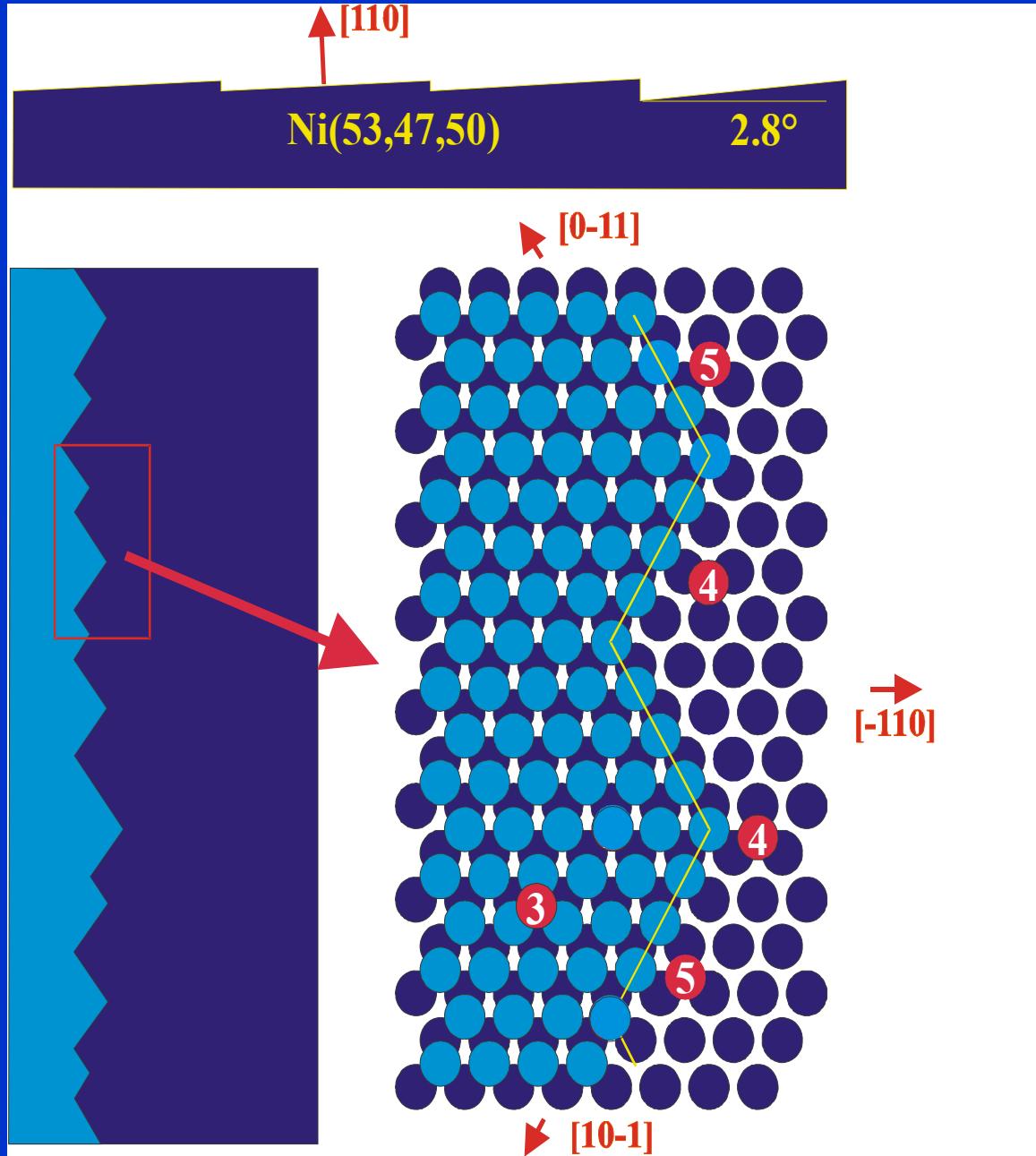
EFG:

Parameters in measurement:
 $|V_{zz}|$, η , angles (α , $[\beta]$, γ)



Cubic environment: $V_{zz} = 0$

1



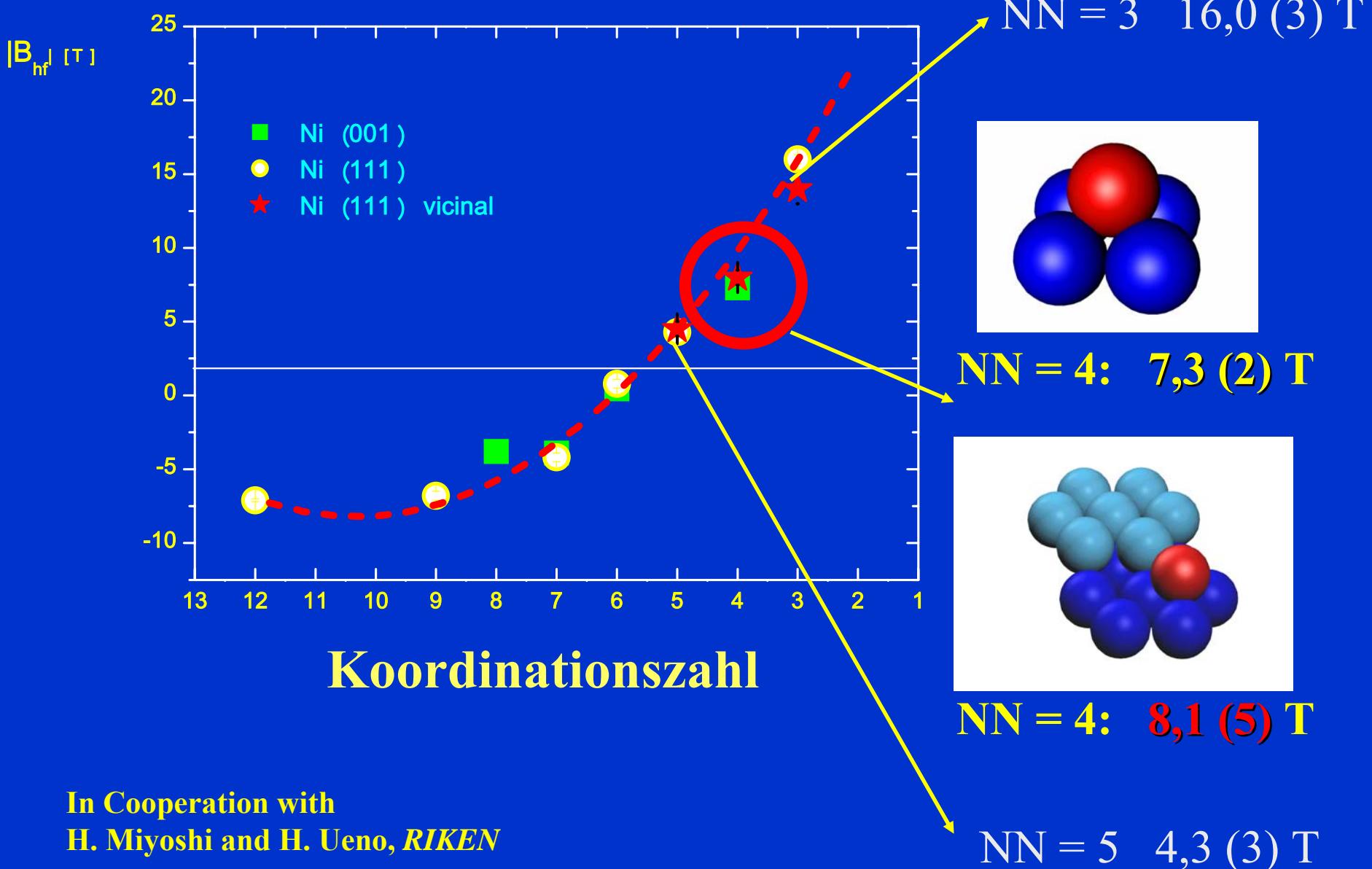
S.C. Ni

Positions of guest atoms on the vicinal $\text{Ni}_{\nu}(111)$ surface

Adatom position ($\text{NN} = 3$),
and atoms in front of step
($\text{NN} = 4$ and $\text{NN} = 5$)

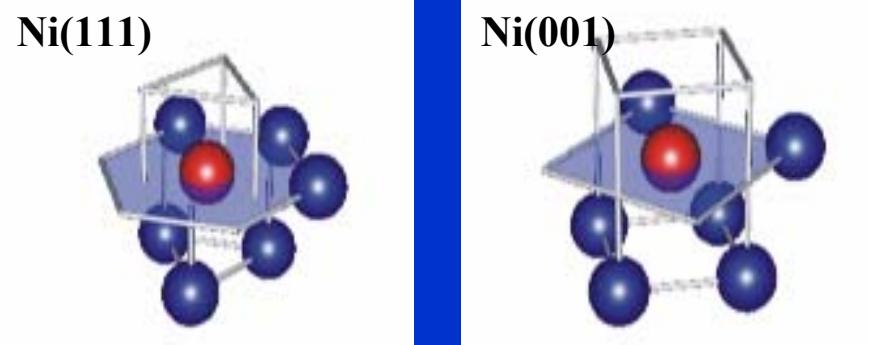
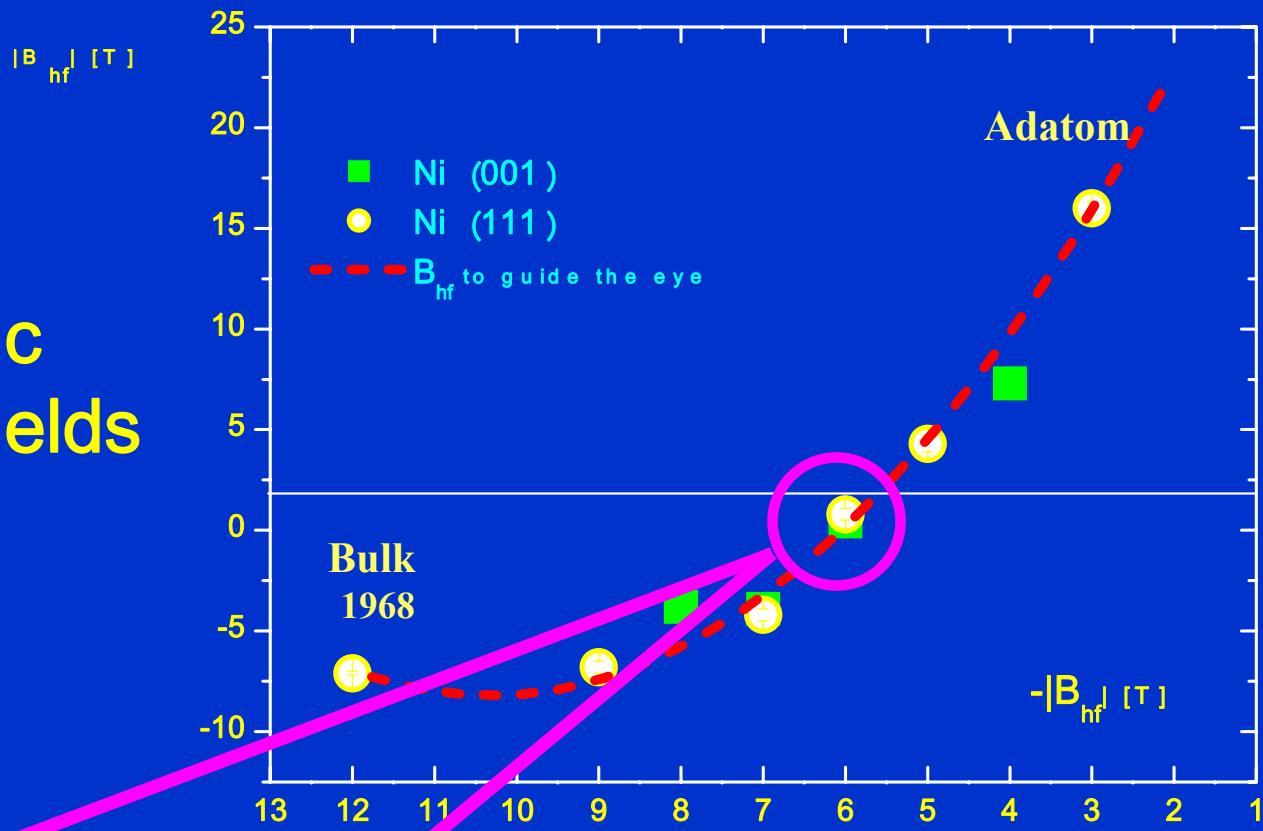
Experimental Results

APL 85, (2004) 76-78



Coordination number dependence of $|B_{hf}|$ of Cd on Ni

magnetic
hyperfine fields
 $|B_{hf}|$



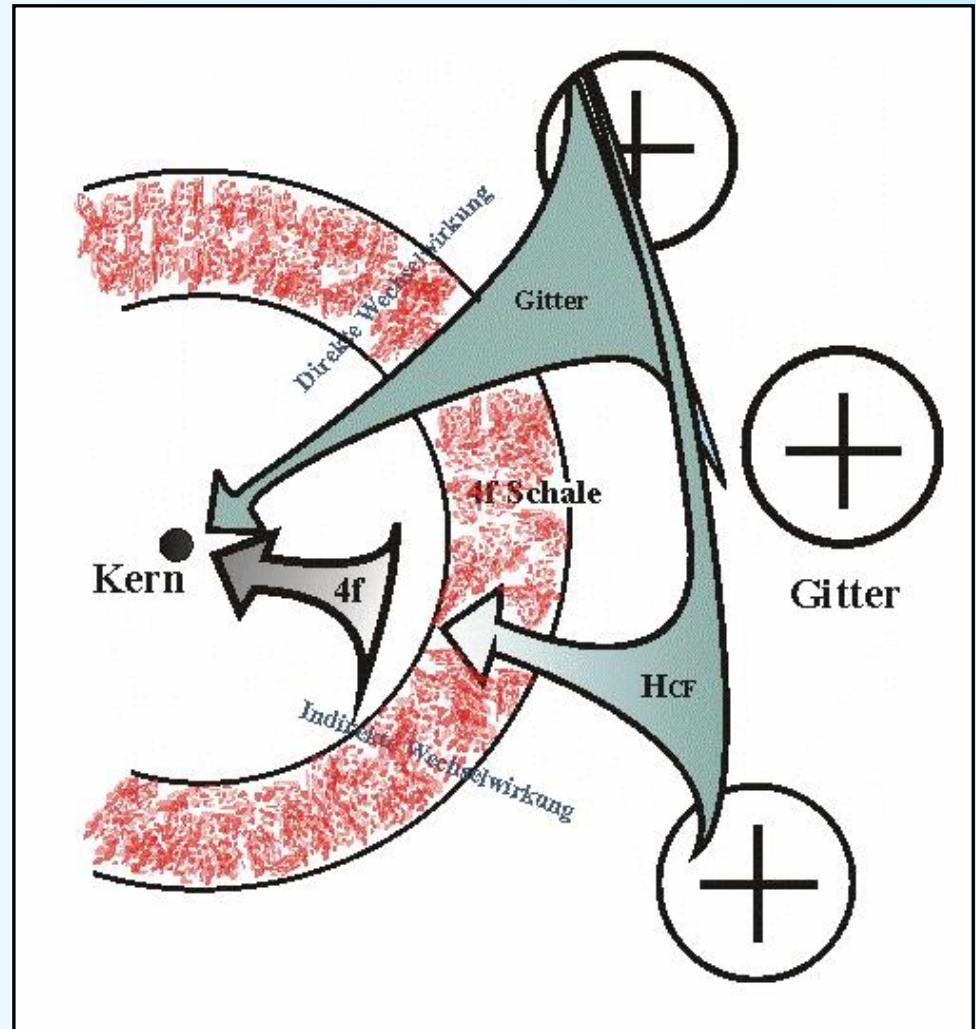
Koordinationszahl

K. Potzger, Ph.D. thesis (2001)
Potzger et al., PRL 88, (2002) 247201
Potzger et al., Phys. Rev. B, 72 (2005) 054435

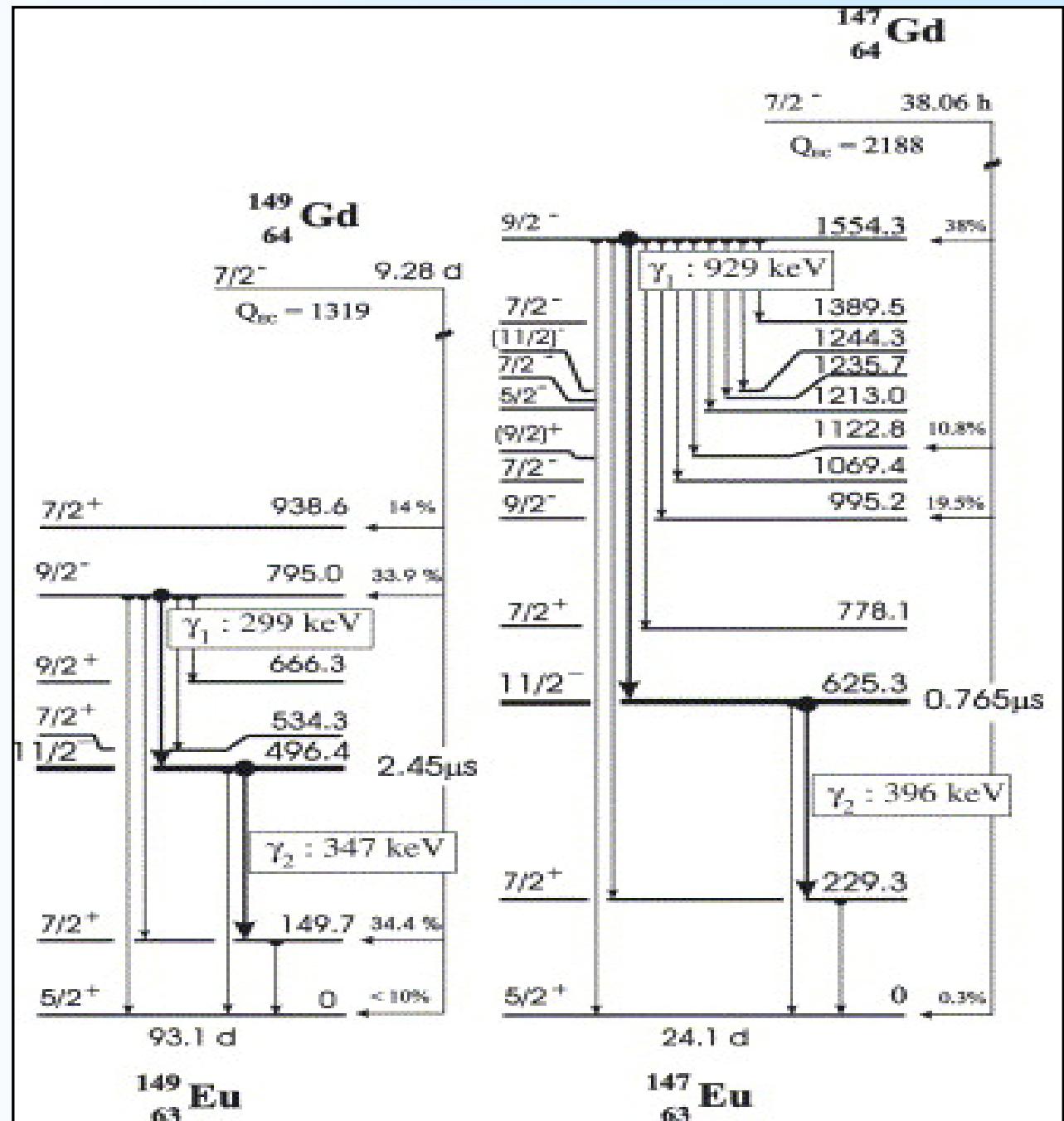
Interaction of the nucleus with its environment

The 4f-moments are not quenched, but they experience changes due to the interaction with the lattice.

This interaction can lead to valence changes or instabilities and even to the reduction of the observed moments by spin fluctuations and by the Kondo-effect.



Nuclear Level Schemes



Hyperfine fields of free 4f ions

n	Ion	S L J	B _{int} [T]	V _{zz} ^{4f} [10 ¹⁷ V/cm ²]
0	La ³⁺	0 0 0	0	0
1	Ce ³⁺	1/2 3 5/2	189.3	22.8
2	Pr ³⁺	1 5 4	335.4	26.2
3	Nd ³⁺	3/2 6 9/2	429.6	11.4
4	Pm ³⁺	2 6 4	419.9	11.7
5	Sm ³⁺	5/2 5 5/2	335.6	-24.5
6	Eu ³⁺	3 3 0	0	0
7	Eu ²⁺	7/2 0 7/2	-34.2	0
7	Gd ³⁺	7/2 0 7/2	-32.1	0
8	Tb ³⁺	3 3 6	311.6	51.1
9	Dy ³⁺	5/2 5 15/2	559.8	55.3
10	Ho ³⁺	2 6 8	724.1	23.8
11	Er ³⁺	3/2 6 15/2	765.3	-25.7
12	Tm ³⁺	1 5 6	662.5	-69.0
13	Yb ³⁺	1/2 3 7/2	412.5	-74.1
14	Lu ³⁺	0 0 0	0	0

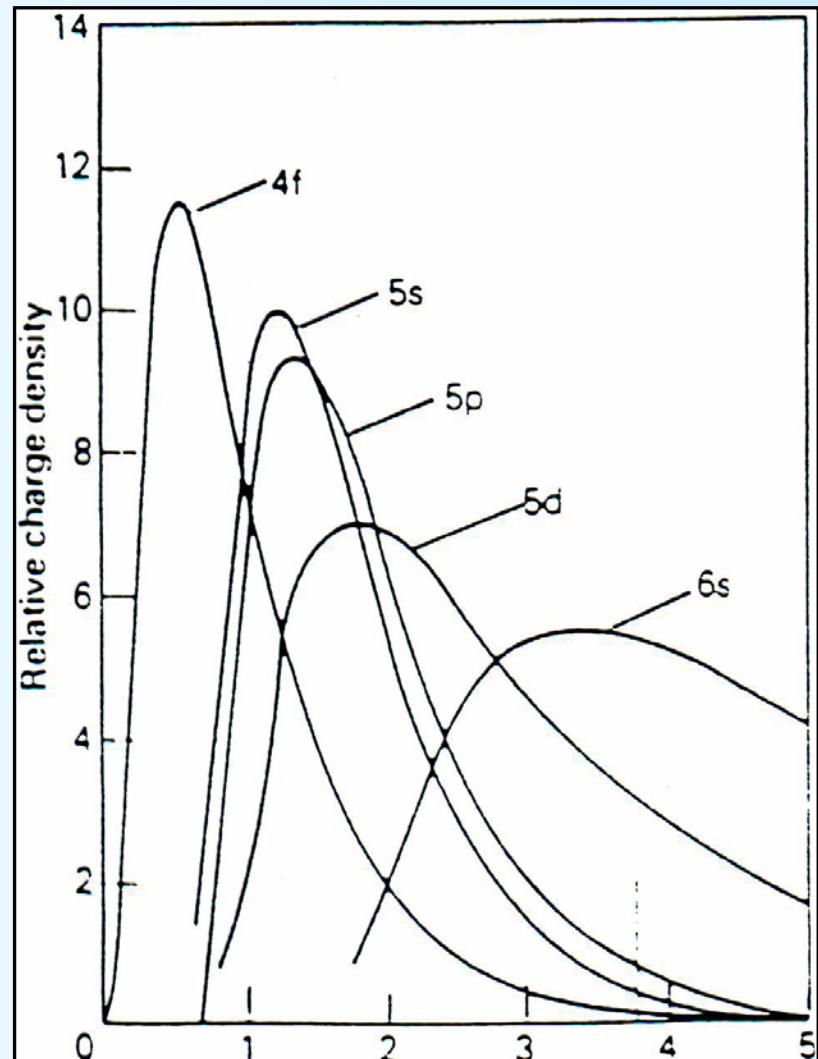
$$^{2S+1}L_J$$

Ref.:G.A.Steward, Materials Forum
18 (1994) 177.



Radial part of electronic densities in Gd

- The vertical dotted line stands for $a = 3.636 \text{ \AA}$ of Gd metal
- Most 4f orbitals are localised in crystals
- The electronic moments in the 4f orbitals are coupled according to Hund's rules and are less affected by the interactions in the lattice than electrons in the d-shells.



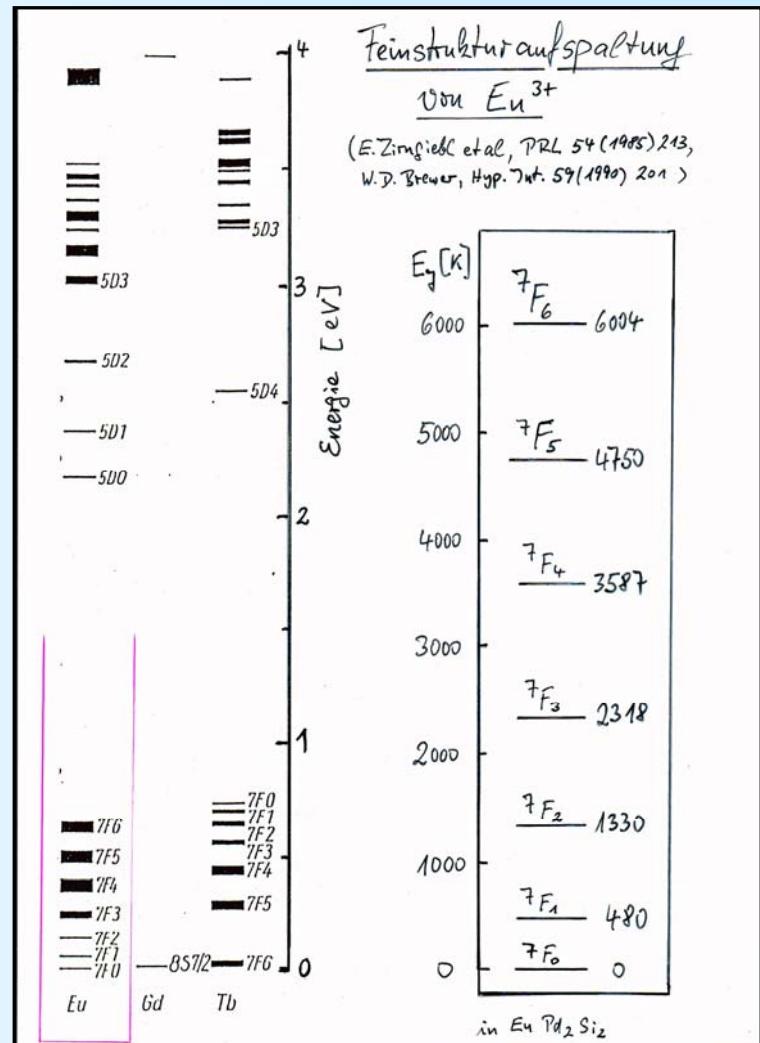
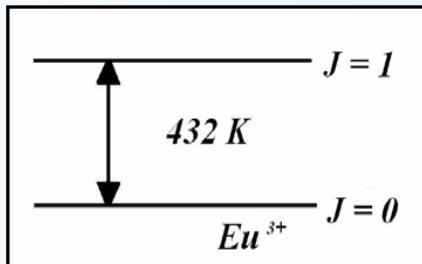
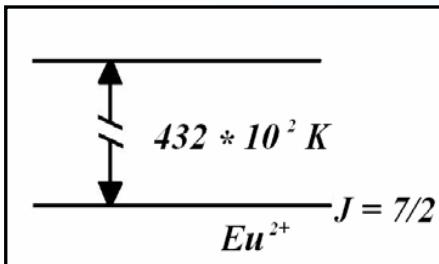
Rare Earth - Eu²⁺, Eu³⁺

Among the rare earth elements, Eu is a special case. According to the occupancy in the 4f-shell, europium can be either trivalent, Eu³⁺: [Xe]4f⁶(5d6s)³, or divalent, Eu²⁺: [Xe]4f⁷(6s)².

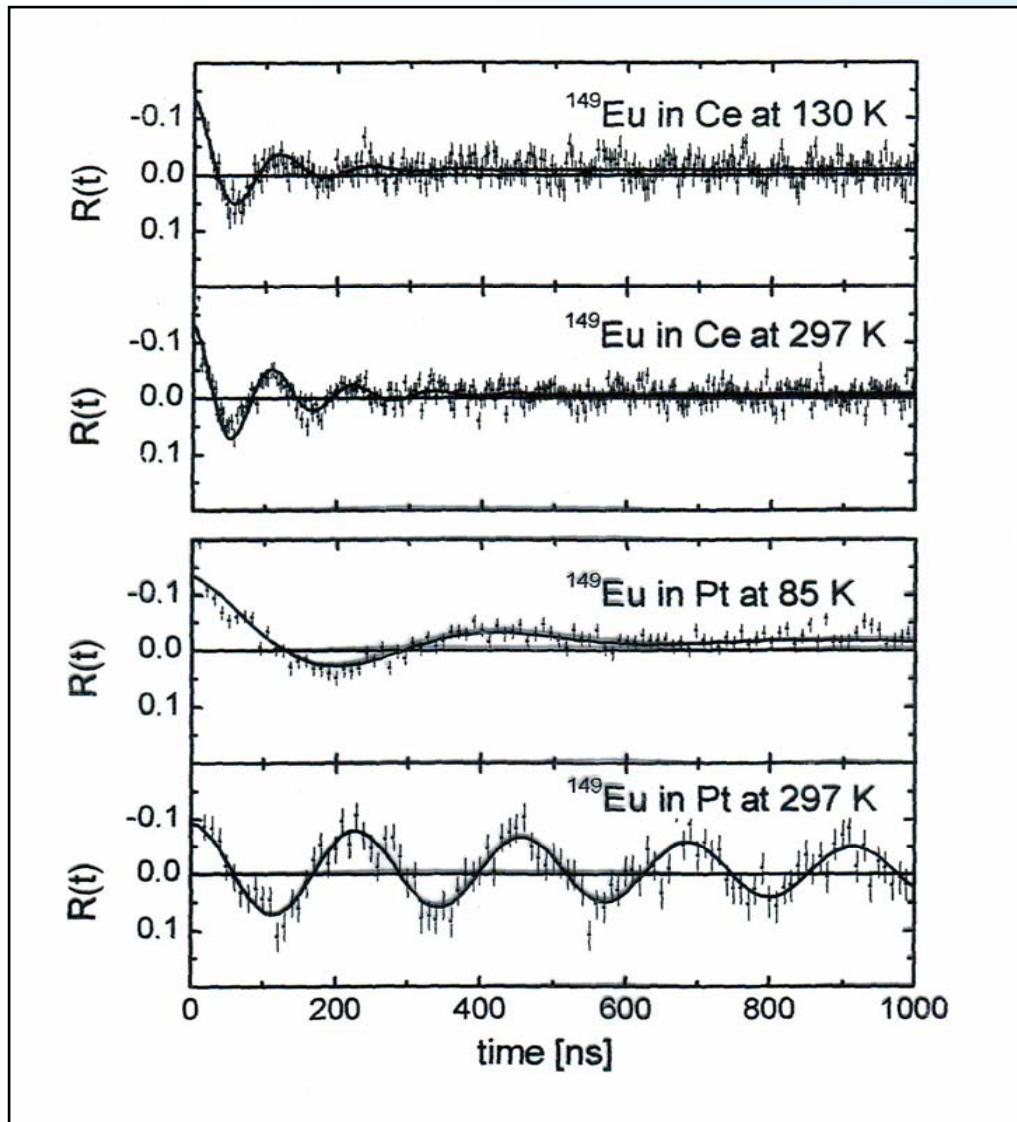
If trivalent, Eu has strong spin and orbital moments of S = 3 and L = 3 which couple to the non-magnetic ground state of J = 0

The susceptibility, which is observed under certain conditions arises from Van Vleck contributions mixing neighboring levels.

The divalent case , however, Eu²⁺ resembles Gd³⁺ by showing the pure spin magnetism of S = J = 7/2.



PAC spectra for Europium (^{149}Eu) in Cerium und Platinum at different temperatures



- in Platinum:
trivalent Europium (Eu^{3+})
with the non-magnetic
ground state ($J=0$)
- in Cerium:
divalent Europium (Eu^{2+})
with $S=J=7/2$ ground state



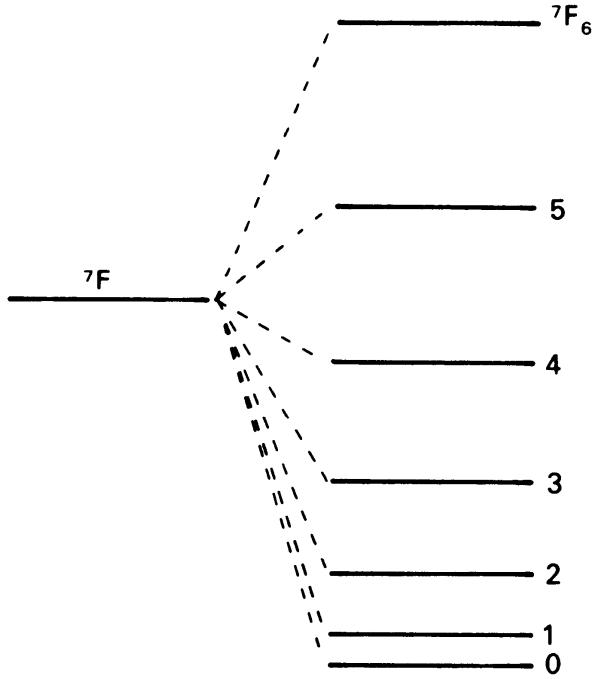
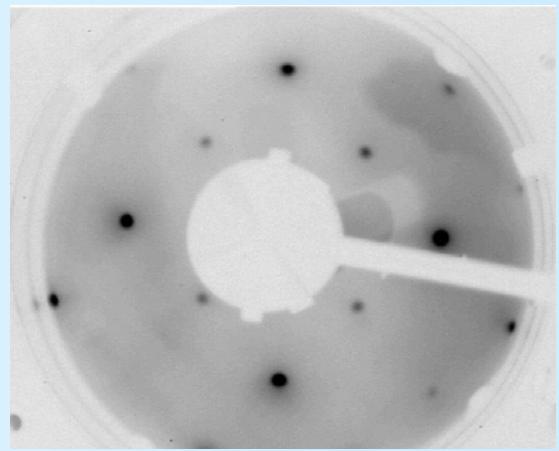
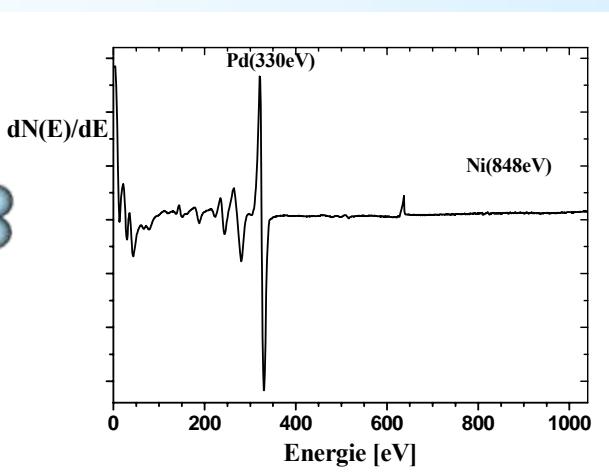
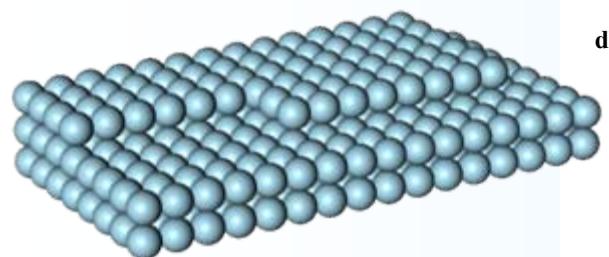
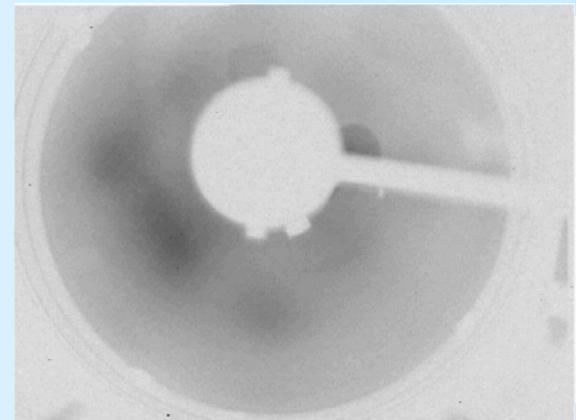
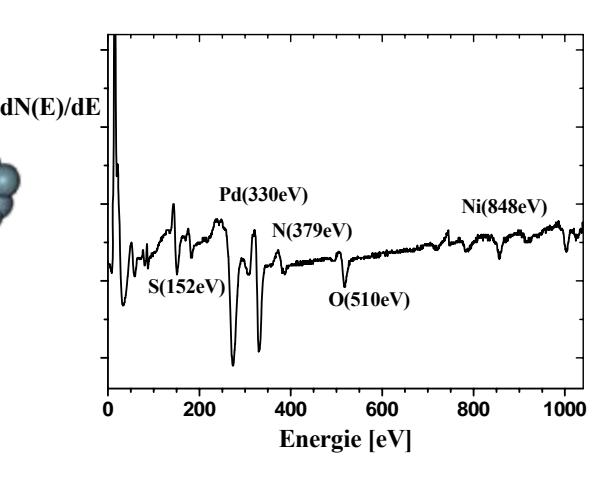
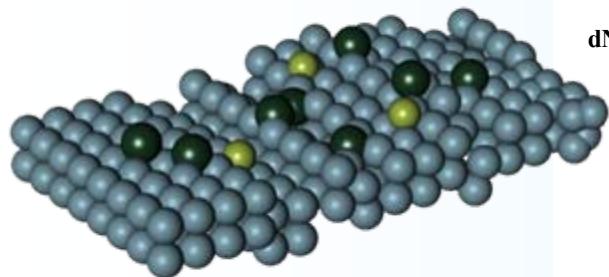
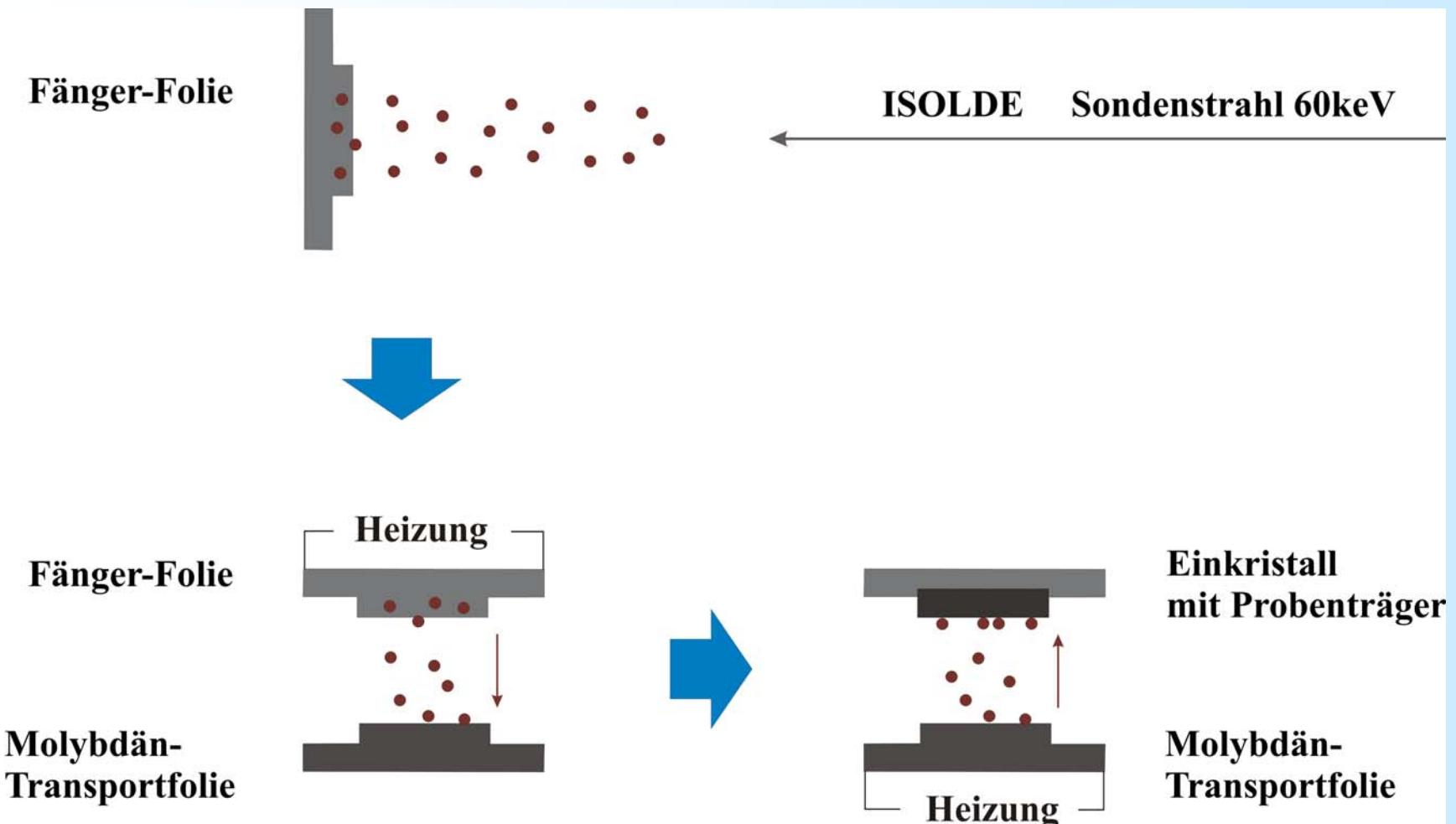


FIG. 8.2. Splitting of the 7F ($L=3, S=3$) term by spin-orbit coupling in the Russell-Saunders approximation. The spin-orbit coupling parameter is assumed positive, as in the ground state of Eu^{3+} (see Fig. 8.1).

Preparation of samples

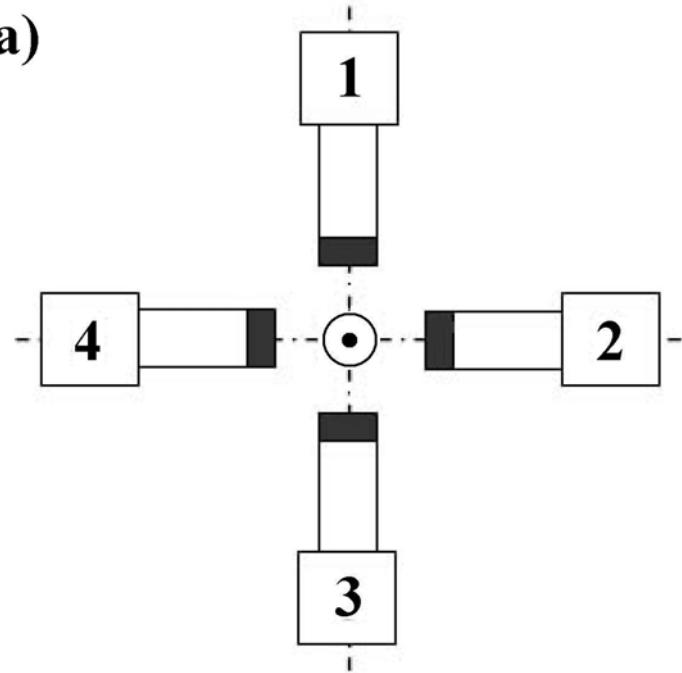


“Soft landing“

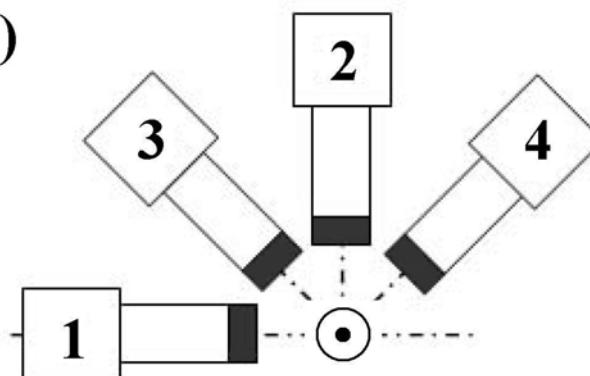


Arrangement of Detektors

a)



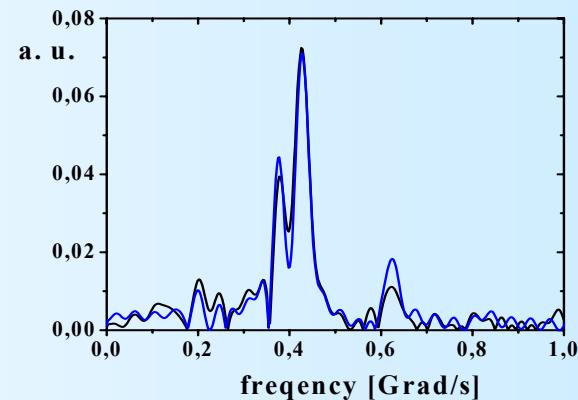
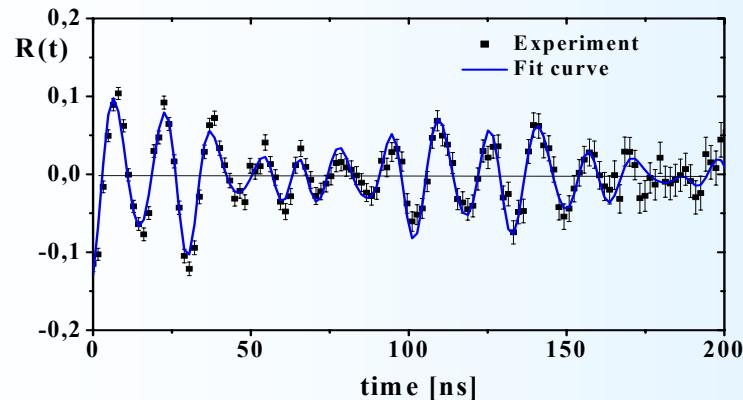
b)



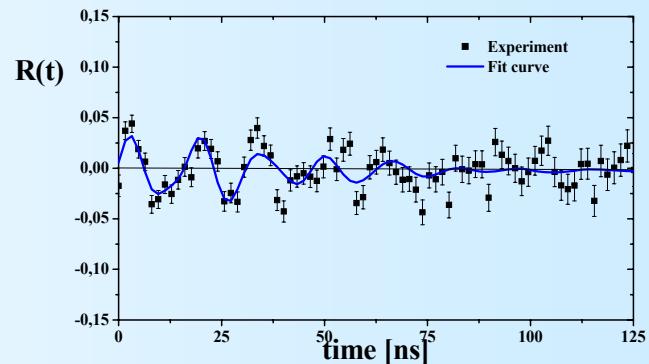
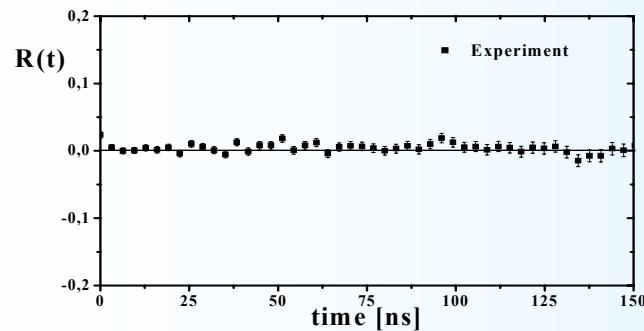
$$R(t) = \frac{W(180^\circ, t) - W(90^\circ, t)}{W(180^\circ, t) + W(90^\circ, t)} = \frac{3A_{22} \cos 2\omega_L t}{4 + A_{22}}$$

$$R(t) = \frac{3A_{22} \sin 2\omega_L t}{4 + A_{22}}$$

Cadmium in Ni(111) Terrace (NN=9)

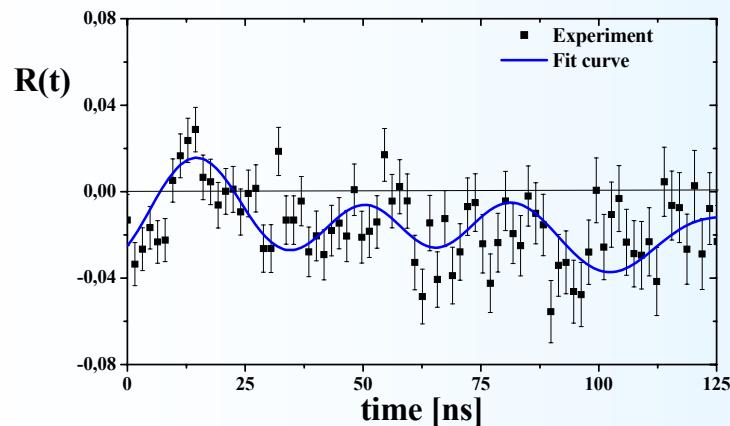


Detektorkonfiguration ($180^\circ/90^\circ$)

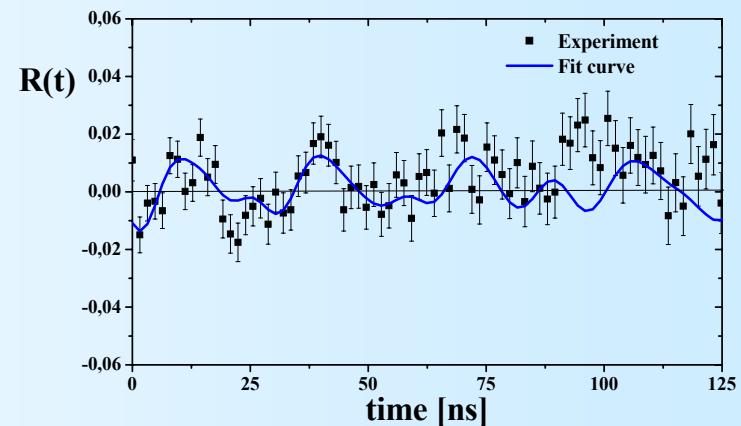


Detektorkonfiguration ($135^\circ/45^\circ$)

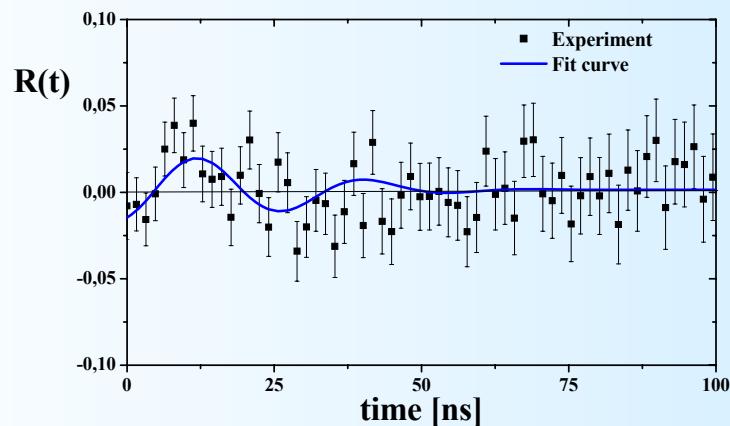
Determination of Signs of the Magnetic Hyperfine Fields



Kink site ($NN=5$) on $\text{Ni}(111)$



Step site ($NN=7$) on $\text{Ni}(111)$



- Adatom site ($NN=4$) on $\text{Ni}(001)$