From theoretical chemistry to nuclear physics – and back

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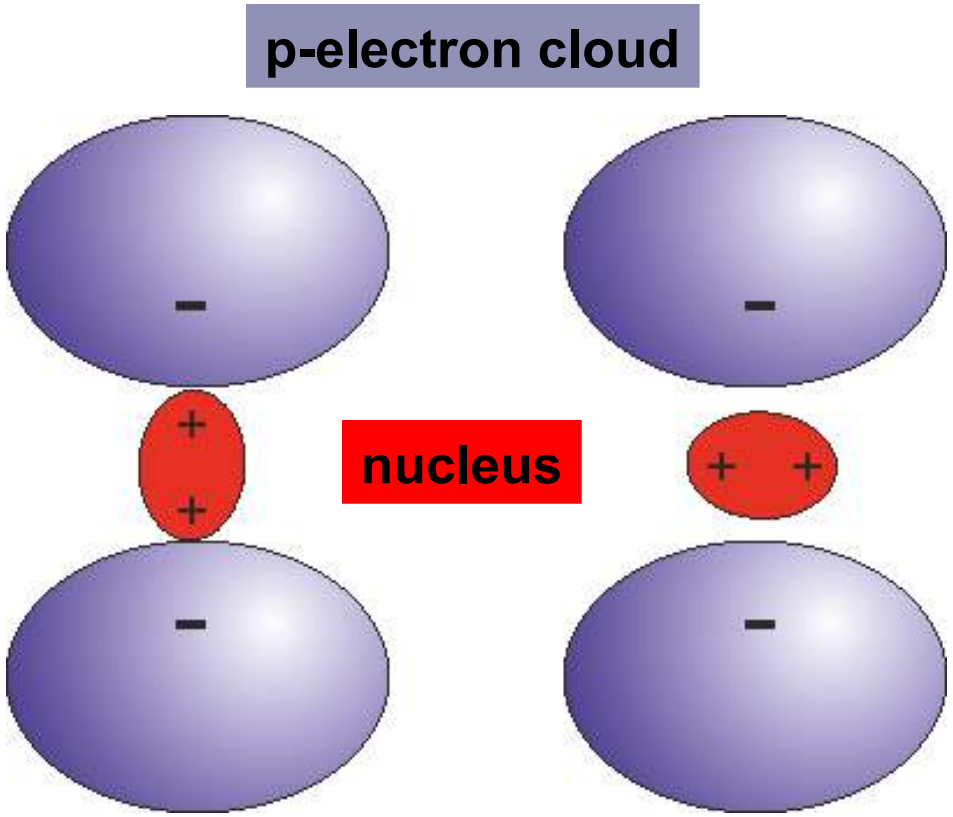
Nuclear quadrupole interaction



electric field gradient (EFG)

$V_{zz} = d_2V/dz^2$ [V/m²]

nuclear quadrupole moment

Q [b]

interaction energy

$E = eQV_{zz}$

Interaction frequency

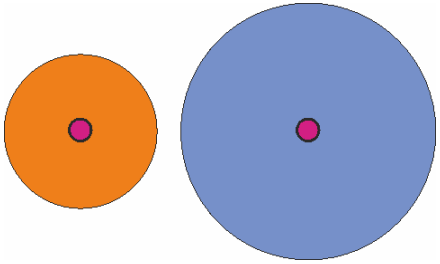
eQV_{zz}/h

typically 100 MHz

RF spectroscopy NQR

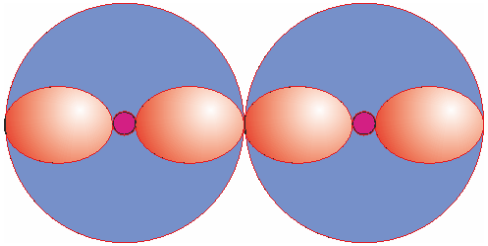
Interest from (theoretical) chemistry:

Ionic bond: NaCl



EFG = 0

Covalent bond: Cl_2



EFG = atomic value

Transition metal halides: $CuCl_2$, $NiCl_2$, ...

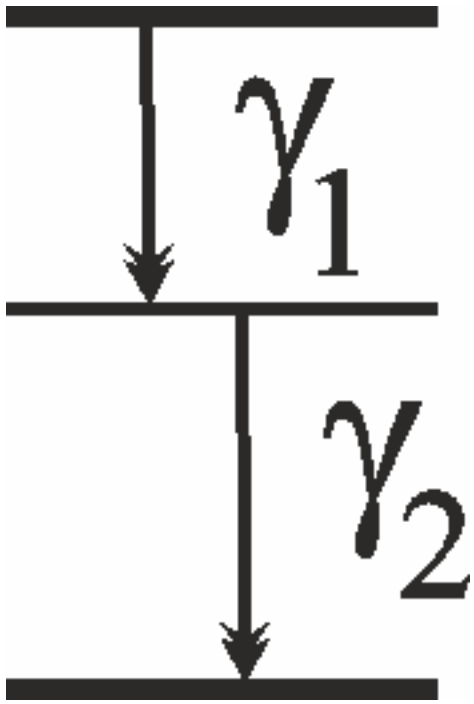
EFG measures covalency !

More interesting: Fluorides

but ^{19}F has I = ½, thus Q = 0 !

Measure other state by nuclear technique !

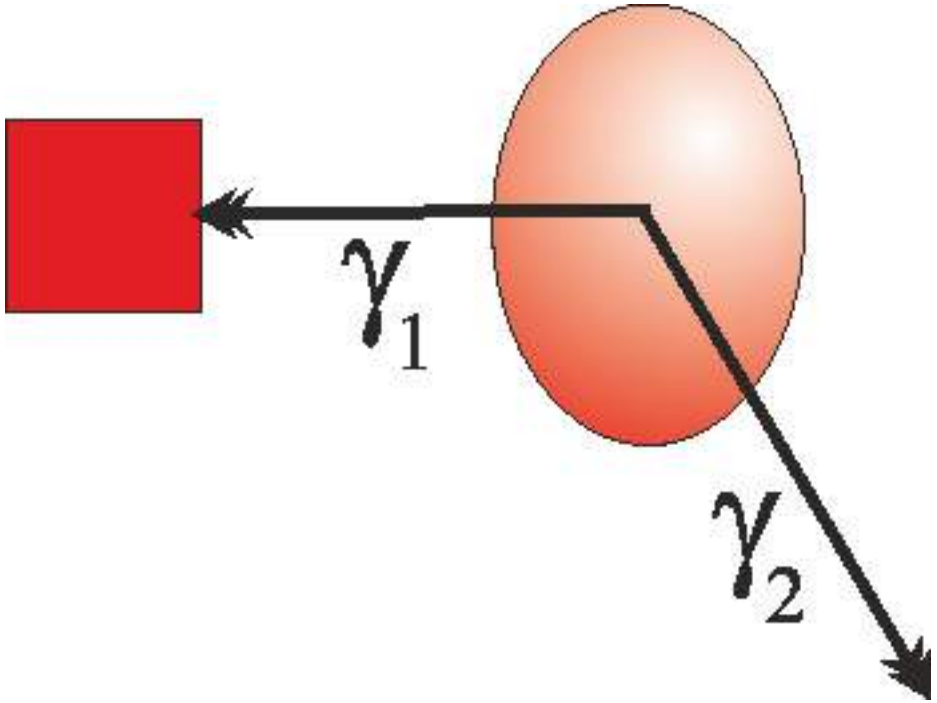
Nuclear decay



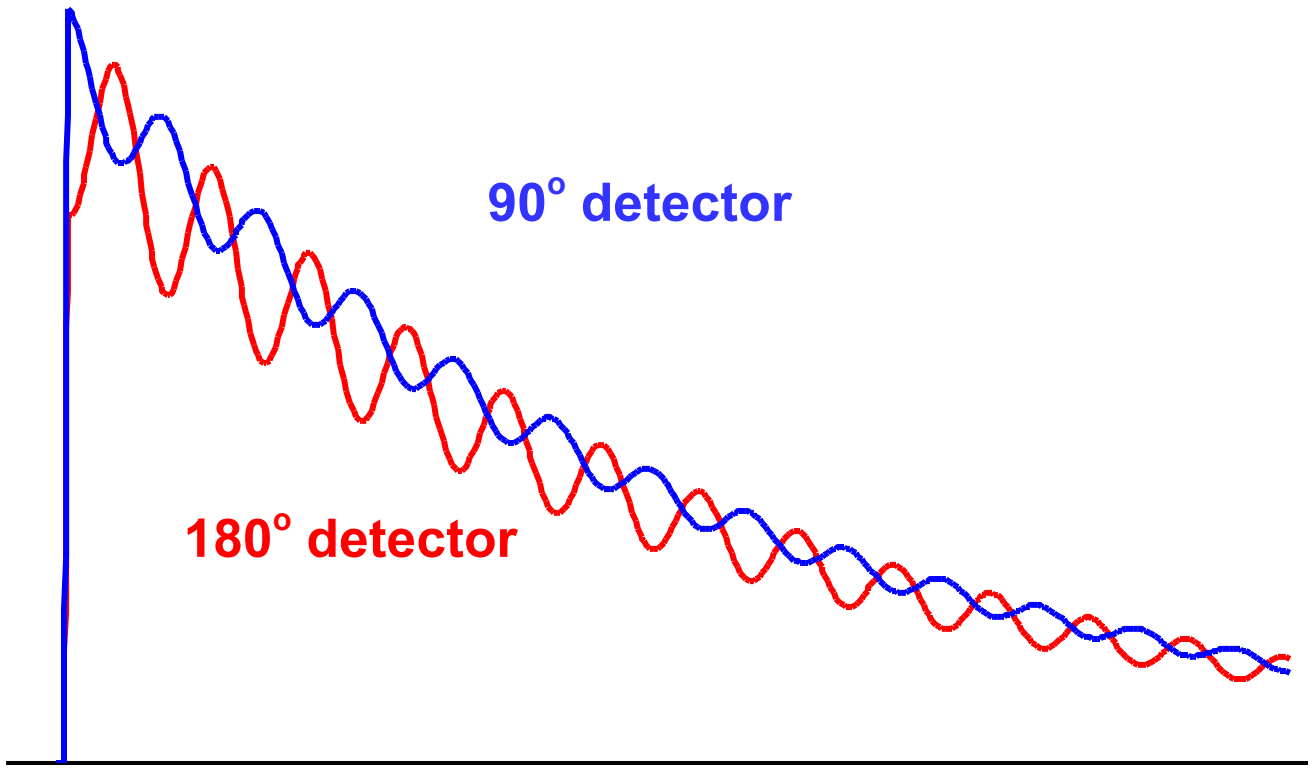
Source (isomeric) state
$T_{1/2}$ 30 seconds to years

PAC state, Spin > 1/2
$T_{1/2}$ 2 ns to 5000 ns

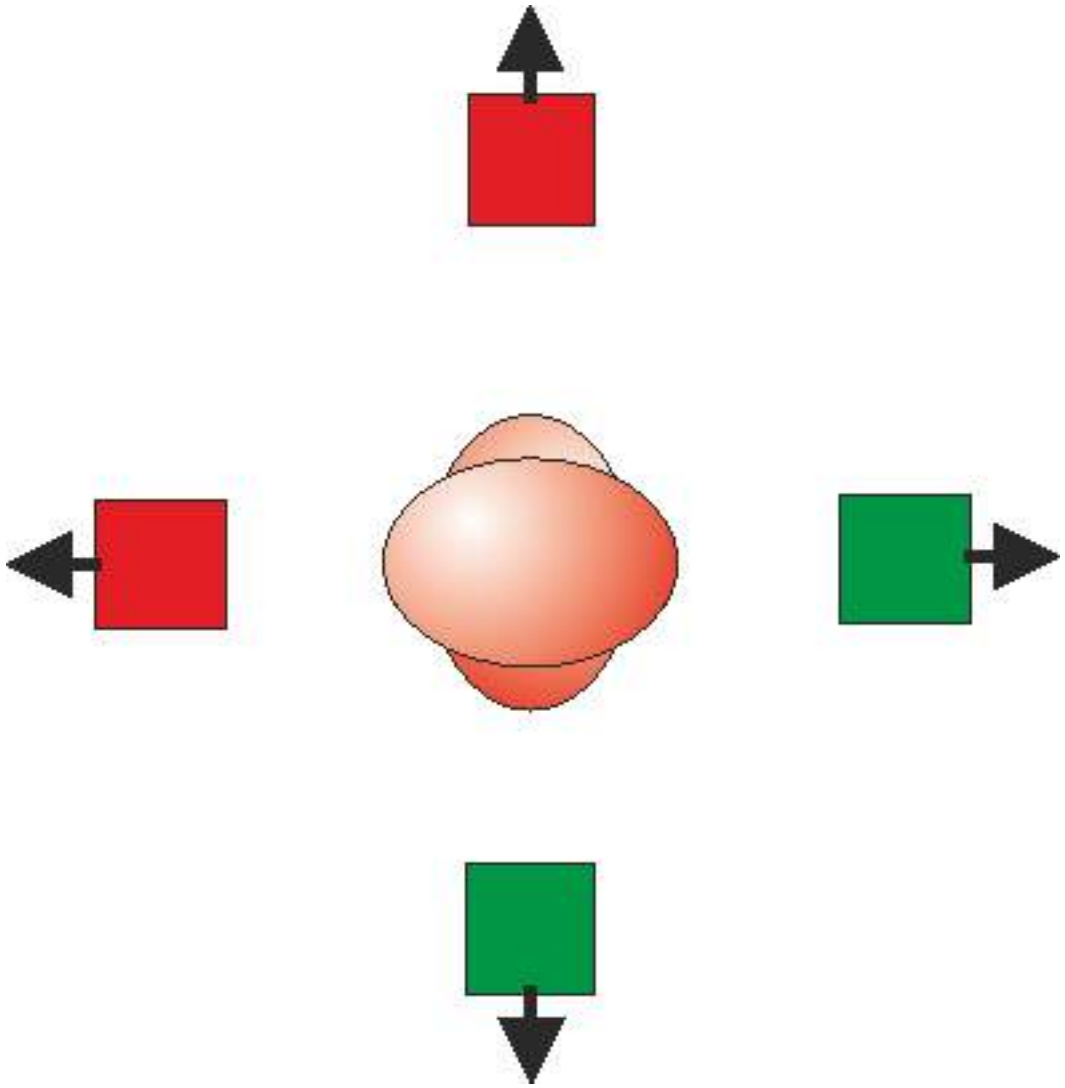
Angular correlation



PAC coincidence time spectrum



The Berkeley “trick”

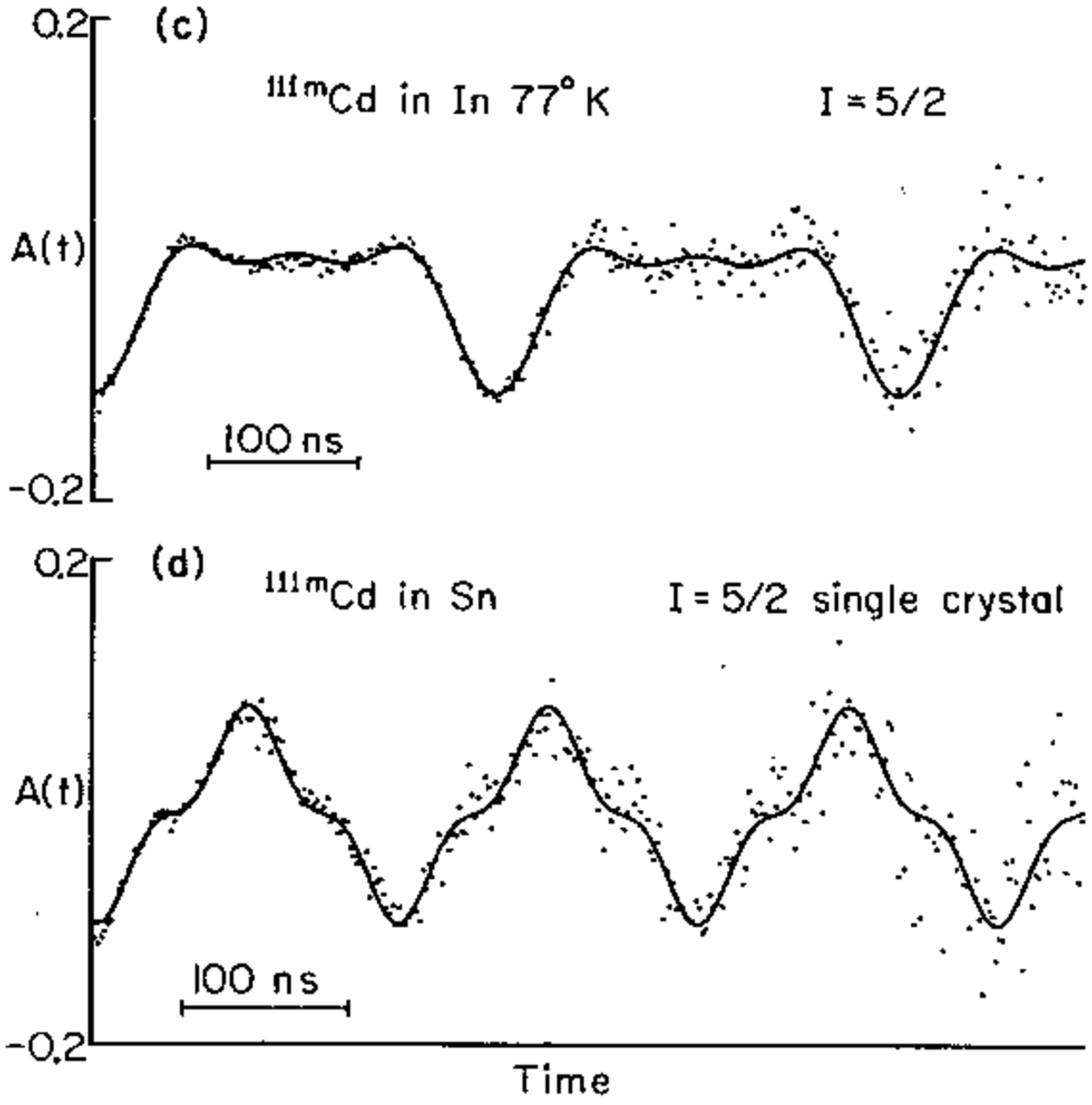


two start detectors
two stop detectors

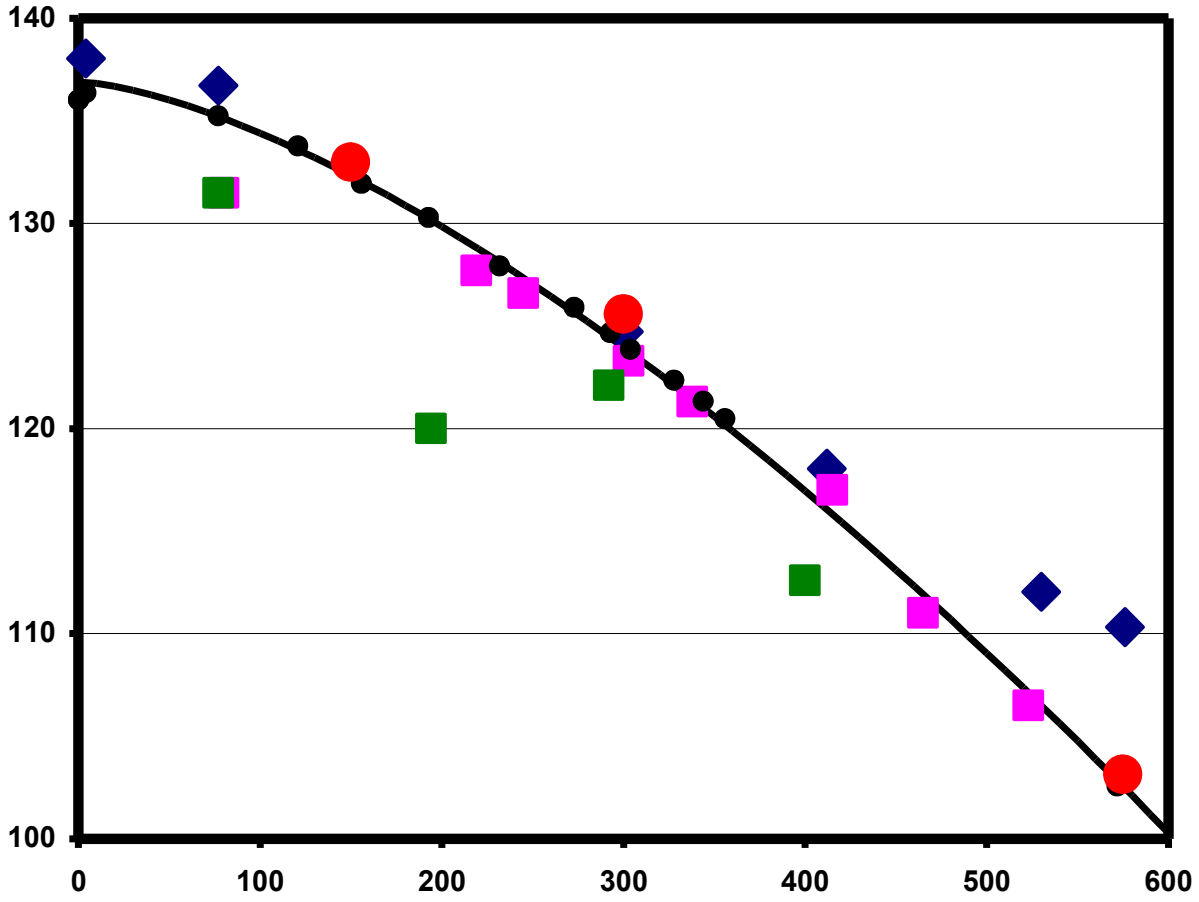
four time spectra
simultaneously !

made possible by
1600 channel MCA,
and of course some
electronics

Typical PAC spectra (Berkeley 1969)

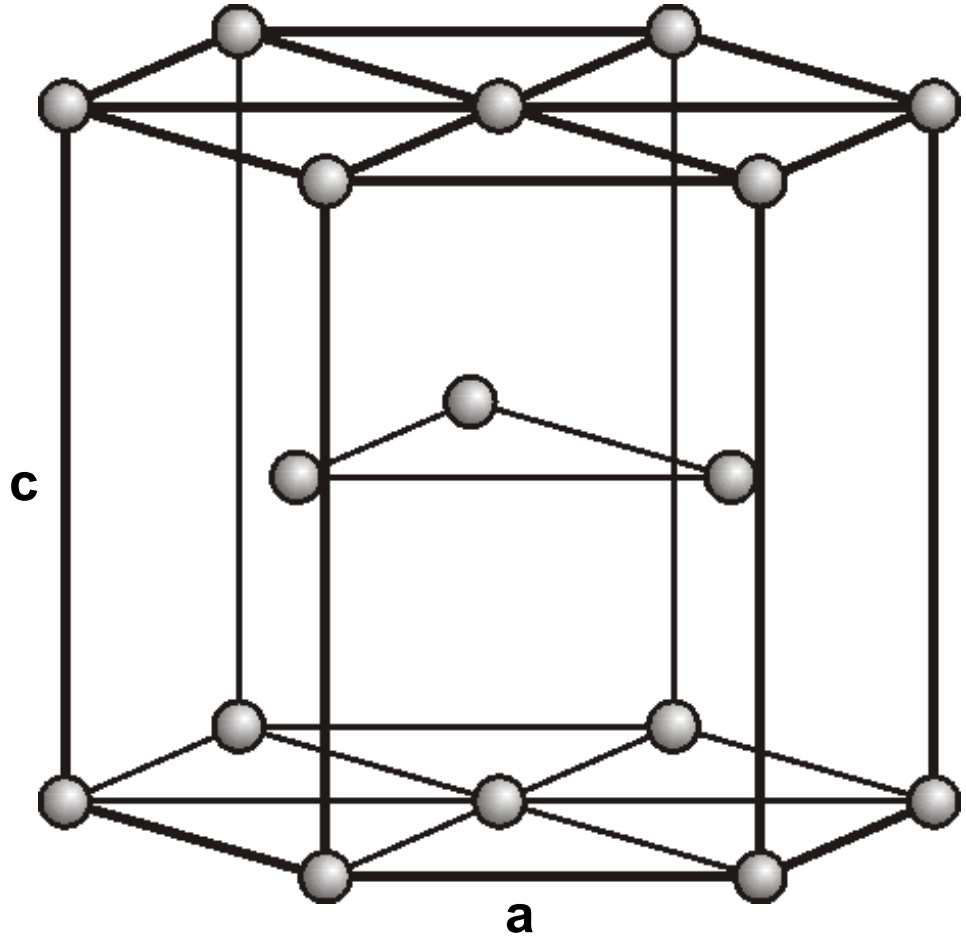


A bit of history: Temperature dependence of QI in Cd



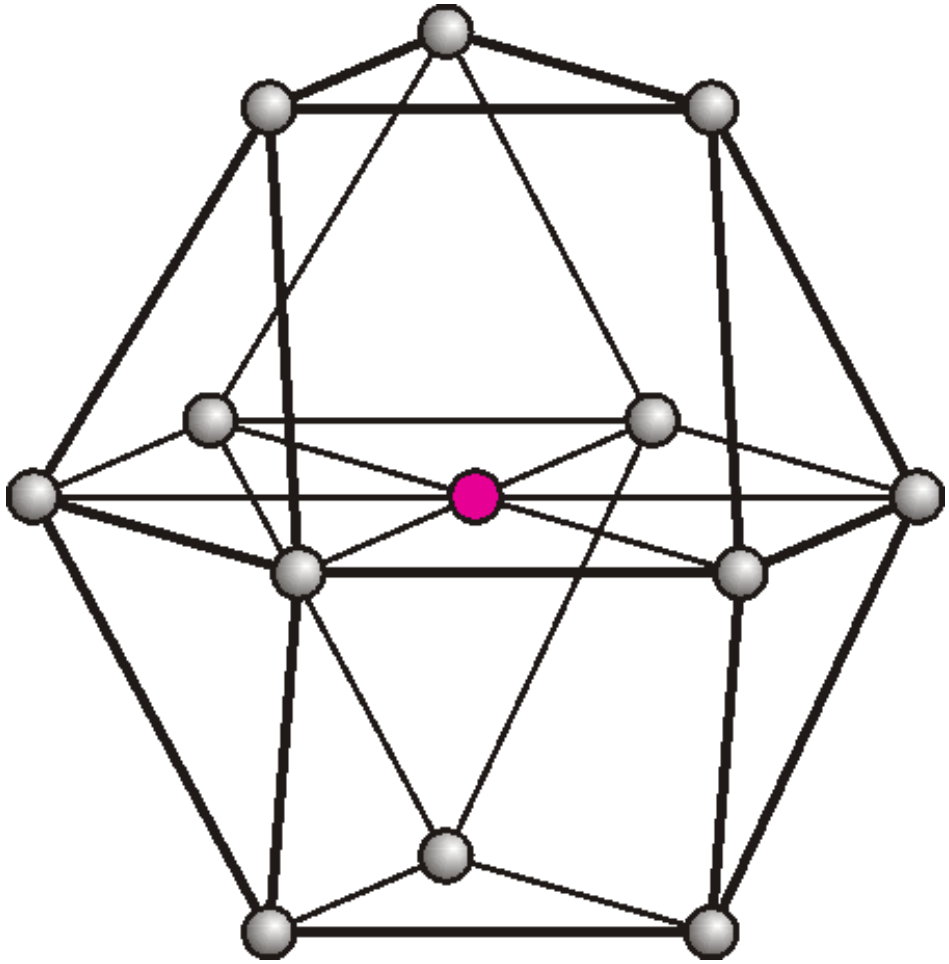
Used $T^{1.5}$ "law" for extrapolation to T=0

The hexagonal crystal structure of Zn and Cd



	Zn	Cd
a[A]	2.6549	2.9631
c[A]	4.8534	5.5189
c/a	1.8281	1.8625
hcp	1.6330	1.6330

nn configuration



Positive point charges would give negative EFG!

The breakthrough in experiment

PHYSICAL REVIEW B VOLUME 13, NUMBER 7 1 APRIL 1976

Sign and magnitude of the quadrupole interaction of ^{111}Cd in noncubic metals: Universal correlation of ionic and electronic field gradients

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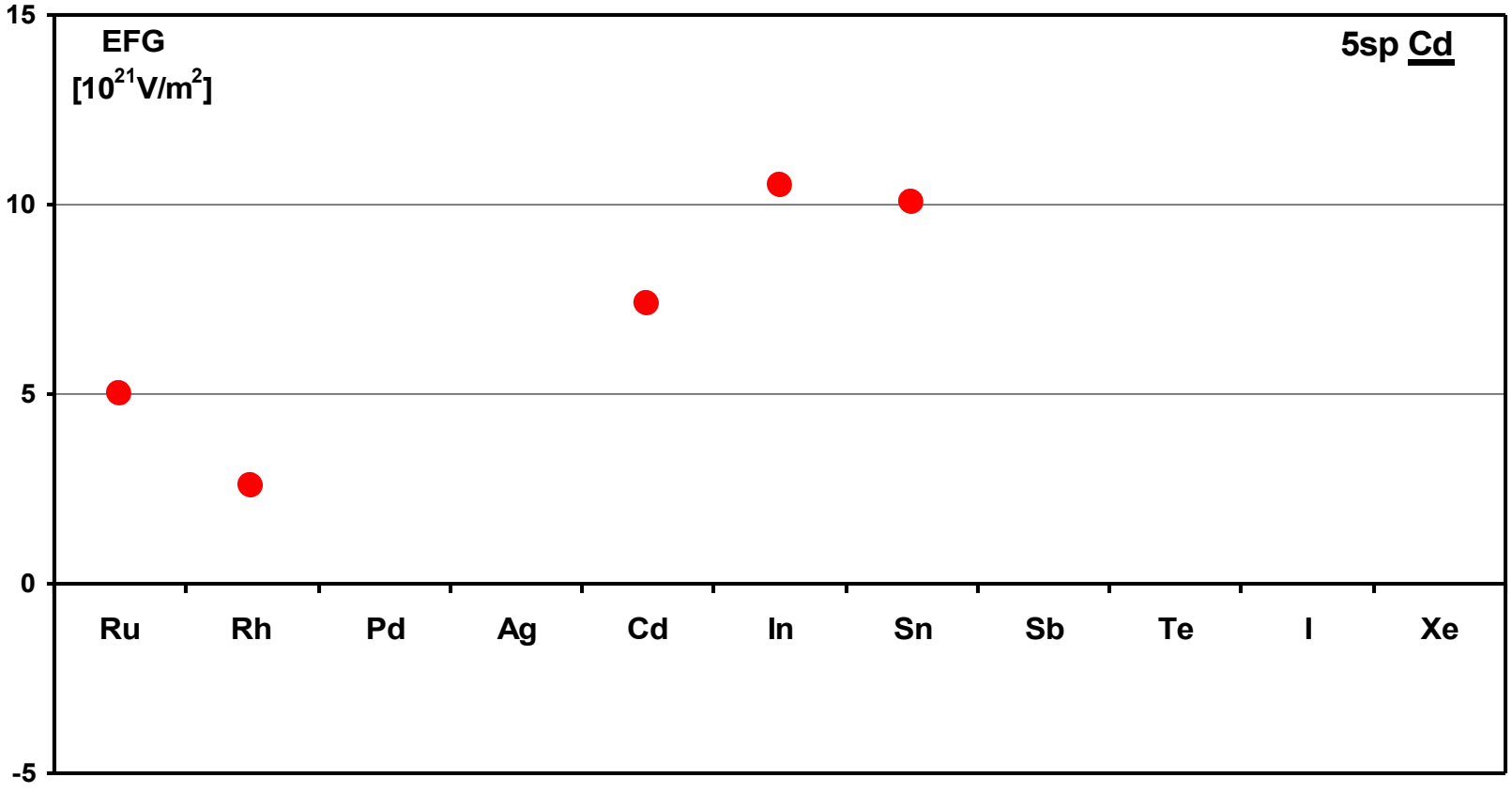
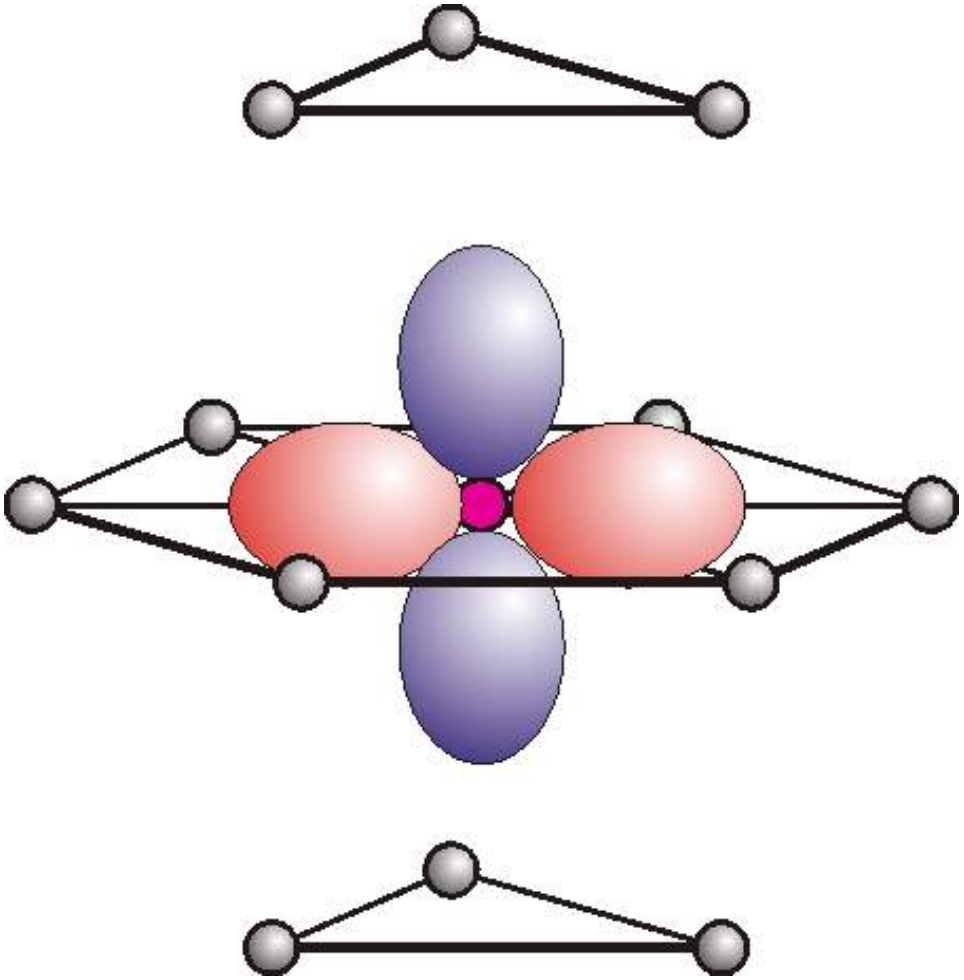
The EFG for Cd in Cd is positive!

EFG at impurities in cadmium: Our data

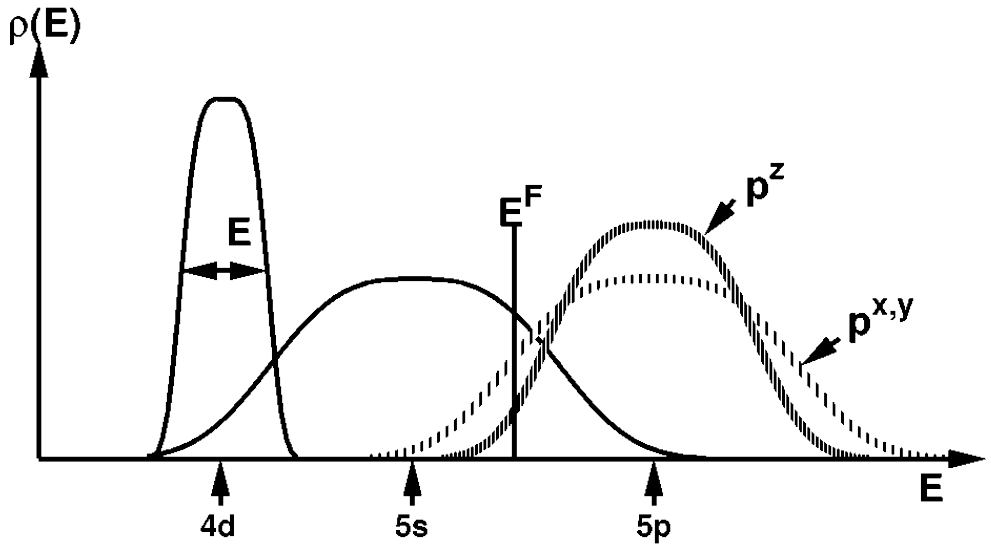


Back to Townes and Dailey:

p orbitals at central atom

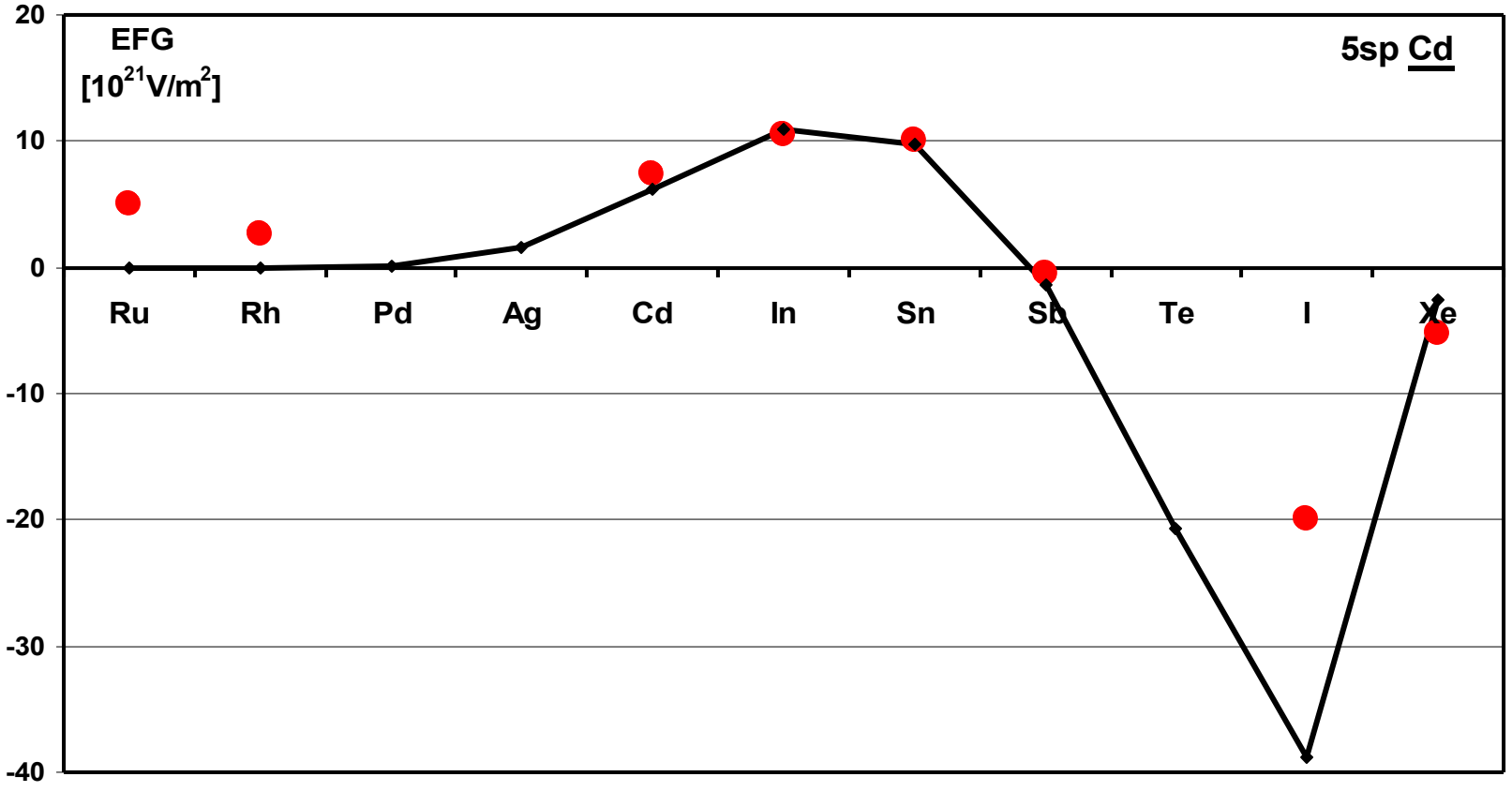


Tight binding model for Cd



$$V_{zz} = \int_0^{E_F} \left(\tfrac{1}{2}\rho(p_x) + \tfrac{1}{2}\rho(p_y) - \rho(p_z) \right) dE \cdot V_{zz}^{p}$$

Model: The whole story



The breakthrough in theory

PHYSICAL REVIEW B VOLUME 37, NUMBER 6 15 FEBRUARY 1988-II

First-principles calculation of the electric-field gradient in hcp metals

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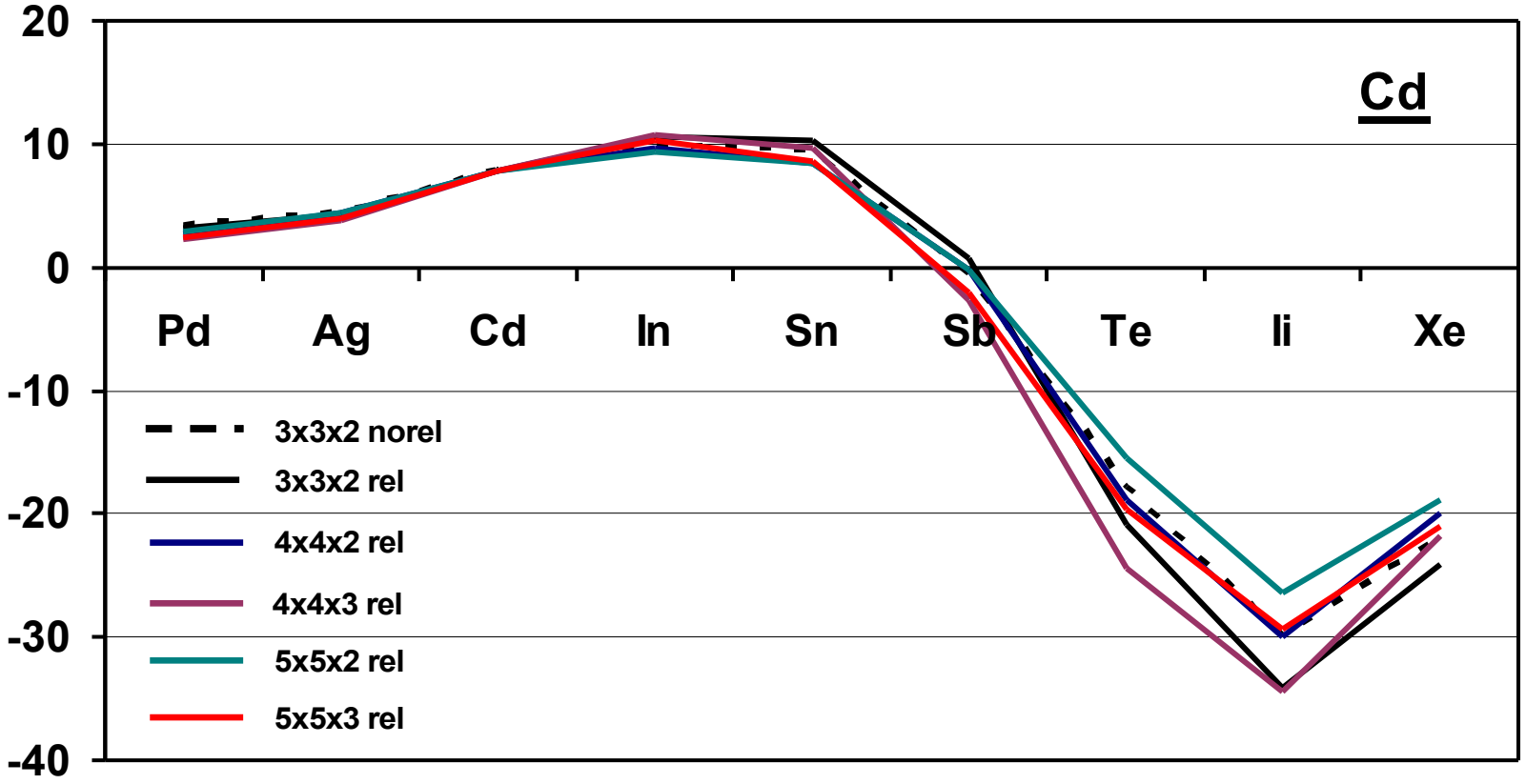
(Received 15 September 1987)

The electric-field gradient (EFG) for all hcp metals from Be to Cd is obtained from energy-band calculations using the full-potential linearized-augmented-plane-wave (LAPW) method. Our first-principles method, which does not rely on any Sternheimer antishielding factor, yields EFG's in good agreement with experiment and predicts also the sign of the EFG's. The EFG was found to be determined mainly by the nonspherical distribution of the valence-electron density close to the nucleus. In general, contributions to the EFG originating from *p* states dominate. This is the case even for transition metals, where the *d* anisotropy is large.

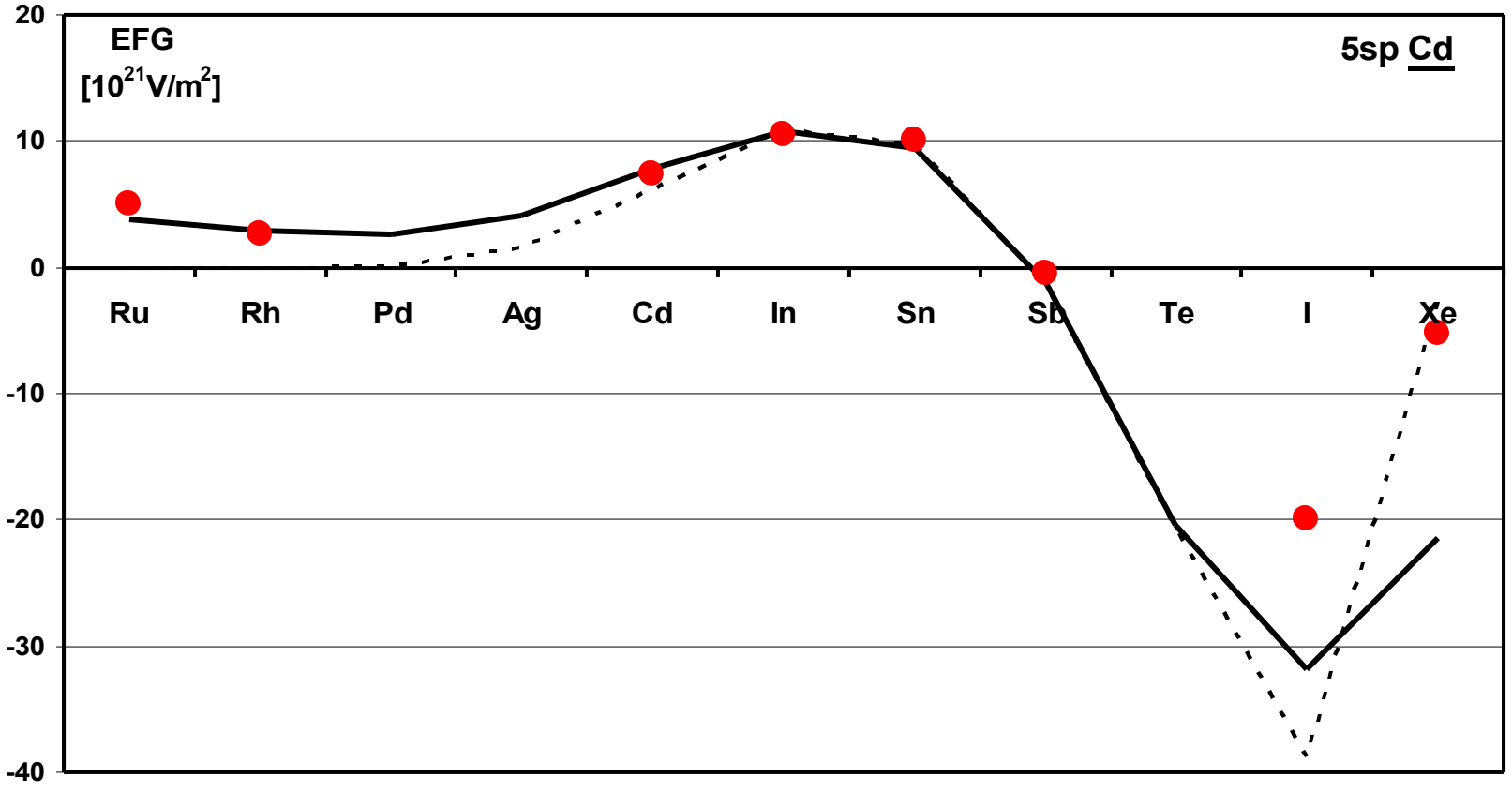
This triggered my retirement project !

Theoretical EFG for 5sp impurities in Cd [10^{21}V/m^2]

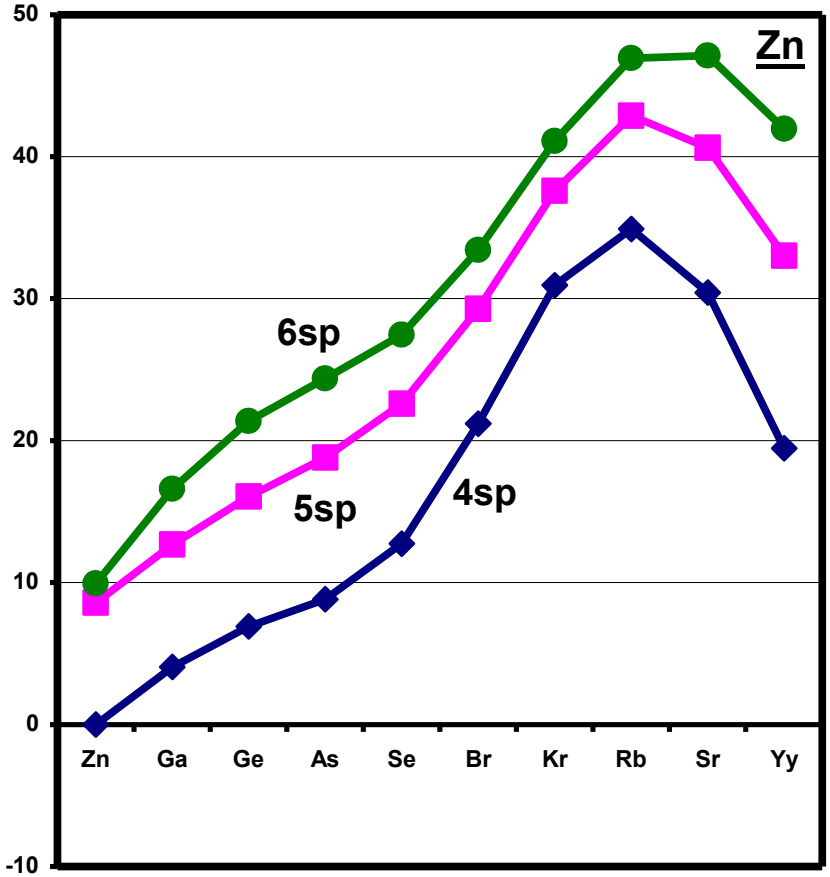


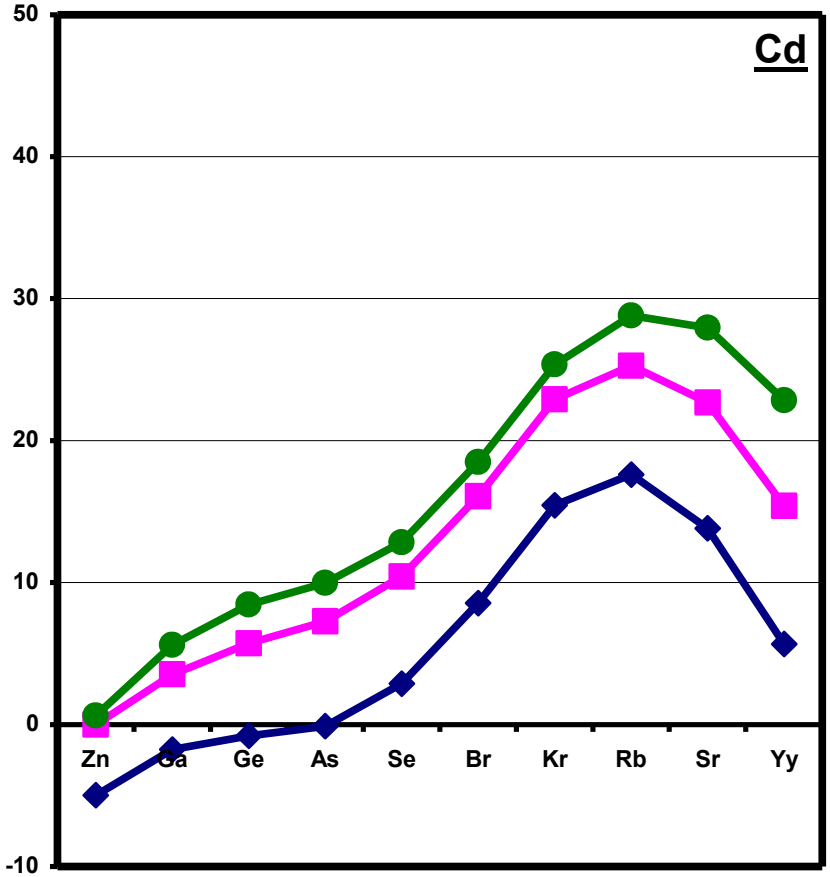
Conclusion: No large dependence on supercell size and local lattice relaxation!

Final FLAPW results

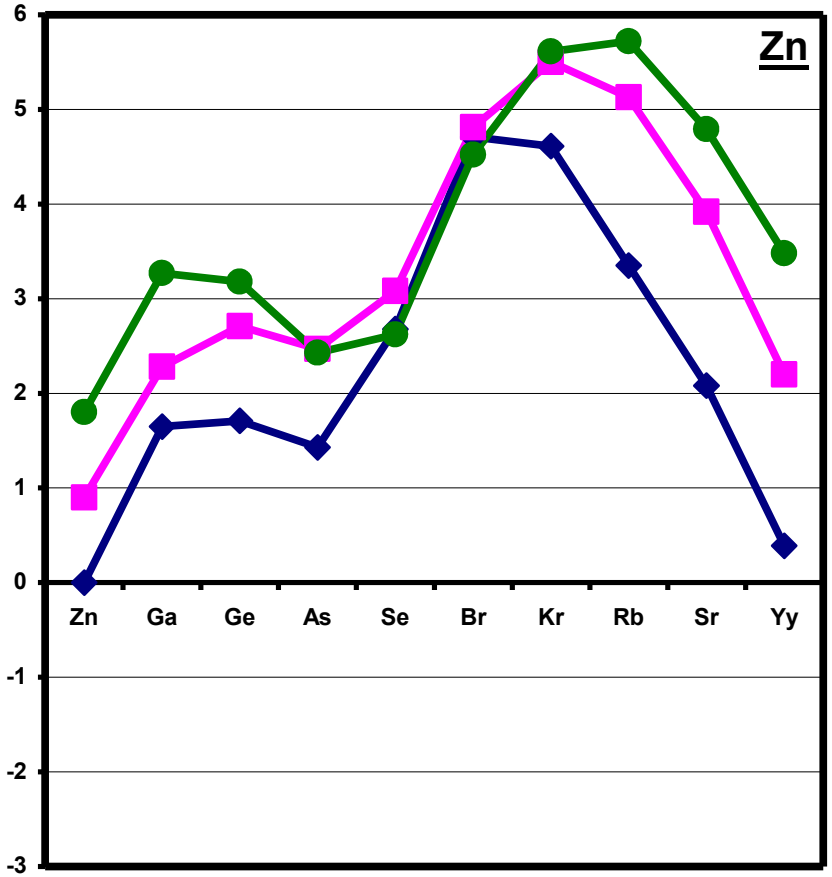


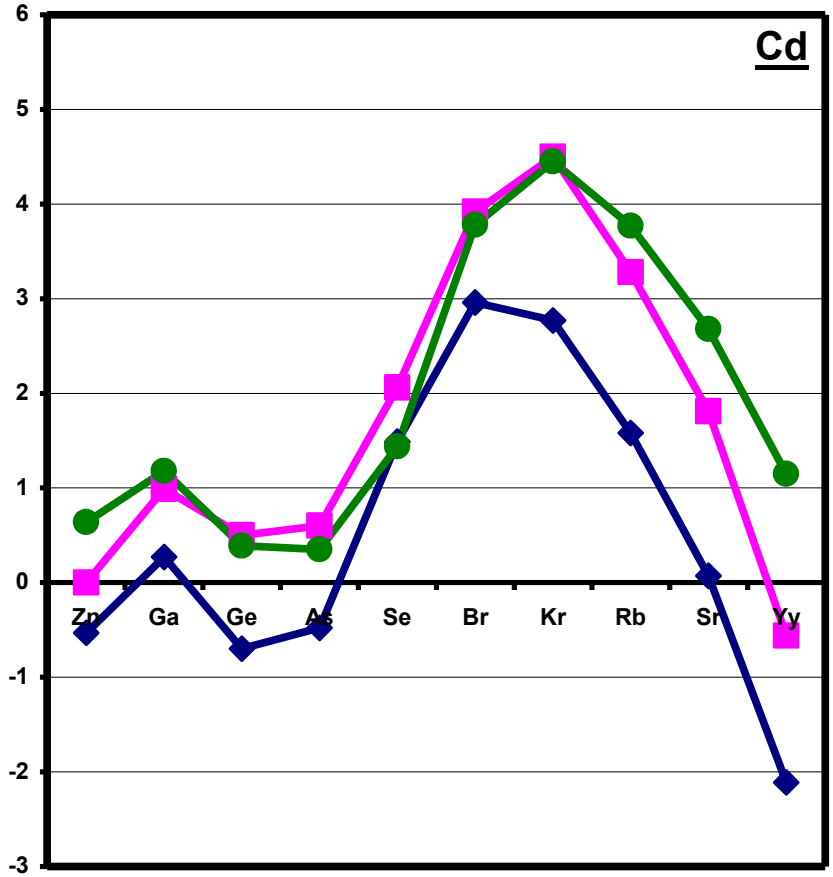
Local volume change (%) by sp impurities



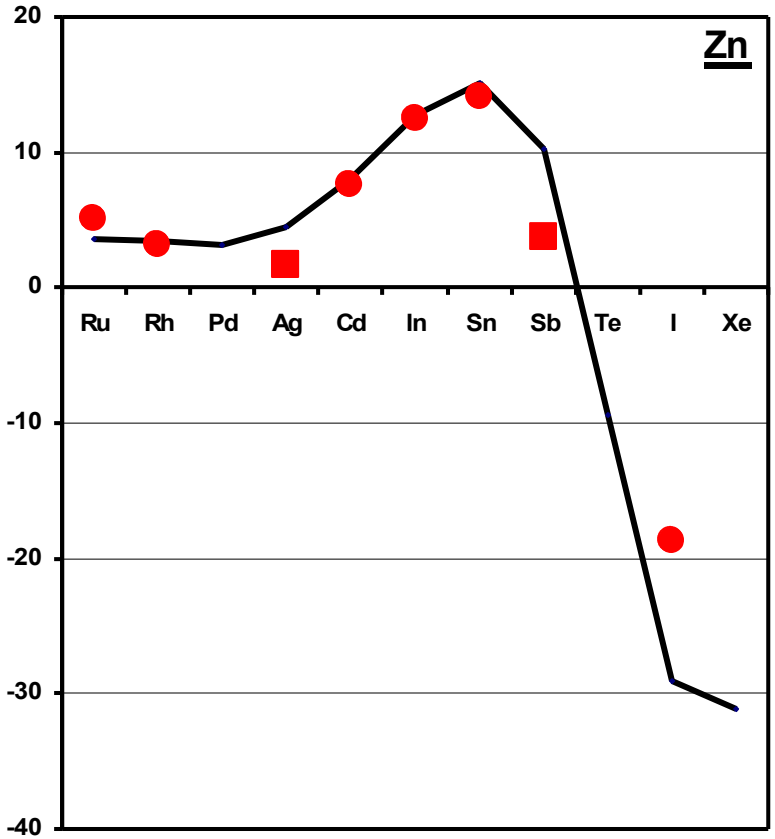


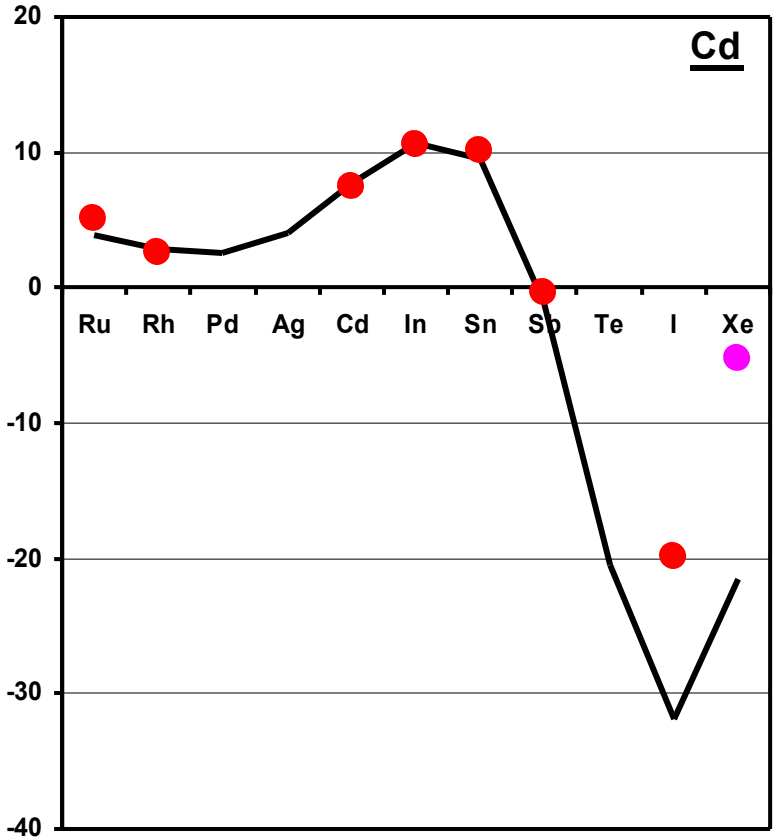
Local c/a change (%) by sp-impurities



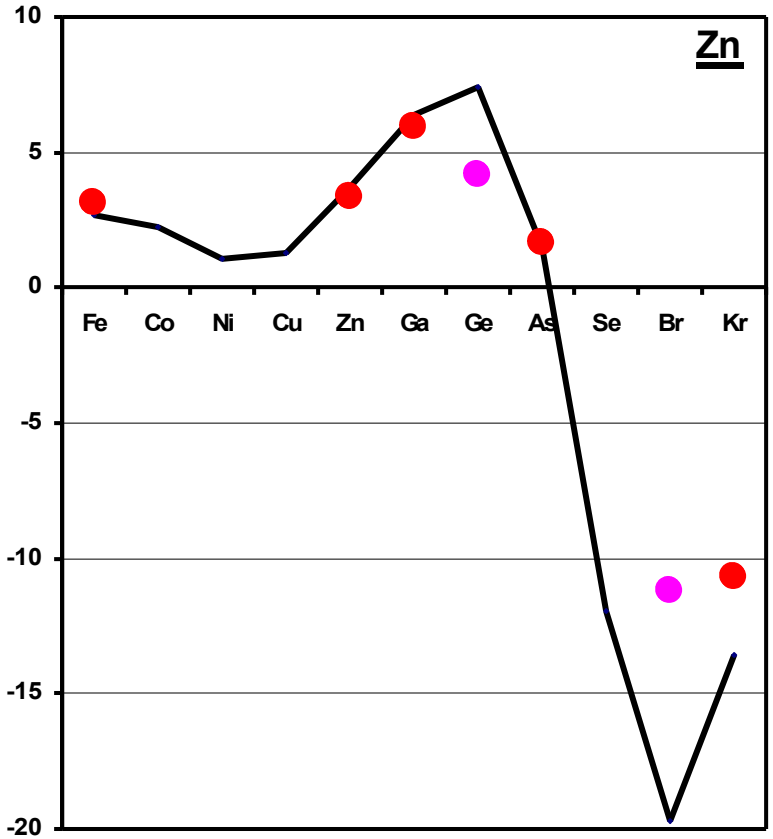


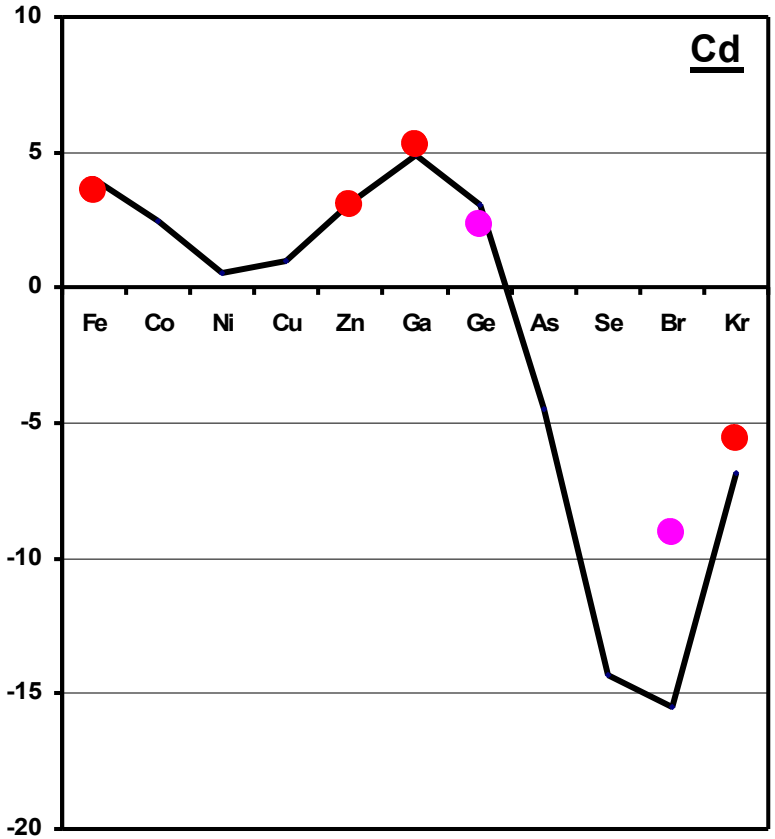
5sp EFG compared to experiments in Zn and Cd





4sp EFG compared to experiments in Zn and Cd





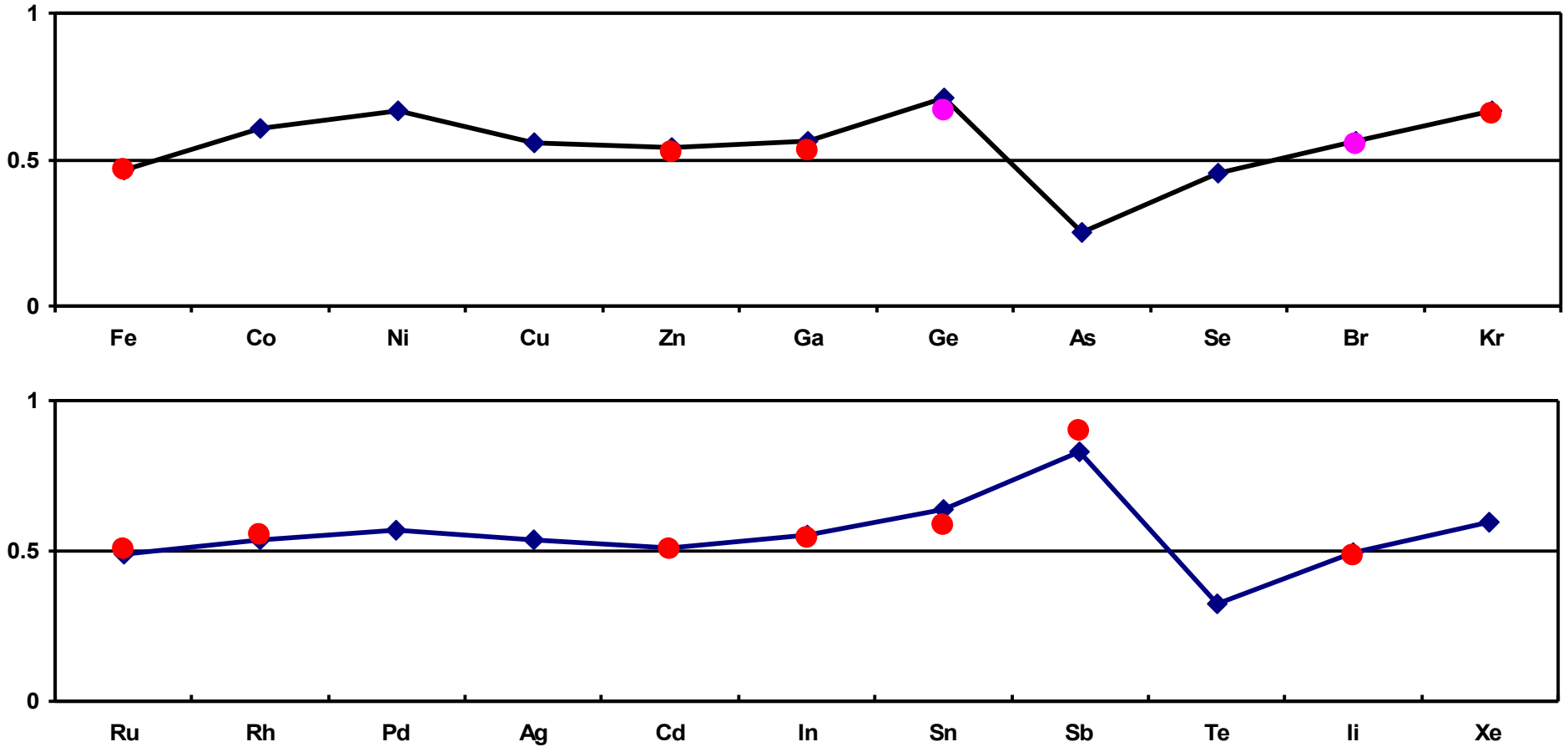
Conclusions from 4sp and 5sp cases

For the cases where the nuclear quadrupole moments (Q) are reliably known the calculations reproduce quantitatively the data, with the exceptions of Sb in Zn and I in Zn and Cd.

Whenever Q has only been estimated, strong disagreement is found. In three cases (^{67}Ge, ^{77}Br, ^{123}Xe) it is felt that the present work results in the first reliable value for Q.

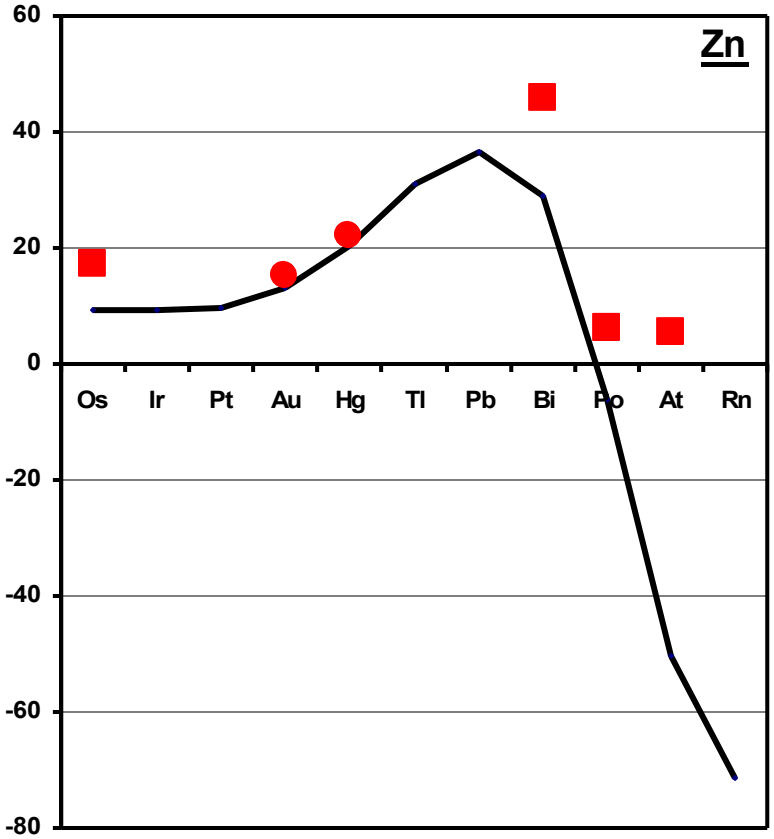
All the qualitative features found in the present investigation can be understood in the rigid band model earlier proposed.

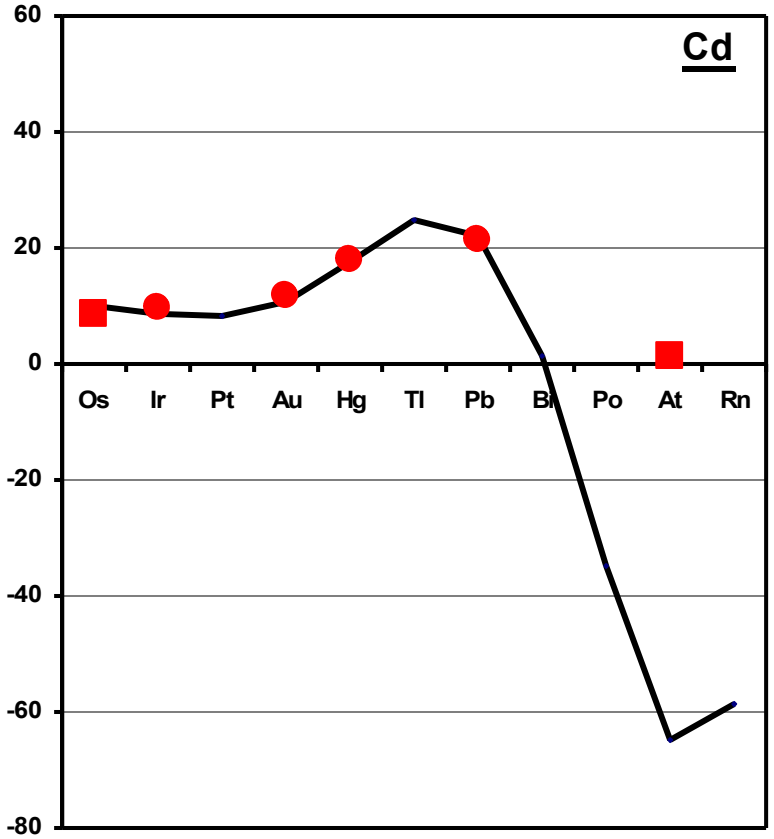
EFG ratio, plotted: XZn / (XZn + XCd)



Also confirms conclusion about incorrect Q values (purple)

6sp EFG compared to experiments





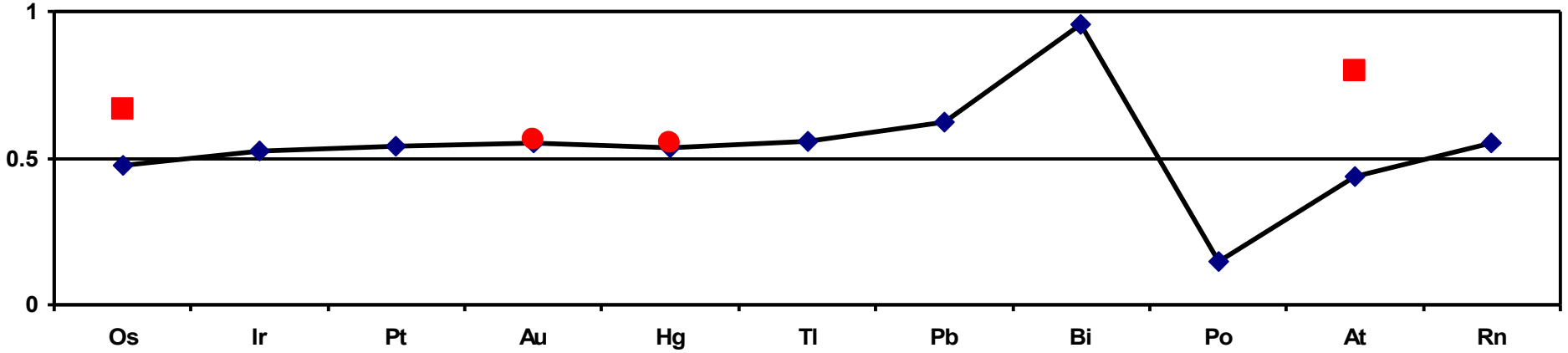
Conclusions from 6sp cases

The inclusion of spin-orbit interaction in the calculations changes the results only by a very small amount, typically 5%.

For the cases measured with time-differential PAC perfect agreement is obtained.

For all cases measured with NO (nuclear orientation) the experiments should be ignored!

6sp EFG ratio, plotted: X<u>Zn</u> / (X<u>Zn</u> + X<u>Cd</u>)



Also confirms conclusion about NO experiments (squares)!

Summary

The electric field gradients (EFG) at the impurities Fe – Kr, Ru – Xe, and Os – Rn in the hcp metals Zn and Cd were calculated with the WIEN2k full-potential linearized augmented plane waves (FLAPW) code. The generalized gradient approximation was used throughout.

Supercells with 36(45), 64(48), 96(15), 100(14) and 150(21) atoms were constructed with the low temperature lattice constants for all cases in order to test the influence on the resultant EFG (number of k-points in the reduced Brillouin zone in parentheses).

The positional parameters were relaxed to small resultant forces acting on all atoms in the supercell, requiring typically 3-4 structural iterations.

The calculations reproduce the experiments remarkably well !

Thank you

Dave !

(for putting me on the track)