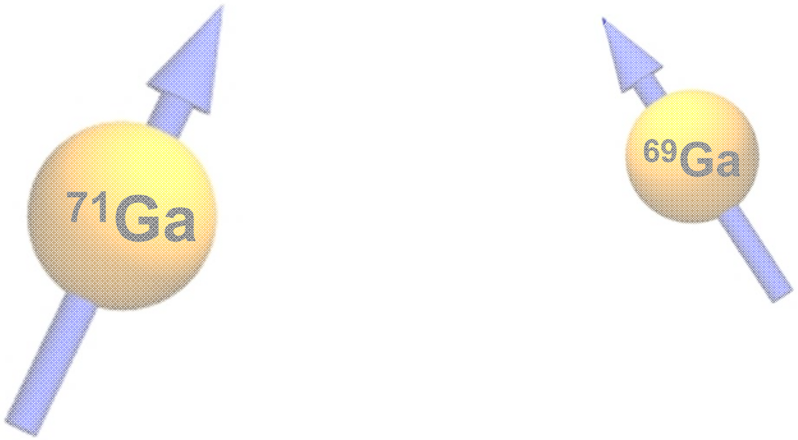
RWTH AACHEN UNIVERSITY

IAC

Festkörper-NMR-Spektroskopie in der Anorganischen Chemie



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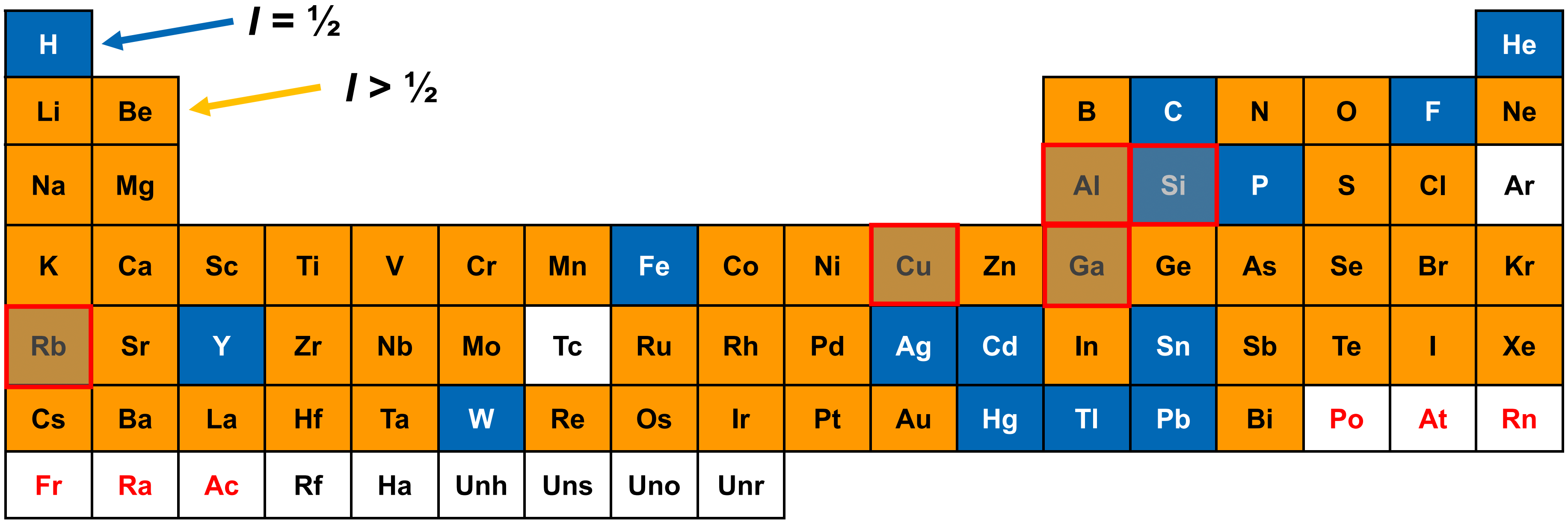
http://www.nmr.ac.rwth-aachen.de

Solid state NMR

(Active elements)

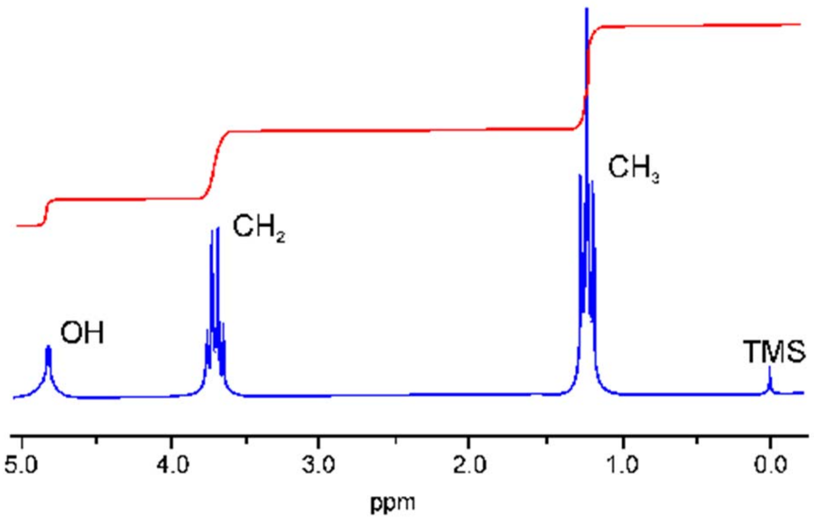


I = ½ magnetic couplings only

I > ½ magnetic and electric couplings

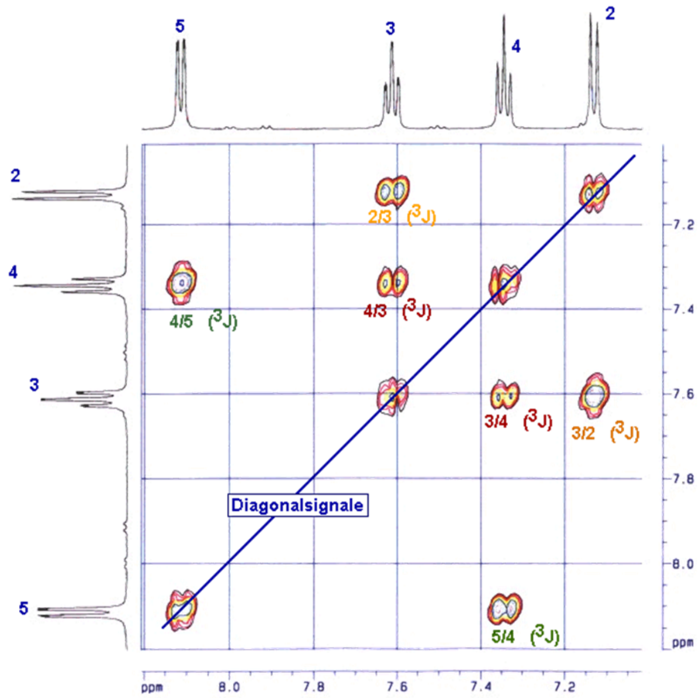
Liquid state NMR-spektroskopy

1D-NMR



⇒ **NMR signal as fingerprint (basic analytik)**

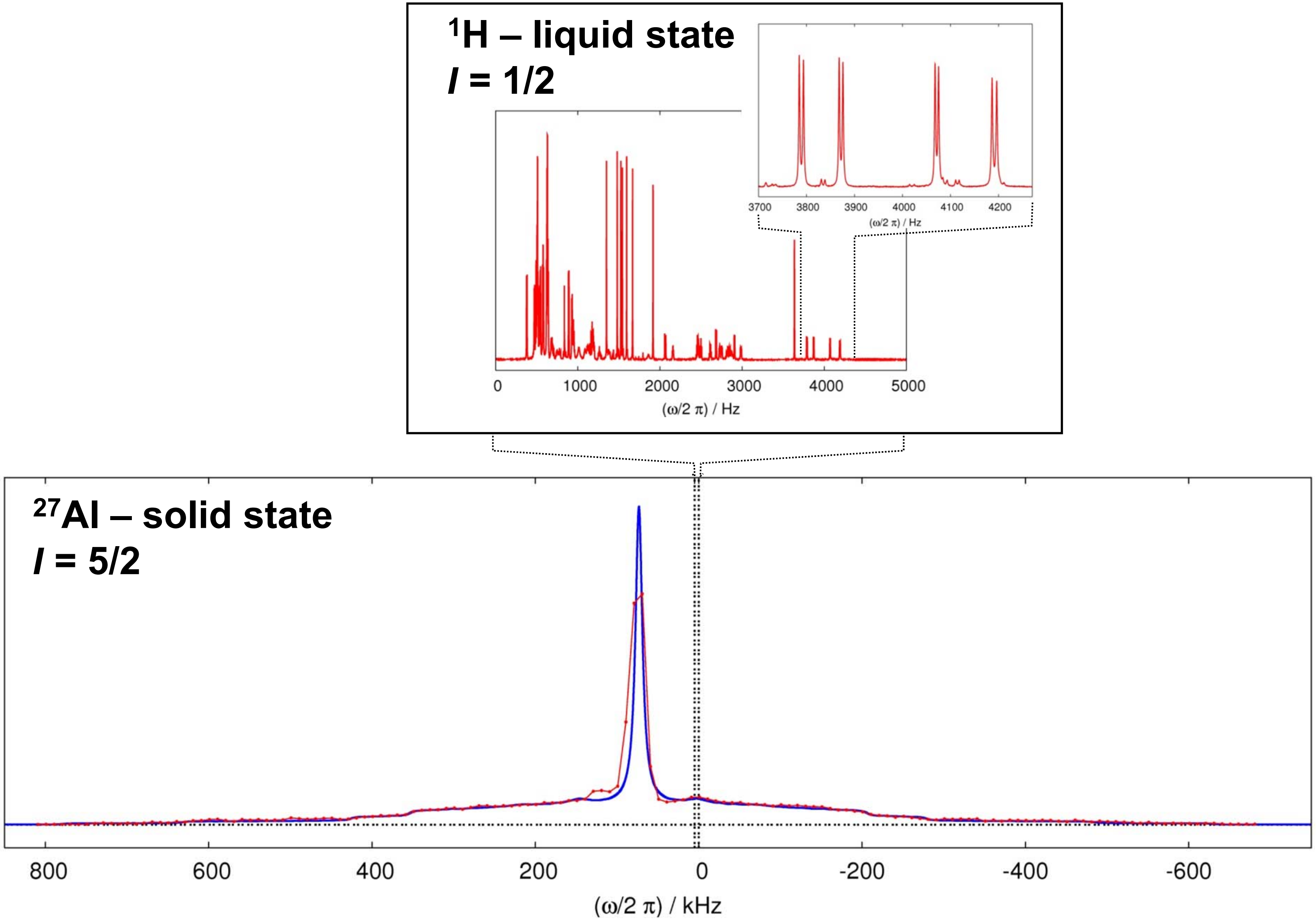
2D-NMR



⇒ **signal assignment**

⇒ **structure determination**

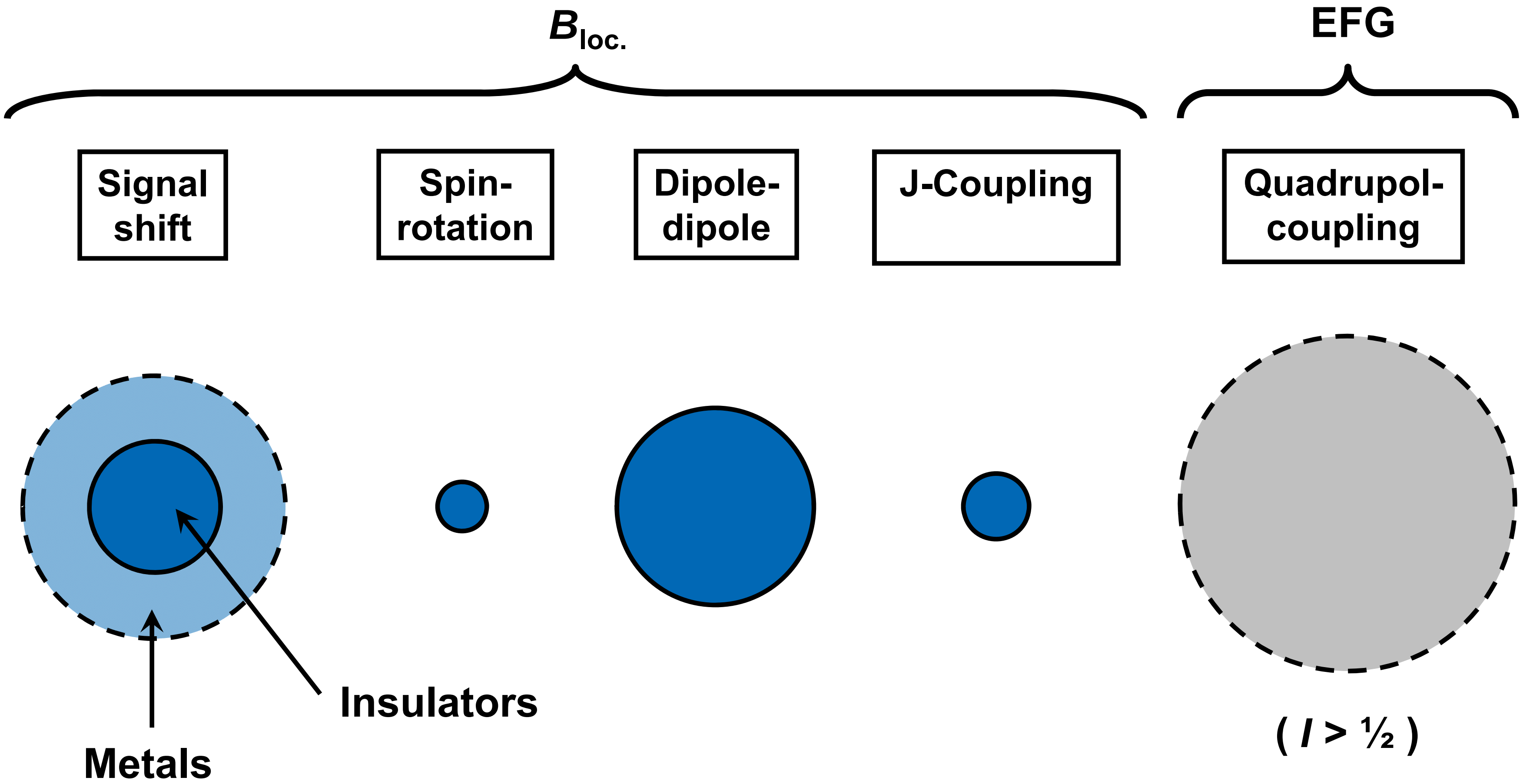
Liquid state vs. solid state



Couplings

External couplings: B_0 and B_{rf}

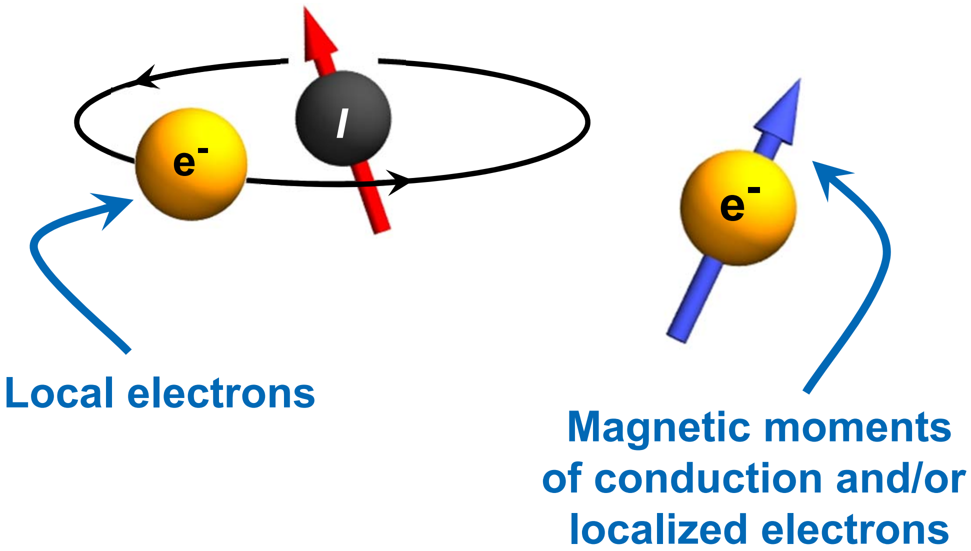
Internal couplings:



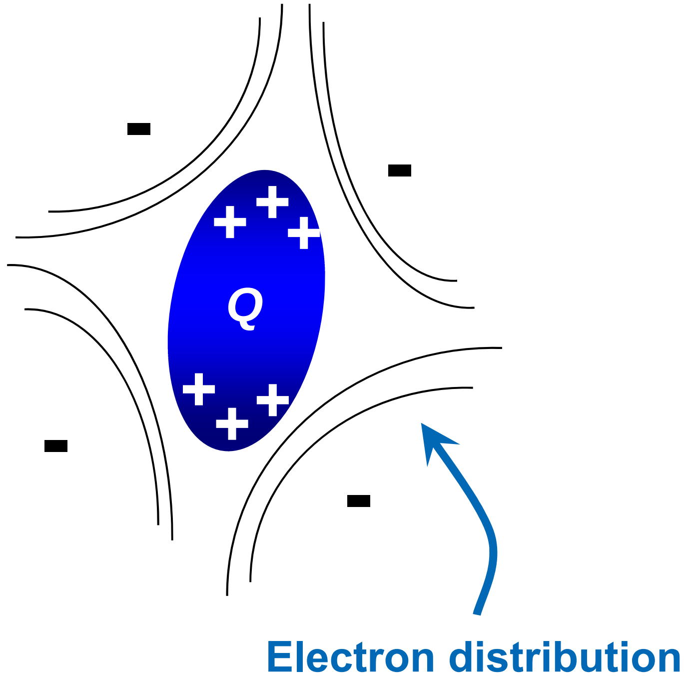
Solid state NMR

(*Basic interactions*)

Magnetic $I \neq 0$



Electric $I > ½$



Local magnetic field at nuclear site (B_{loc})

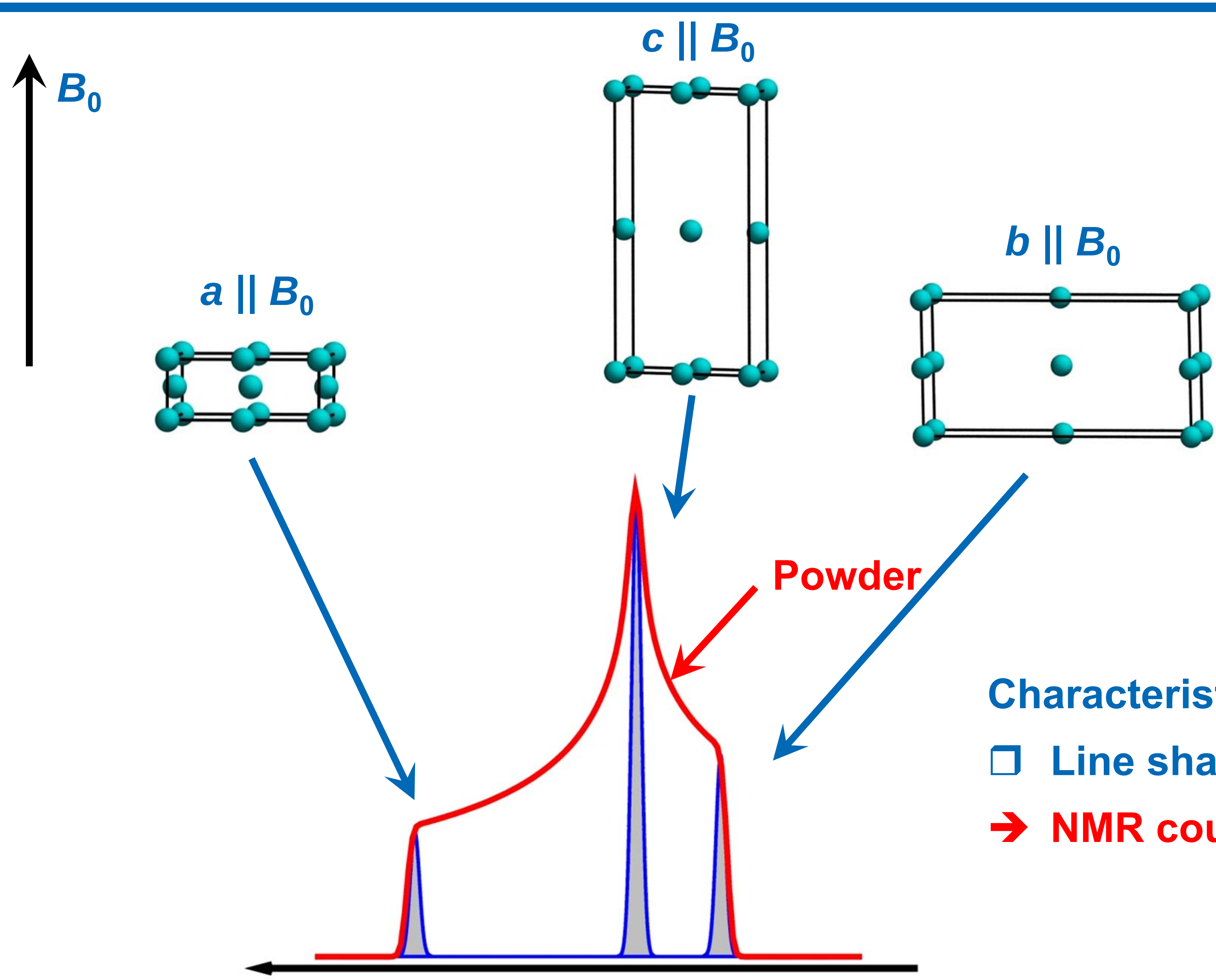
- ❒ Chemical shielding
- ❒ *Knight*-Shift
- ❒ Magnetism

Charge distribution

- ❒ Quadrupole coupling

Solid state NMR

(*Anisotropic interactions*)



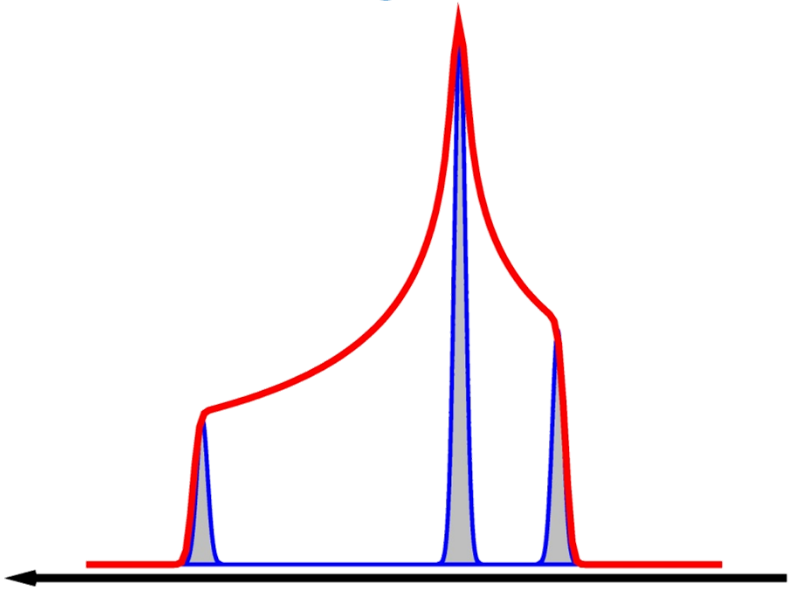
Characteristic line shape

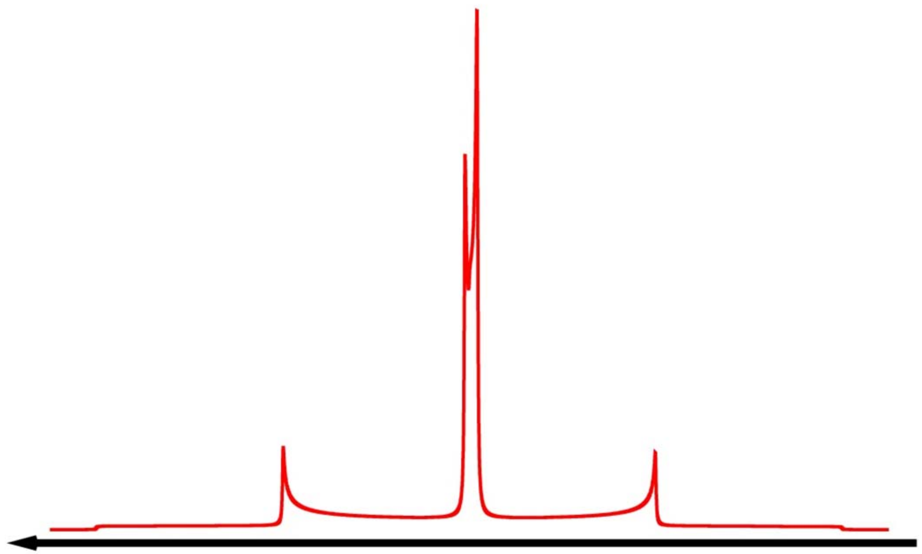
❒ **Line shape analysis**

➔ **NMR coupling parameters**

Solid state NMR
(*Coupling parameter*)

Magnetic $I \neq 0$ | **Electric $I > ½$**





Chemical shielding δ | ***Knight* shift K** | **Quadrupole coupling**

$$\delta_{iso} = ⅓\,(\delta_{XX} + \delta_{YY} + \delta_{ZZ}) \qquad K_{iso} = ⅓\,(K_{XX} + K_{YY} + K_{ZZ}) \qquad \Delta_{iso}$$

$$\Delta_\delta = \delta_{ZZ} - \delta_{iso} \qquad \Delta_K = K_{ZZ} - K_{iso} \qquad \Delta_{aniso}$$

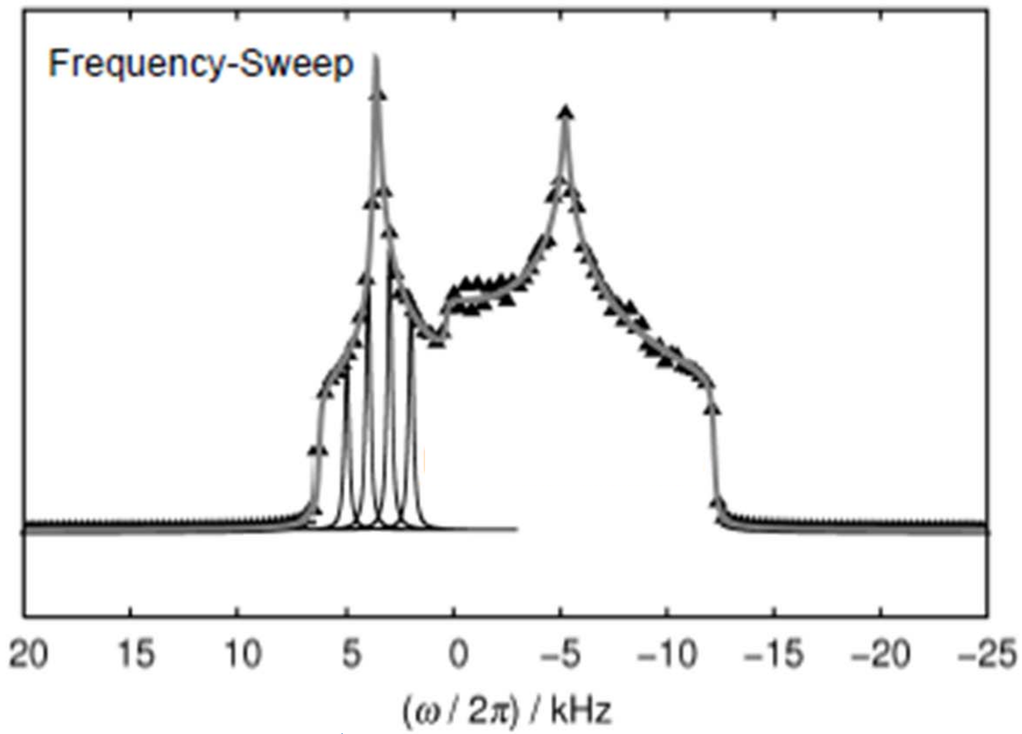
$$\eta_\delta = \frac{\delta_{XX} - \delta_{YY}}{\delta_{ZZ}} \qquad \eta_K = \frac{K_{XX} - K_{YY}}{K_{ZZ}} \qquad \eta_\Delta$$

$$C_Q = \frac{|V_{ZZ}|\, e\, Q}{h}$$

$$\eta_Q = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$$

Mesaurement strategies

(Wideline and ultra wideline)

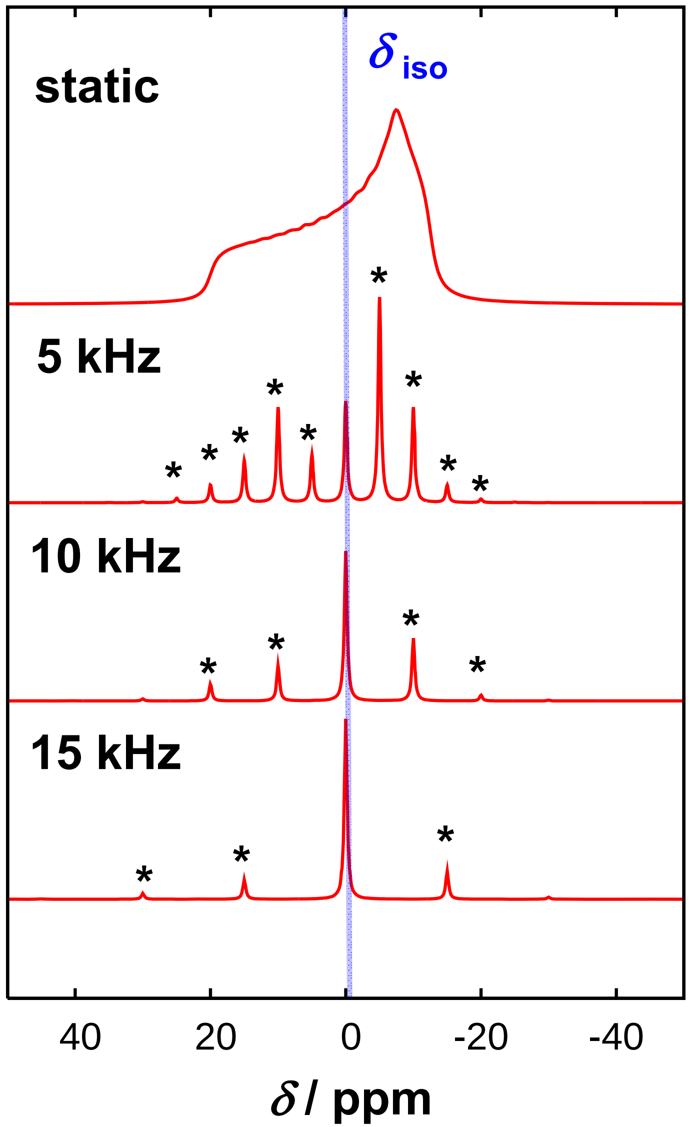


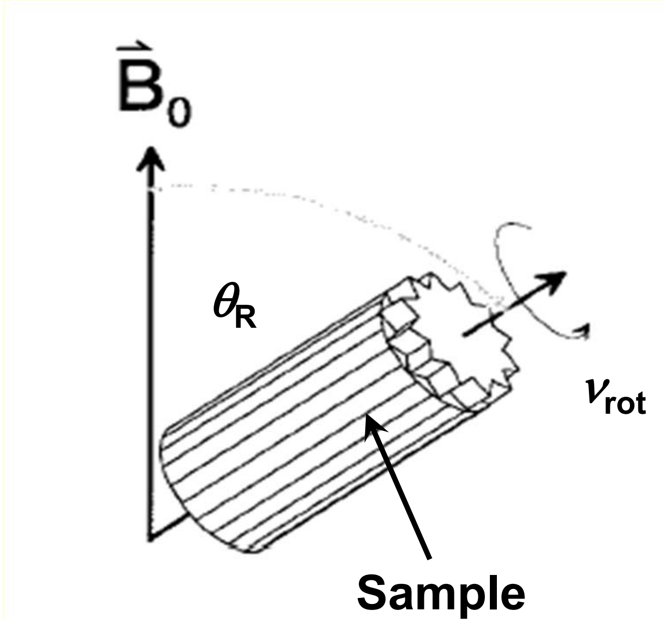
Δν < 200 kHz → **Echo experiment**

Δν > 200 kHz → **Sequence of selective excitation echo experiments**

Mesaurement strategies

(Magic angle spinning – MAS)





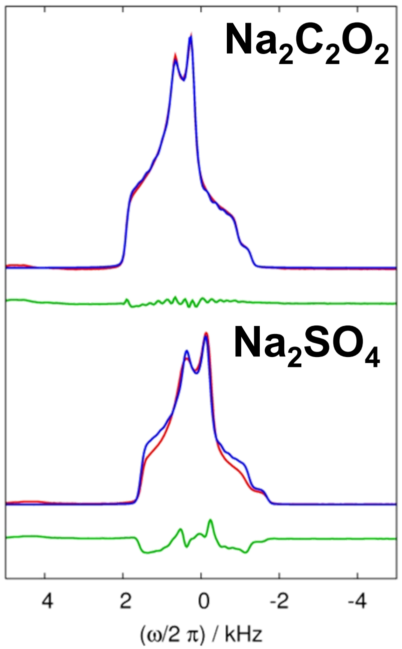
Experimental:

Ø 4 mm ν_{rot} = 15 kHz
Ø 2.5 mm ν_{rot} = 35 kHz
Ø 1.2 mm ν_{rot} = 65 kHz

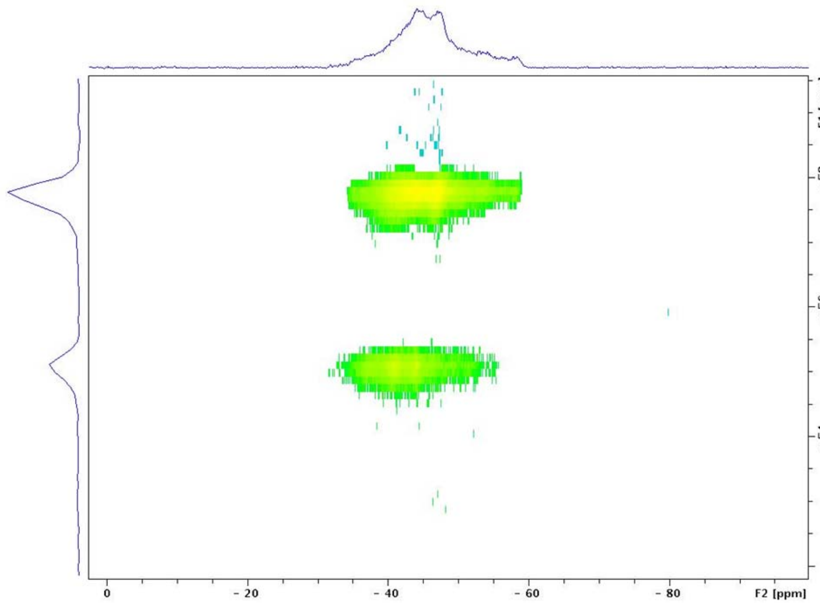
- ➢ **Increase of resolution**
- ➢ **Increase of S/N**

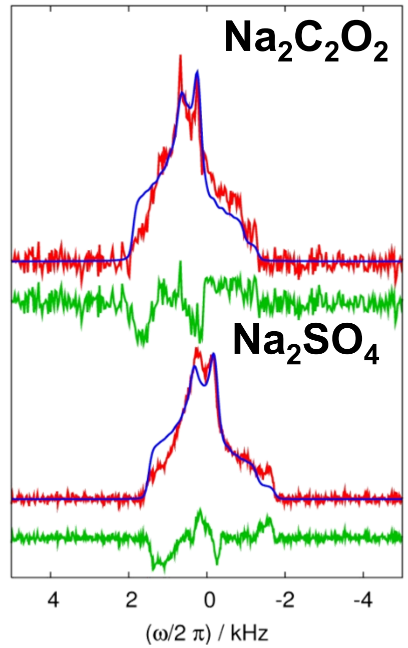
Multi Quantum MAS

Signals



2D – MQMAS



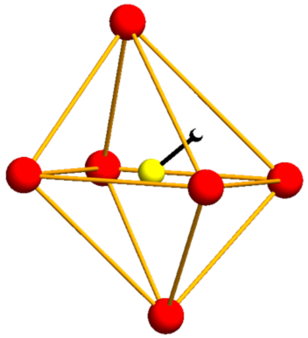


- **additional increase of resolution by double rotation (DOR) θ_1 = 54.7° and θ_2 = 30.6° / 70.1°)**

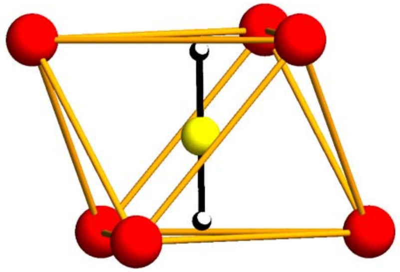
Dynamic disorder

*M*HS with
M = Na, K, Rb

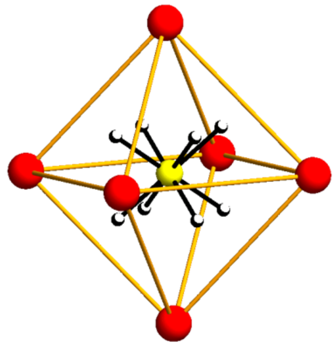
TTM



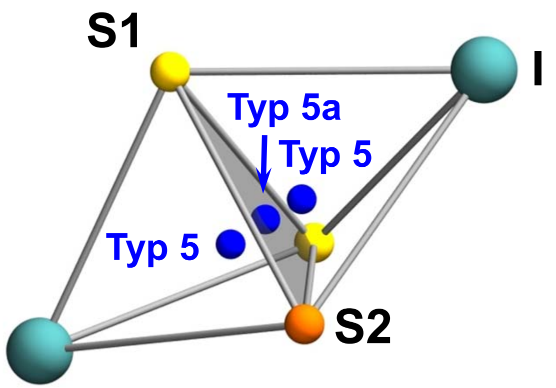
MTM

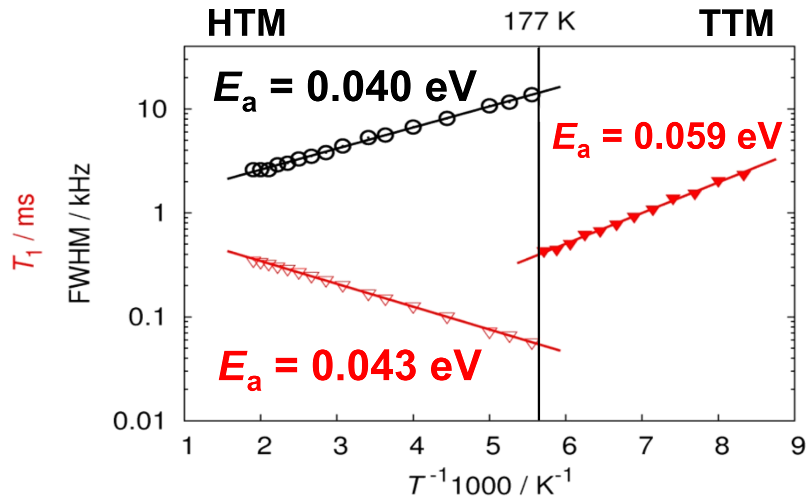


HTM



$Li_{7-x}PS_{6-x}I_x$

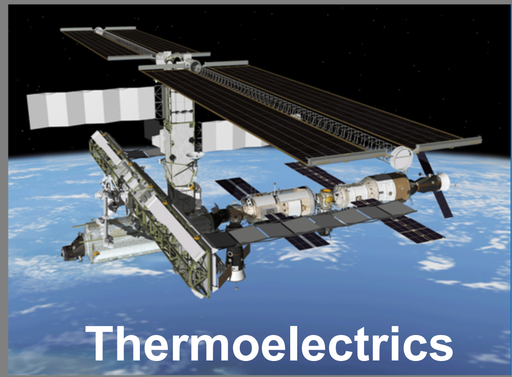


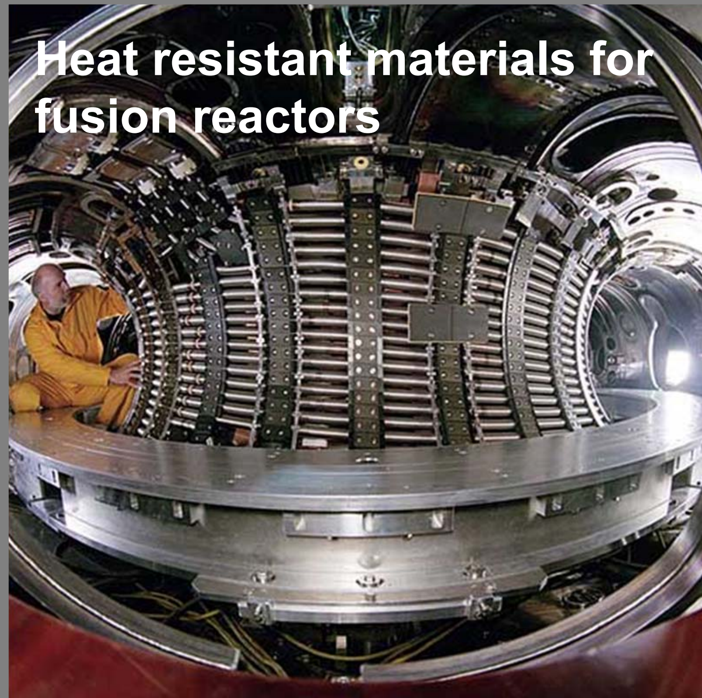


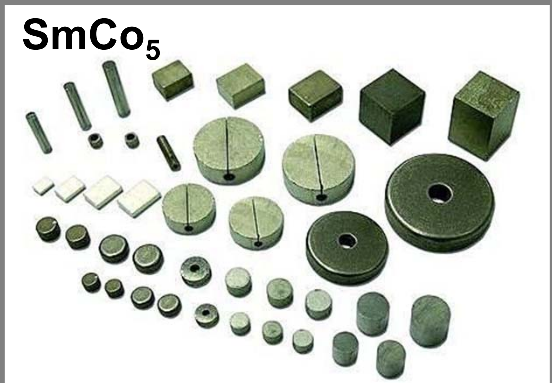
[1] F. Haarmann, H. Jacobs, J. Senker, E. Rössler. *J. Chem. Phys.* (2002) 117, 1269.
[2] F. Haarmann, H. Jacobs, W. Kockelmann, J. Senker, P. Müller, C. A. Kennedy, R. A. Marriott, L. Qiu, M. A. White. *J. Chem. Phys.* (2002) 117, 4961.
[3] O. Pecher, S.-T. Kong, T. Goebel, V. Nickel, K. Weichert, C. Reiner, H.-J. Deiseroth, J. Maier, F. Haarmann, D. Zahn. *Chem. Eur. J.* (2010) 16, 8347.
[4] D. Bräunling, O. Pecher, D. M. Trots, A. Senyshyn, D. A. Zherebtsov, F. Haarmann, R. Niewa. *Z. Anorg. Allg. Chem.* (2010) 636, 936.

Intermetallic materials

(Why?)





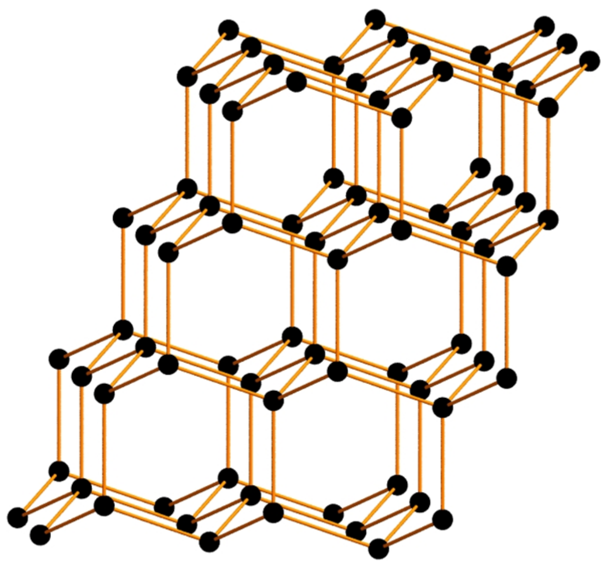


Fun

Intermetallic materials

(*What's interesting: chemical bonding*)

Inorganic materials



Intermetallic materials

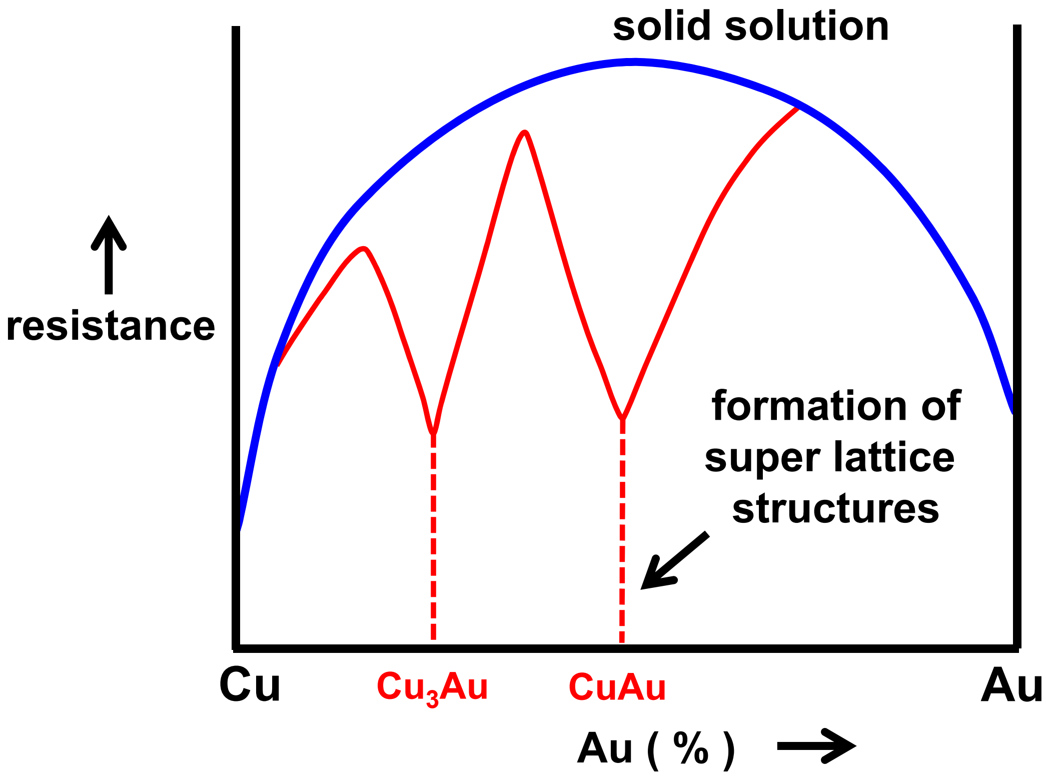
Intermetallic phases have long been among the black sheep in the family of chemical compounds. Their chemical bonding has eluded description by the valence rules, which otherwise are extremely effective. As a result, understanding of the structure-bonding relationships in these phases to date has remained nebulous, even though they form the largest group of inorganic compounds. Their broad industrial applicability and richly varied structural chemistry call for new approaches for explaining their structures, electronic structures, and physical properties...

Reinhard Nesper *Angew. Chem. Int. Ed.* (1991) 30, 789.

➔ **Structure property relationship**

Motivation

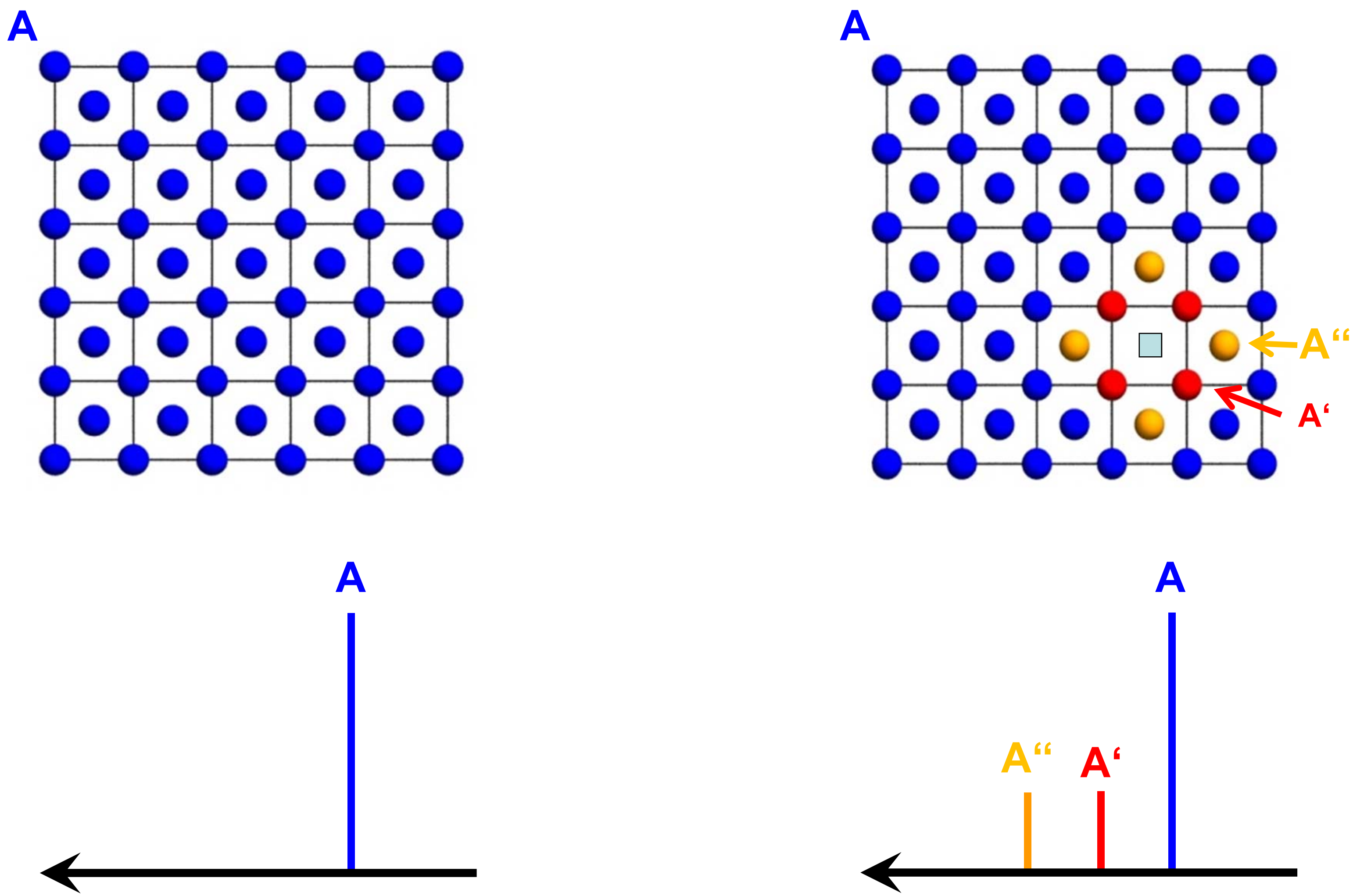
(Properties of materials)



- conductivity
- mechanical properties
- electronic properties of semiconductors
- ion conductivity

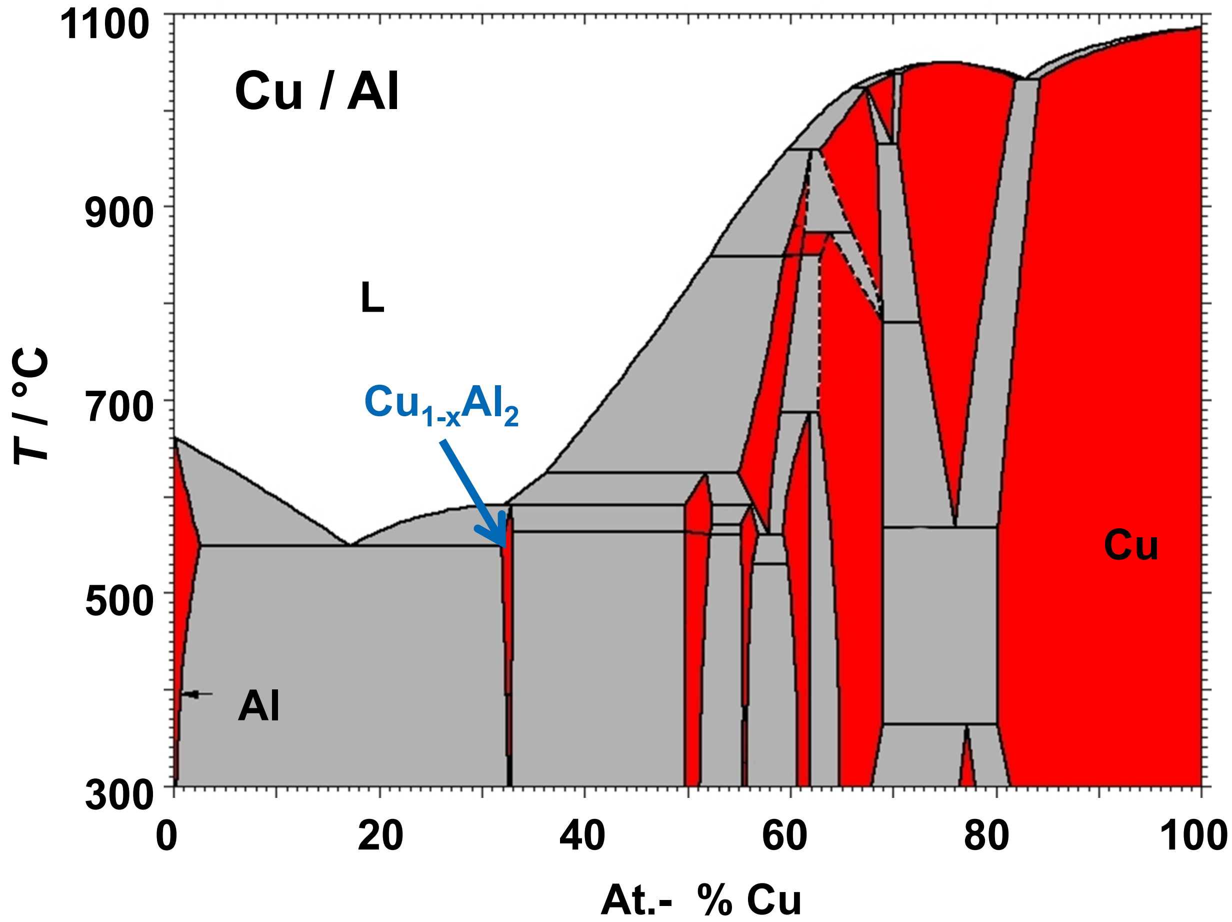
Motivation

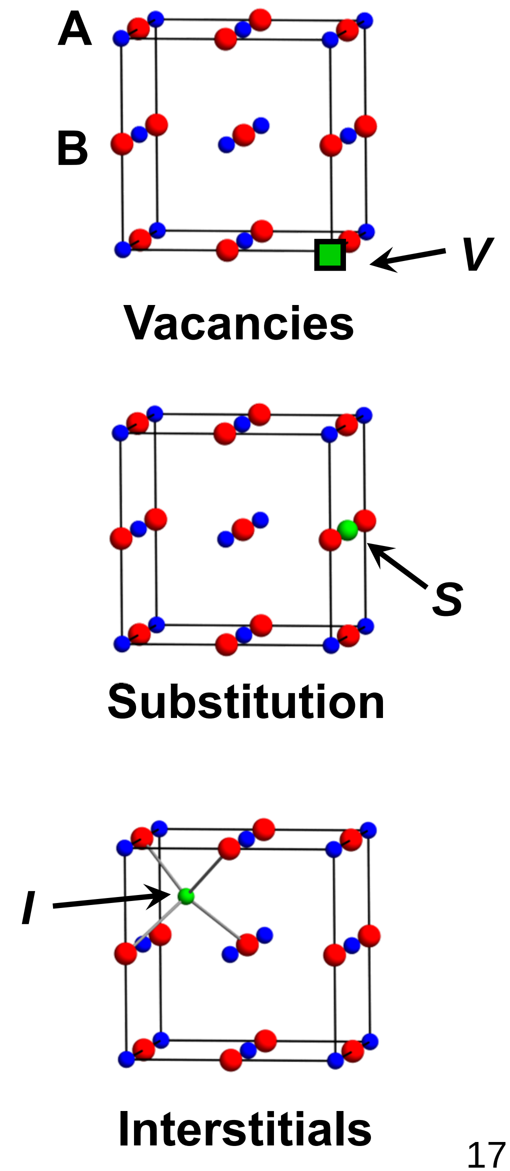
(Local probe NMR – naive picture about signal shift)



Motivation

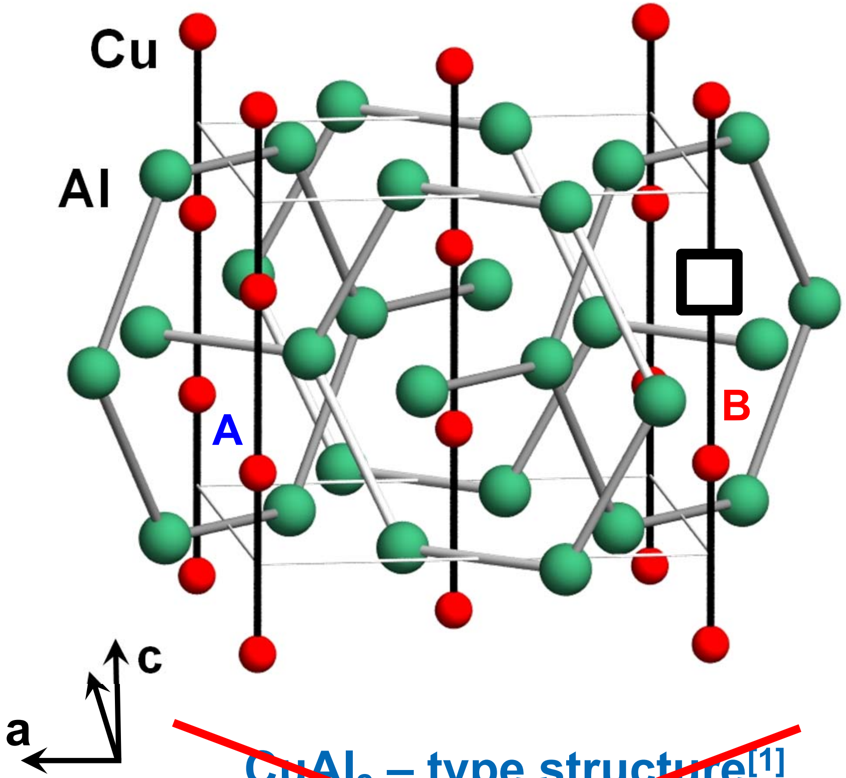
(*Pointdefects*)



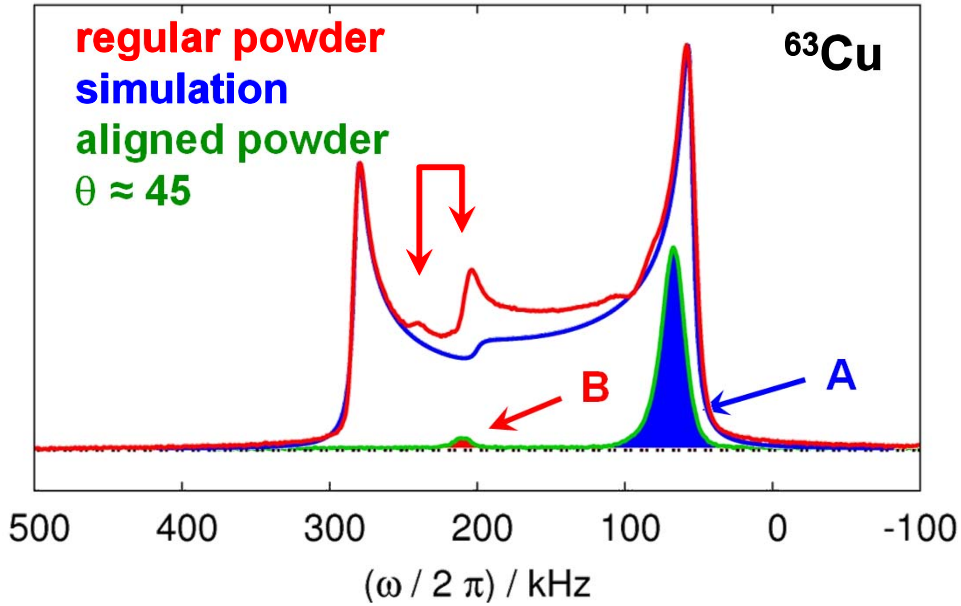


J. L. Murray *Int. Metal Rev.* (1985) 30, 211.

$Cu_{1-x}Al_2$
(*Local order*)



~~$CuAl_2$ – type structure[1]~~
~~1 x Al-position~~
~~1 x Cu-position~~



- ➔ additional Cu sites
- ➔ Cu vacancies[2]
- ➔ different Cu EFGs result in resolved NMR signals

[1] B. Friauf *J. Am. Chem. Soc.* (1927) 49, 3107.
[2] Haarmann, Armbrüster, Grin *Chem. Mat.* (2007) 19, 1147.

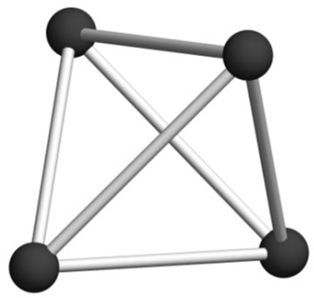
Selected silicides of the alkali metals and barium

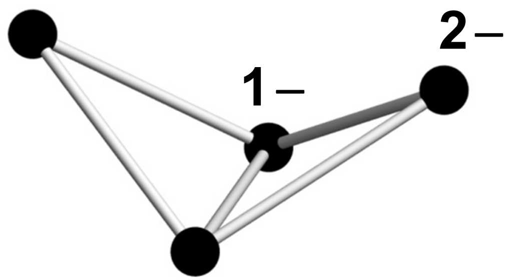
(Crystal structures)

Compound	Type of structure
Na_4Si_4 [1]	NaSi
K_4Si_4 [2]	KGe
Rb_4Si_4 [2]	KGe
Cs_4Si_4 [2]	KGe
Ba_2Si_4 [3]	$BaSi_2$
Ba_3Si_4 [4]	Ba_3Si_4

Structural motifs

Si_4^{4-}





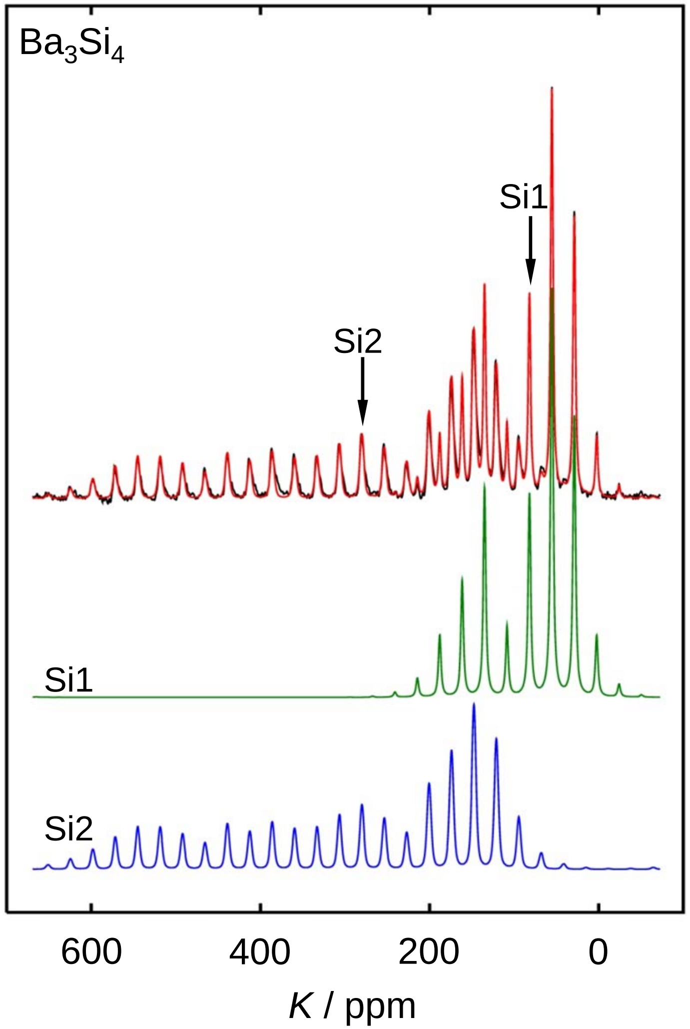
Si_4^{6-}

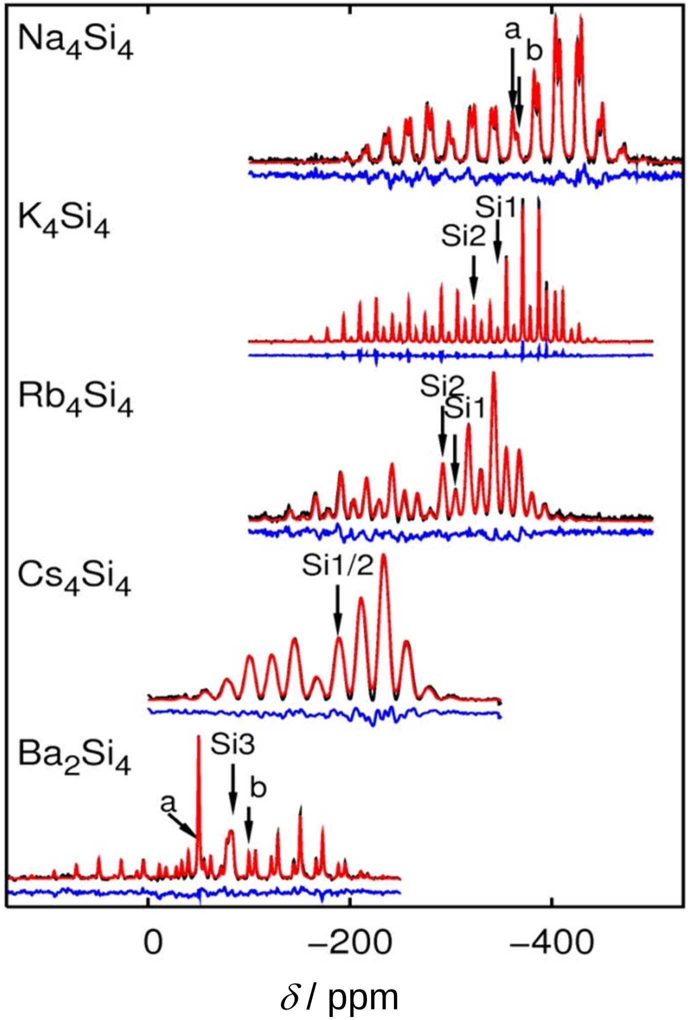
How does the chemical bonding change within the anions?

[1] J. Witte, H.G. von Schnering, W. Klemm *Z. Anorg. Allg. Chem.* (1964) *327*, 260.
[2] E. Busmann *Z. Anorg. Allg. Chem.* (1961) *313*, 90.
[3] K. H. Janzon, H. Schäfer, A. Weiss *Z. Anorg. Allg. Chem.* (1970) *372*, 87.
[4] U. Aydemir, A. Ormeci, H. Borrmann, B. Böhme, F. Zürcher, B. Uslu, T. Goebel, W. Schnelle, P. Simon, W. Carrillo-Cabrera, F. Haarmann, M. Baitinger, R. Nesper, H. G. von Schnering, Yu. Grin *Z. Anorg. Allg. Chem.* (2008) *634*, 1651.

Silicides

(^{29}*Si MAS NMR*)



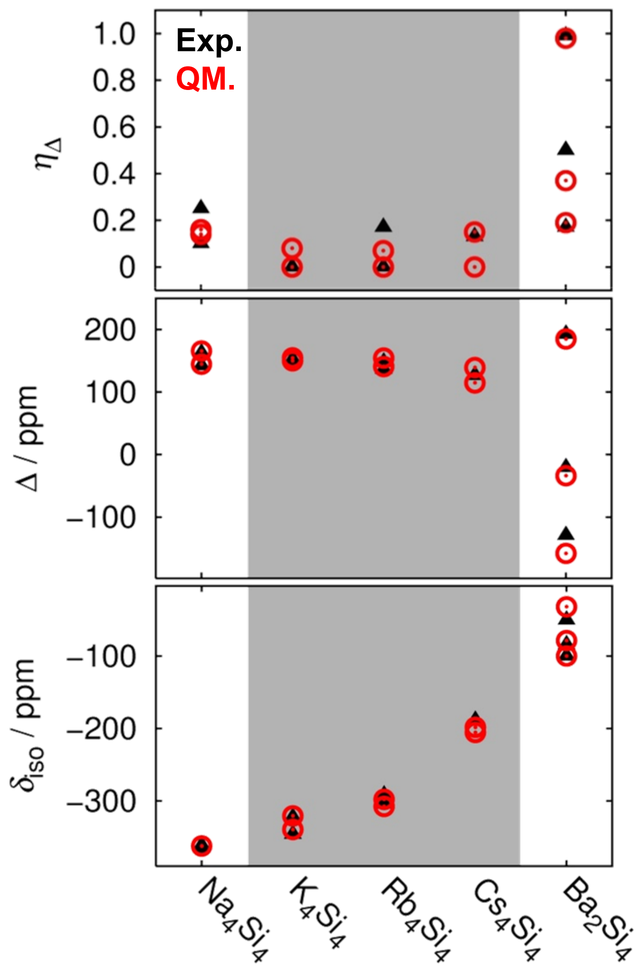


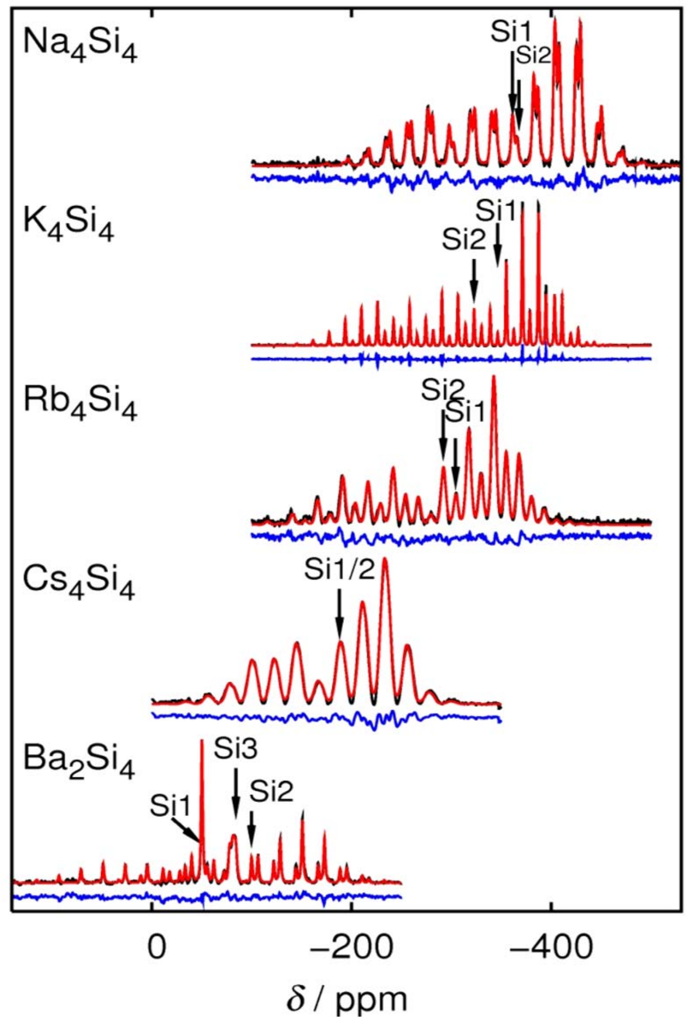
- ❐ **Line shape analysis**
- ➔ ***Knight shift***

➔ **Systematic signal shift with increasing atomic number of *M***

Silicides

(*Quantum mechanical calculations – NMR CASTEP*[1,2])





➔ **Agreement of NMR and QM**

➔ **Signal assignment**

➔ **Systematic signal shift with increasing atomic number of *M***

[1] **C. J. Pickard, F. Mauri, *Phys. Rev.* B (2001) 63, 245101.**
[2] **J. R. Yates, C. J. Pickard, F. Mauri, *Phys. Rev.* B (2007) 76, 024401.**

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Silicides – signal shift

(*Intermediate summary*)

IAC

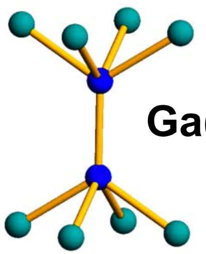
- Signal shift
  - *Knight shift* in metallic Ba_3Si_4
  - Chemical shielding in semiconducting silicides
- Signal assignment by QM calculations of chemical shielding
- Systematic increase of NMR signal shift

➔ Drawback – currently no chemical information

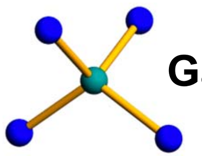
Model system

(*Binary gallides*)

$NaGa_4$[1]			
$CaGa_4$[2]	$Ca_{3-x}Ga_{8+3x}$	$CaGa_2$[2], $Ca_{1-x}Ga_{2+3x}$	-
$SrGa_4$[3]	$Sr_{3-x}Ga_{8+3x}$[4]	$Sr_{1-x}Ga_{2+3x}$[5]	Sr_8Ga_7[3]
$BaGa_4$[3]	-	$BaGa_2$[3]	Ba_8Ga_7[3]

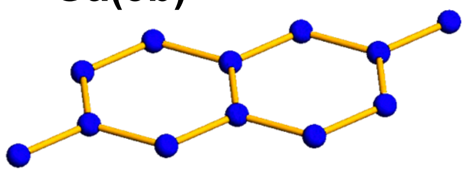


Ga(5b)

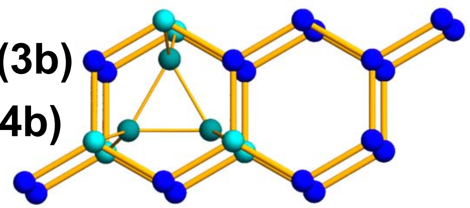


Ga(4b)

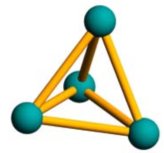
Ga(3b)



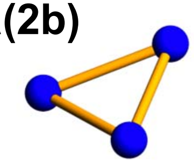
Ga(3b)
Ga(4b)



Ga(3b)



Ga(2b)



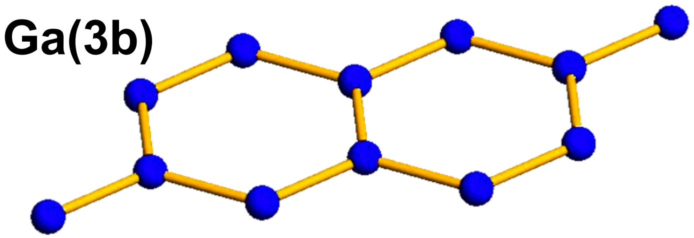
[1] G. Bruzzone, *Acta Cryst.* (1969) B25 1206.
[2] G. Bruzzone, M. L. Fornasini, F. Merlo, *J. Less-Common Met.* (1989) 154, 67.
[3] G. Bruzzone, *Boll. Sci. Fac. Chim. Ind. Bologn.* (1966) 24, 113.
[4] F. Haarmann, Yu. Prots, S. Göbel, H. G. von Schnering, *Z. Kristallogr. NCS* (2006) 221, 257.
[5] F. Haarmann, Yu. Prots, *Z. Anorg. Allg. Chem.* (2006) 632, 2135.

Comparison: Experiment and theory

(MGa$_2$ and MGa$_4$)

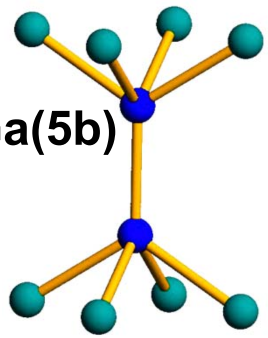
***M*Ga$_2$**

Ga(3b)

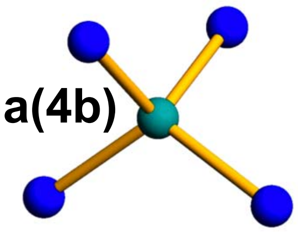


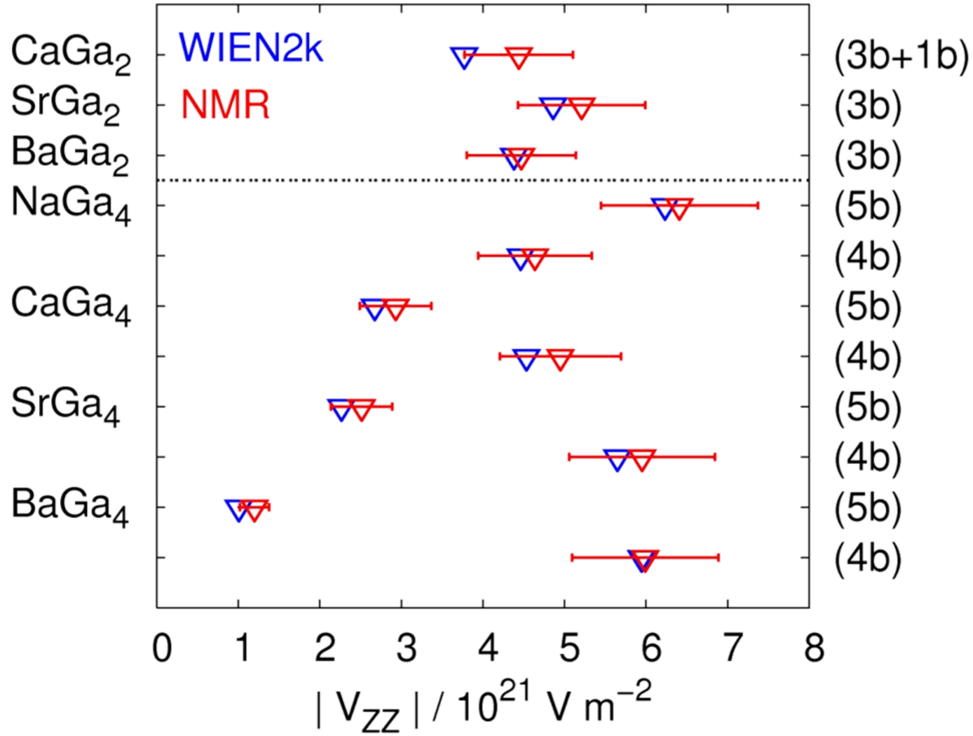
***M*Ga$_4$**

Ga(5b)



Ga(4b)





- ➔ **good agreement**
- ➔ **unambiguous assignment of the signals**

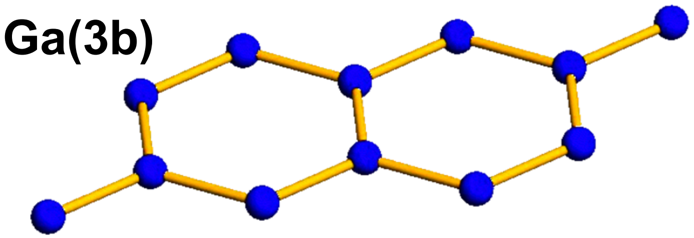
[1] **F. Haarmann, K. Koch, D. Grüner, W. Schnelle, O. Pecher, R. Cardoso-Gil, H. Borrmann, H. Rosner, Yu. Grin *Chem. Eur. J.* 2009, *15*, 1673.**
[2] **F. Haarmann, K. Koch, P. Jeglič, O. Pecher, H. Rosner, Yu. Grin, *Chem. Eur. J.* (2011) 17, 7560.**
[3] **F. Haarmann. Quadrupolar NMR of Intermetallic Compounds. In R. K. Harris, *Enzyclopedia of Magnetic Resonance* (2011).**

Contributions to the EFG

(MGa_2 and MGa_4)

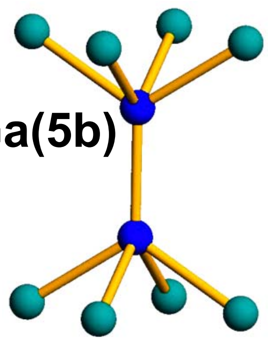
MGa_2

Ga(3b)

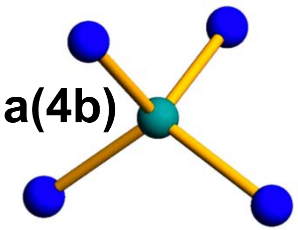


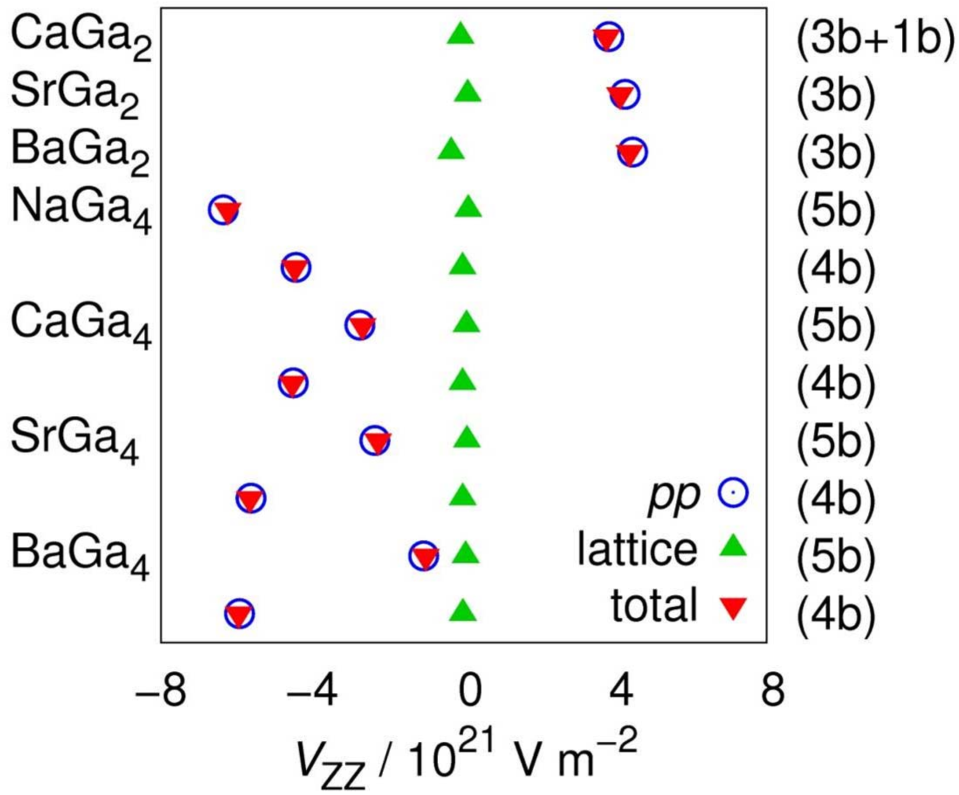
MGa_4

Ga(5b)



Ga(4b)





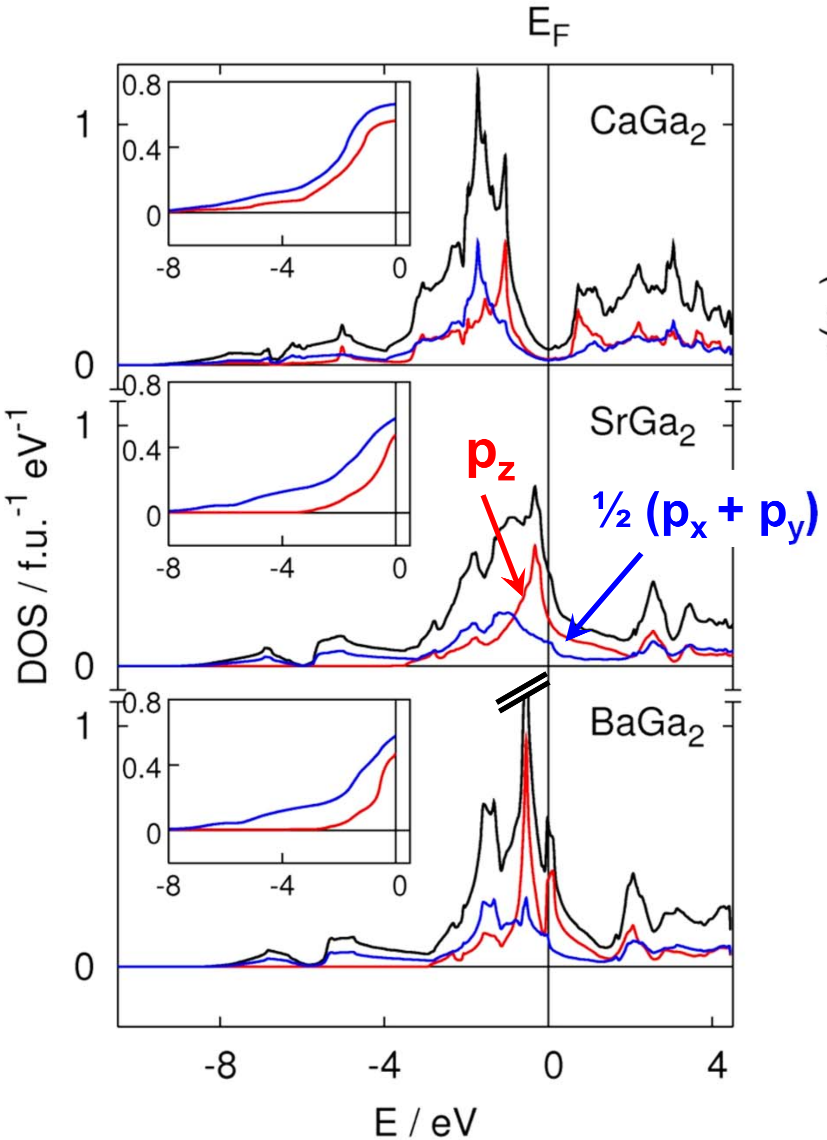
➔ **no lattice contribution**

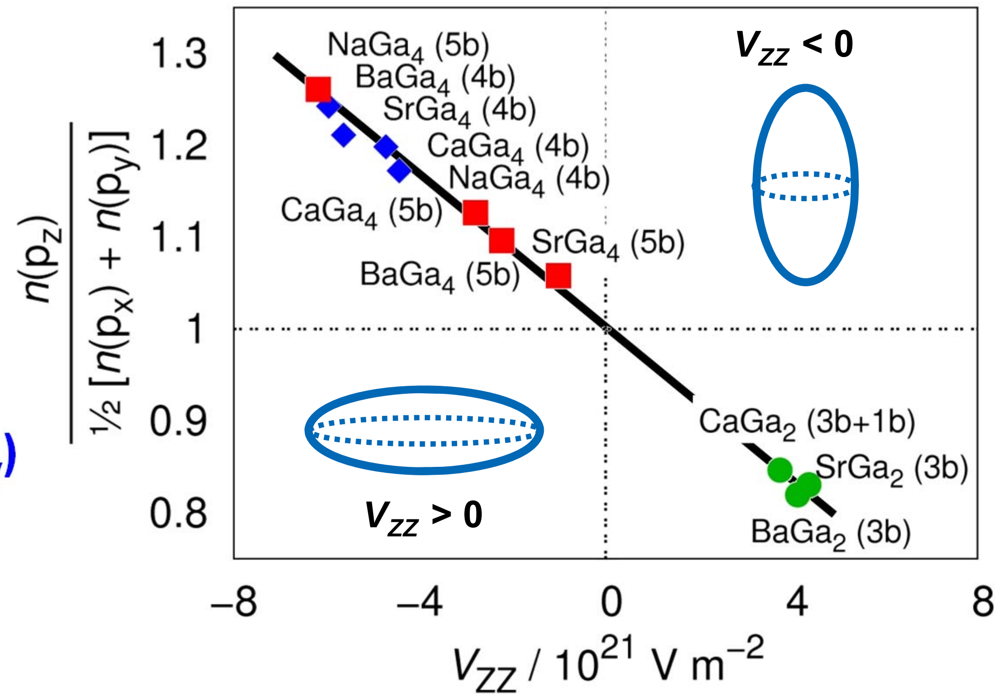
➔ ***p*-states dominate V_{ZZ}**

[1] F. Haarmann, K. Koch, D. Grüner, W. Schnelle, O. Pecher, R. Cardoso-Gil, H. Borrmann, H. Rosner, Yu. Grin *Chem. Eur. J.* 2009, *15*, 1673.
[2] F. Haarmann, K. Koch, P. Jeglič, O. Pecher, H. Rosner, Yu. Grin, *Chem. Eur. J.* (2011) 17, 7560.
[3] F. Haarmann. Quadrupolar NMR of Intermetallic Compounds. In R. K. Harris, *Enzyclopedia of Magnetic Resonance* (2011).

Contributions to the EFG

(MGa_2 and MGa_4)



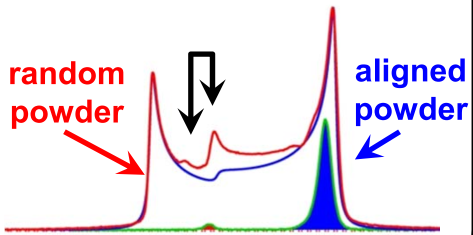


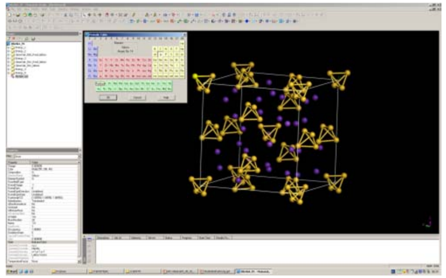
Main contribution to the EFG
➔ valence *p*-states
➔ occupation difference of the *p*-states

[1] F. Haarmann, K. Koch, D. Grüner, W. Schnelle, O. Pecher, R. Cardoso-Gil, H. Borrmann, H. Rosner, Yu. Grin *Chem. Eur. J.* 2009, *15*, 1673.
[2] F. Haarmann, K. Koch, P. Jeglič, O. Pecher, H. Rosner, Yu. Grin, *Chem. Eur. J.* (2011) 17, 7560.
[3] F. Haarmann. Quadrupolar NMR of Intermetallic Compounds. In R. K. Harris, *Enzyclopedia of Magnetic Resonance* (2011).

Strategy for disordered materials

(Combined application of methods)





Diffraction

Chemical bonding in intermetallic compounds

NMR

DFT

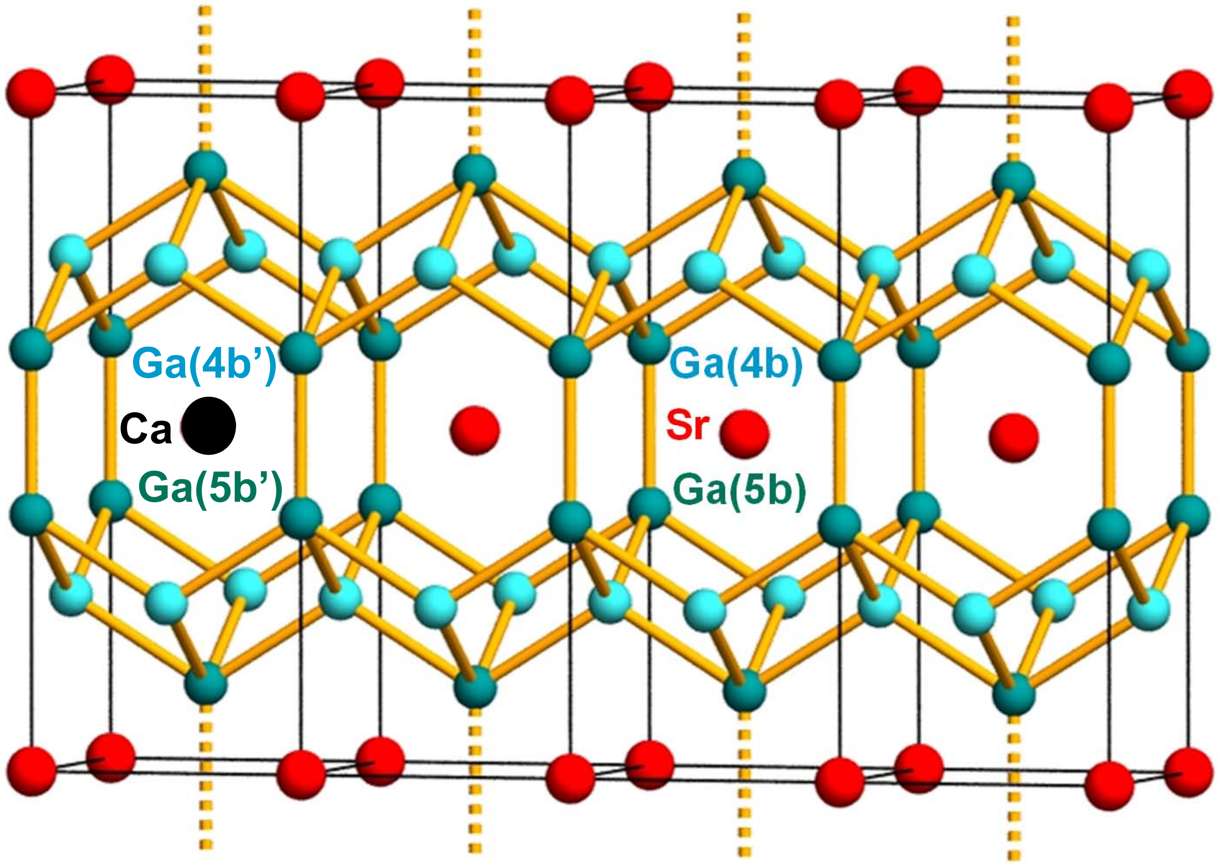
EFG
Chemical shielding

Model systems Di- and Tetragallides

[1] F. Haarmann, K. Koch, D. Grüner, W. Schnelle, O. Pecher, R. Cardoso-Gil, H. Borrmann, H. Rosner, Yu. Grin *Chem. Eur. J.* 2009, *15*, 1673.
[2] F. Haarmann, K. Koch, P. Jeglič, O. Pecher, H. Rosner, Yu. Grin, *Chem. Eur. J.* (2011) 17, 7560.
[3] F. Haarmann. Quadrupolar NMR of Intermetallic Compounds. In R. K. Harris, *Enzyclopedia of Magnetic Resonance* (2011).

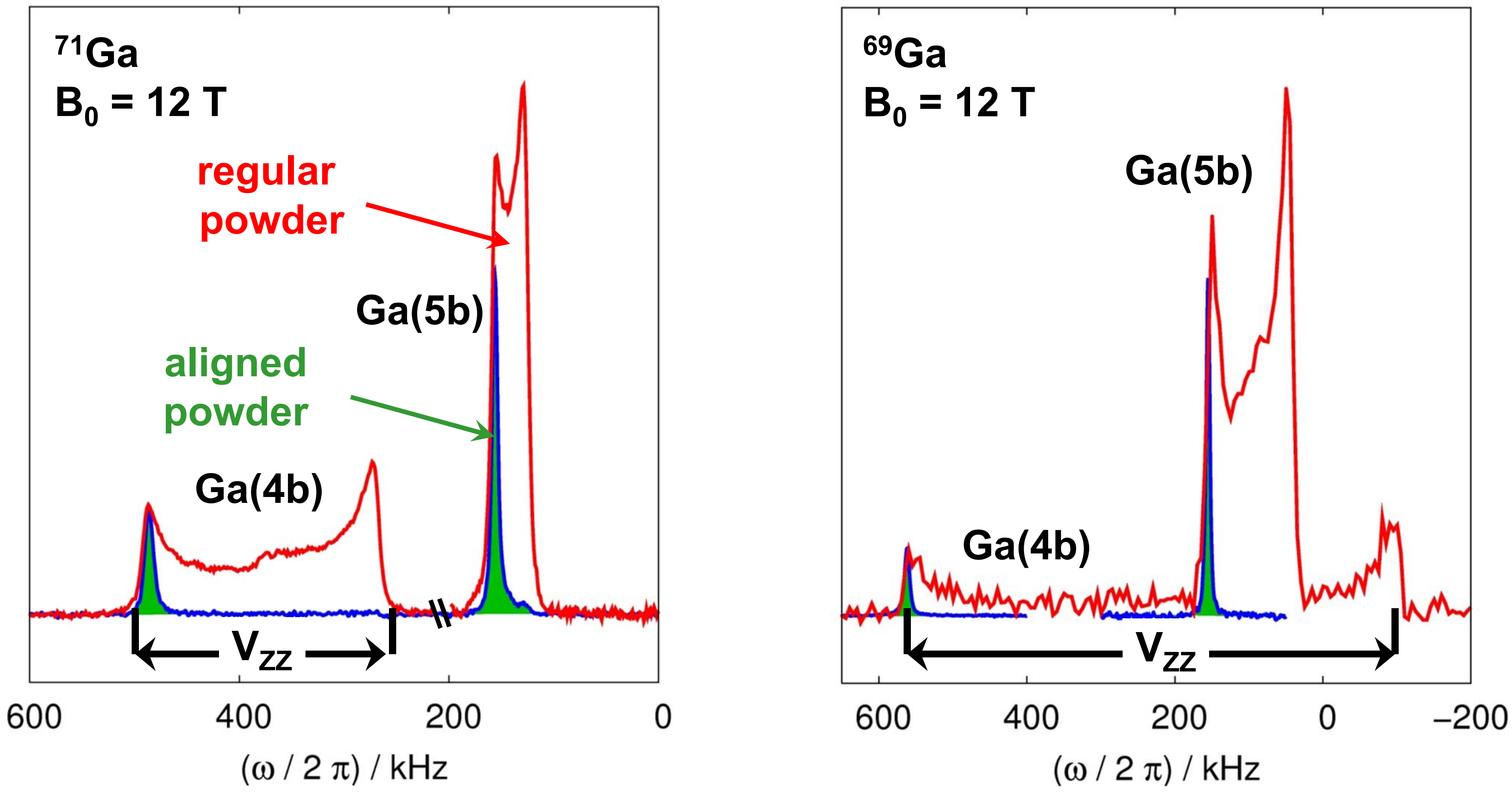
$SrGa_4$ – $CaGa_4$

(Solid Solution – $Ca_xSr_{1-x}Ga_4$)



$Ca_xSr_{1-x}Ga_4$ for $0 \leq x \leq 0.5$

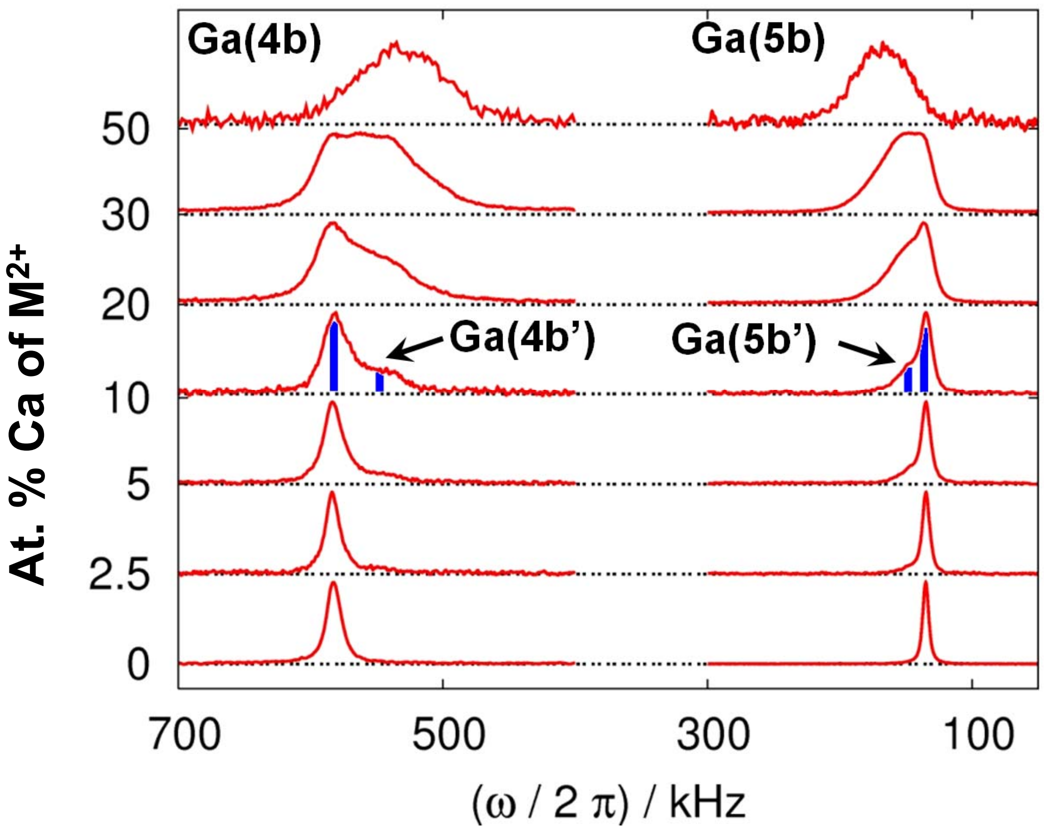
$^{69;71}$Ga – NMR
($SrGa_4$)



B-field aligned samples

($Ca_xSr_{1-x}Ga_4$)

^{69}Ga - B_0 = 7 T

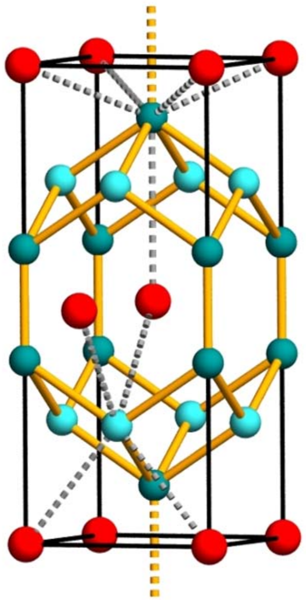


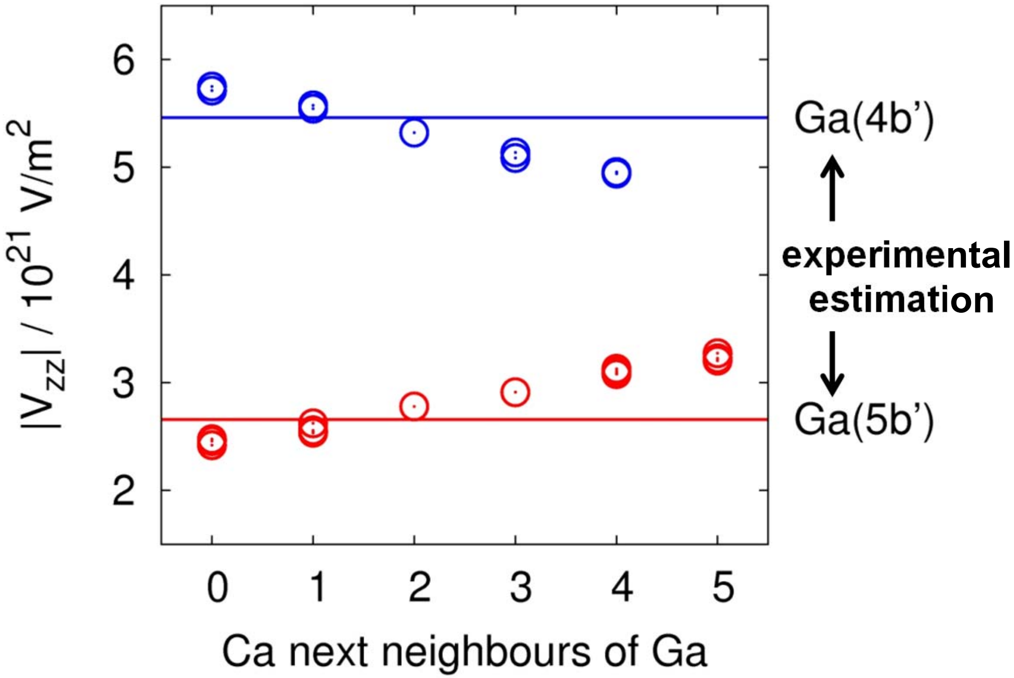
- ➔ **distinguishable signals for Ga(4b), Ga(4b') and Ga(5b), Ga(5b')**
- ➔ **estimation of EFG(V_{ZZ}) for Ga(4b') and Ga(5b')**

Super lattice calculations

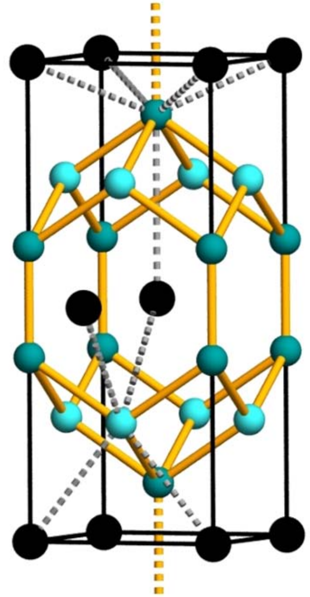
($Ca_xSr_{1-x}Ga_4$)

$SrGa_4$

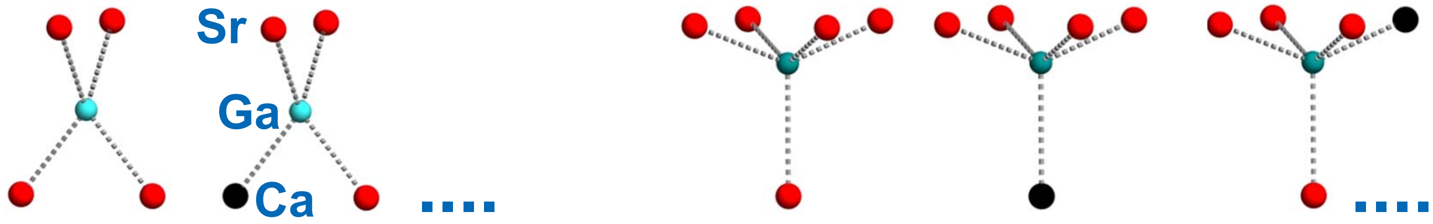




$CaGa_4$(t)

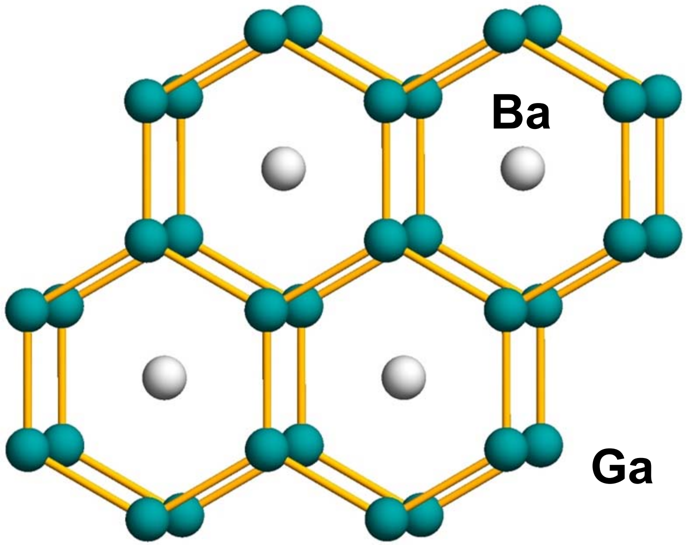


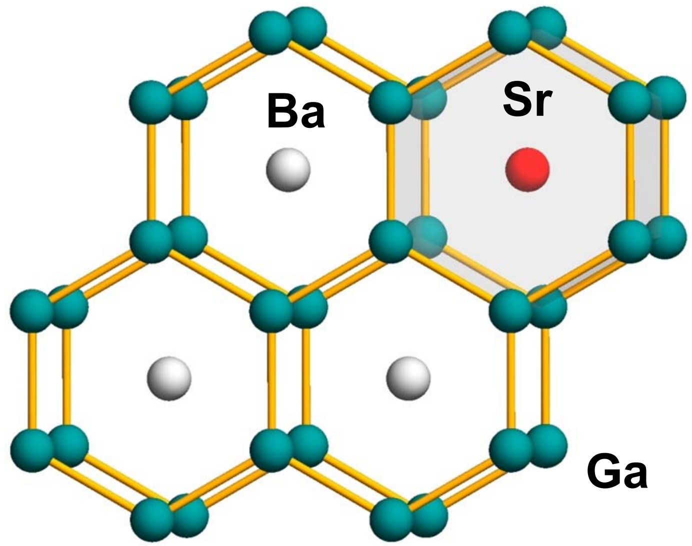
Local atomic arrangements in $Ca_xSr_{1-x}Ga_4$



$SrGa_2$ – $BaGa_2$

(Solid Solution – $Sr_{1-x}Ba_xGa_2$)





$BaGa_2$ / $SrGa_2$

➔ one Ga environment

❒ 12 fold coordination of Ba / Sr

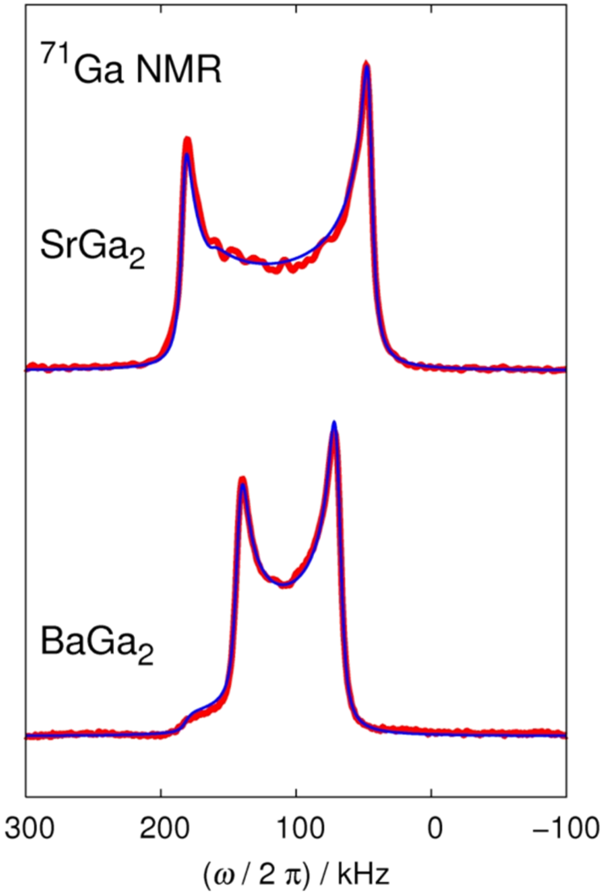
❒ 6 fold coordination of Ga

$x \neq 0$

➔ two Ga environments

B-field aligned samples

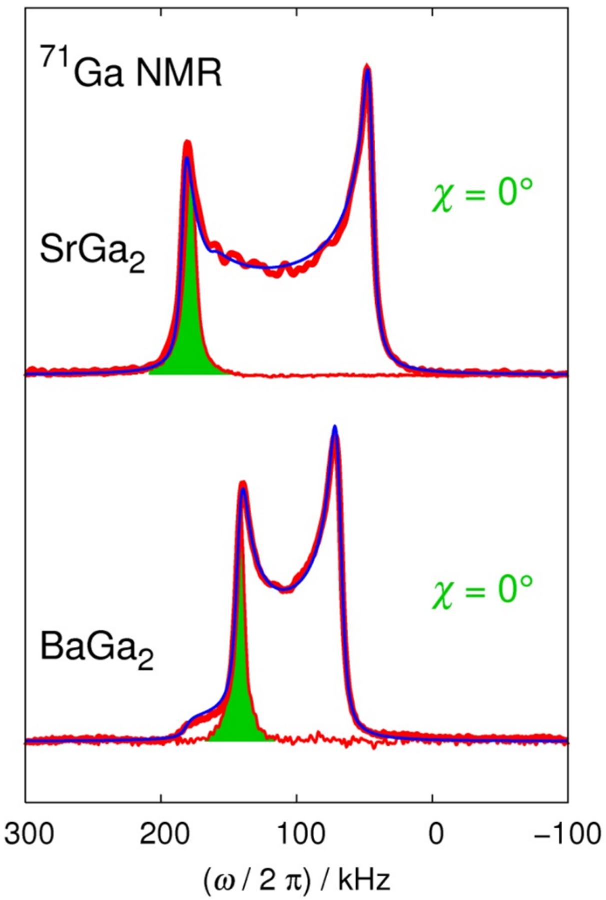
($Sr_{1-x}Ba_xGa_2$)

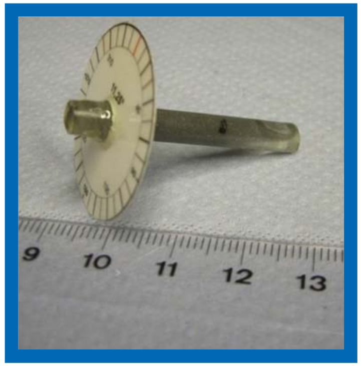


❒ **regular powder**

B-field aligned samples

($Sr_{1-x}Ba_xGa_2$)

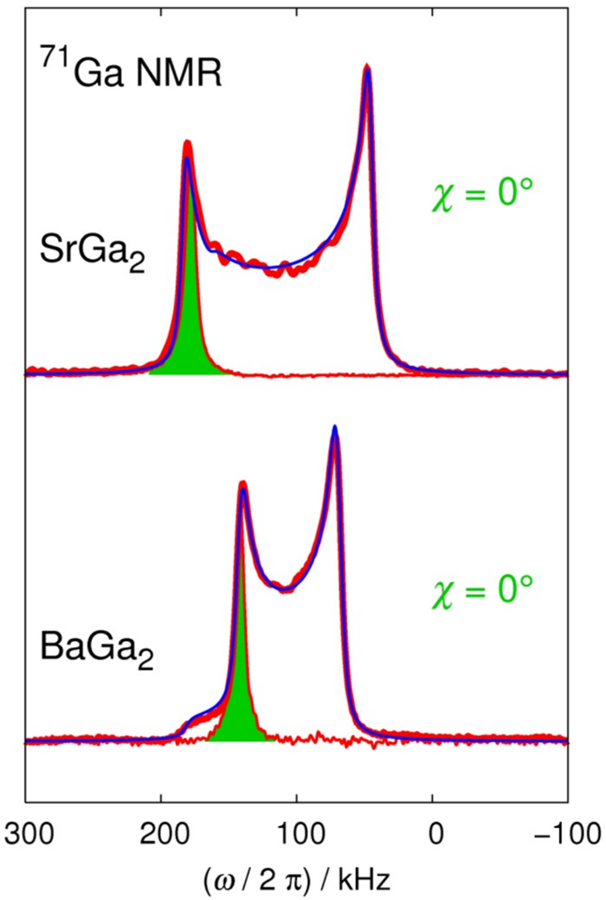


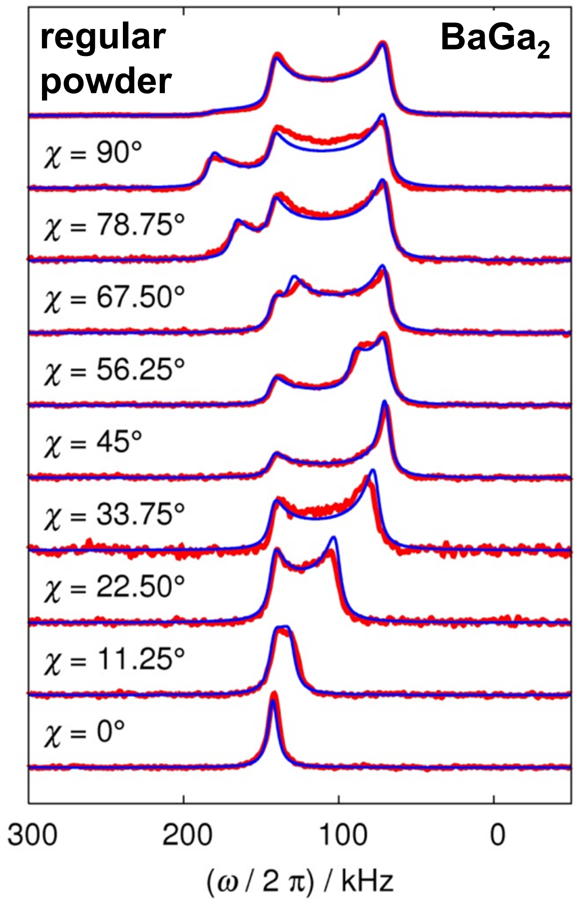


- ❒ **regular powder**
- ❒ **aligned powder**

B-field aligned samples

($Sr_{1-x}Ba_xGa_2$)





- ❒ **regular powder**
- ❒ **aligned powder**

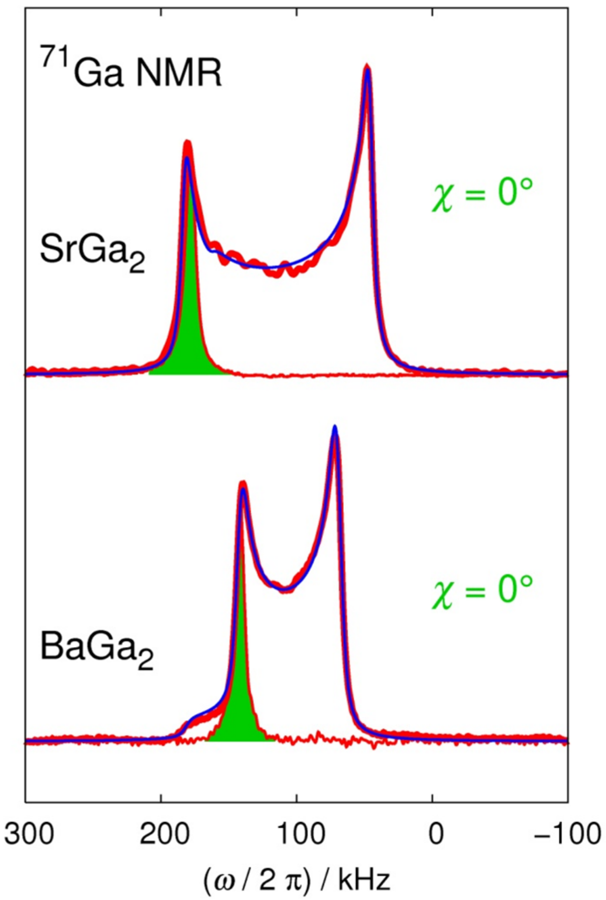
➔ **full determination of EFG**

V_{ZZ} **= 4.48 x 10^{21} Vm^2**

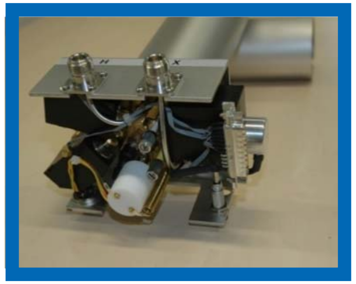
η **= 0**

B-field aligned samples

($Sr_{1-x}Ba_xGa_2$)



ATMG-Wideline Probe[1]



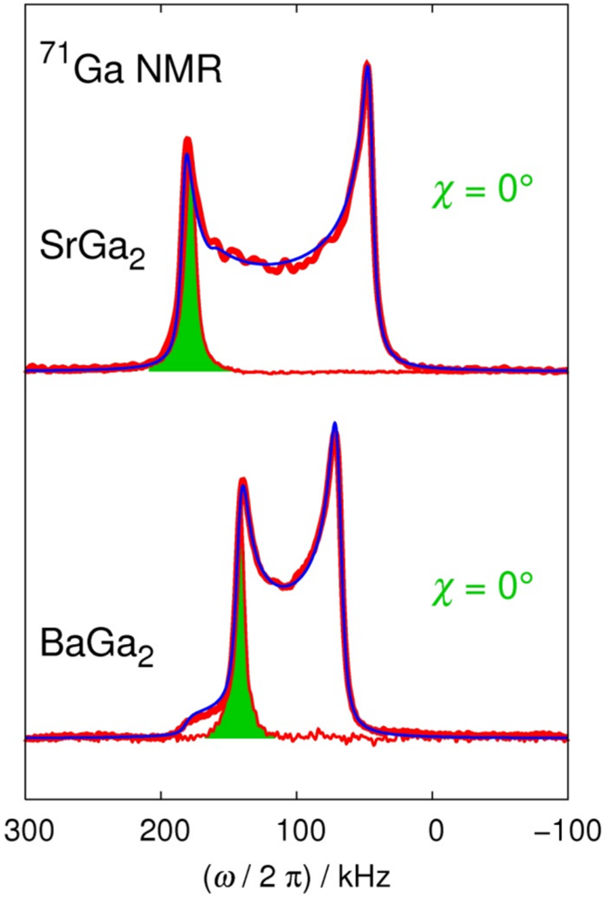
- ❒ regular powder
- ❒ aligned powder

- ❒ automatized tuning and matching of the RF-unit
- ❒ goniometer

[1] O. Pecher, F. Haarmann, *Z. Kristallogr.* 2012, Suppl. 32, 104

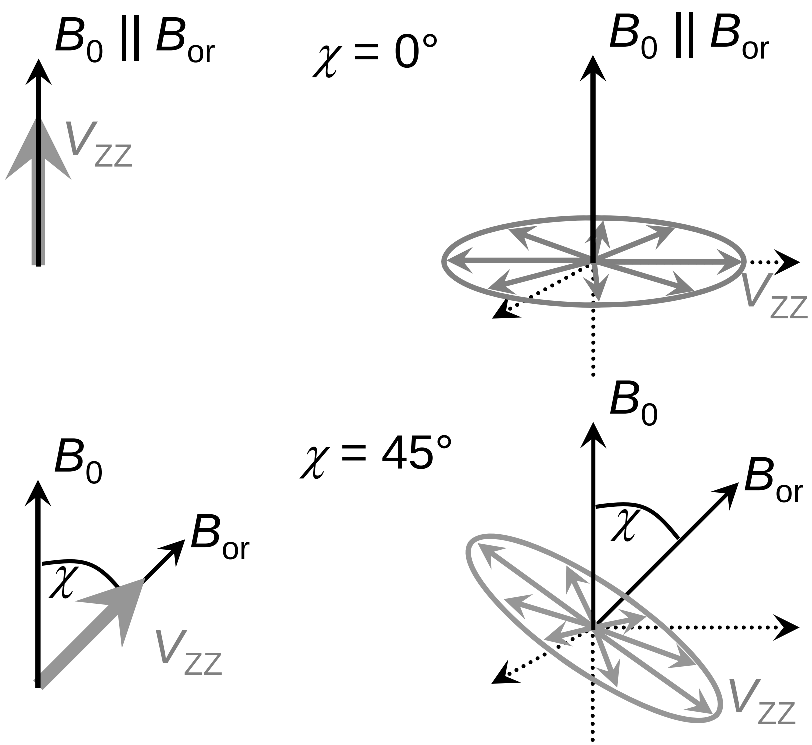
B-field aligned samples

($Sr_{1-x}Ba_xGa_2$)



$V_{ZZ} \parallel B_{or}$ [1,3]

$V_{ZZ} \perp B_{or}$ [2,3]

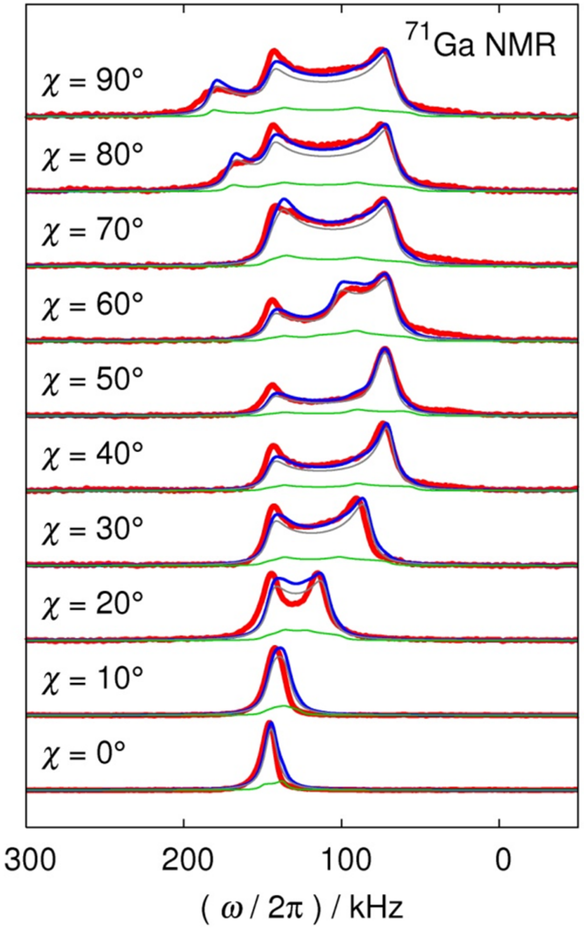


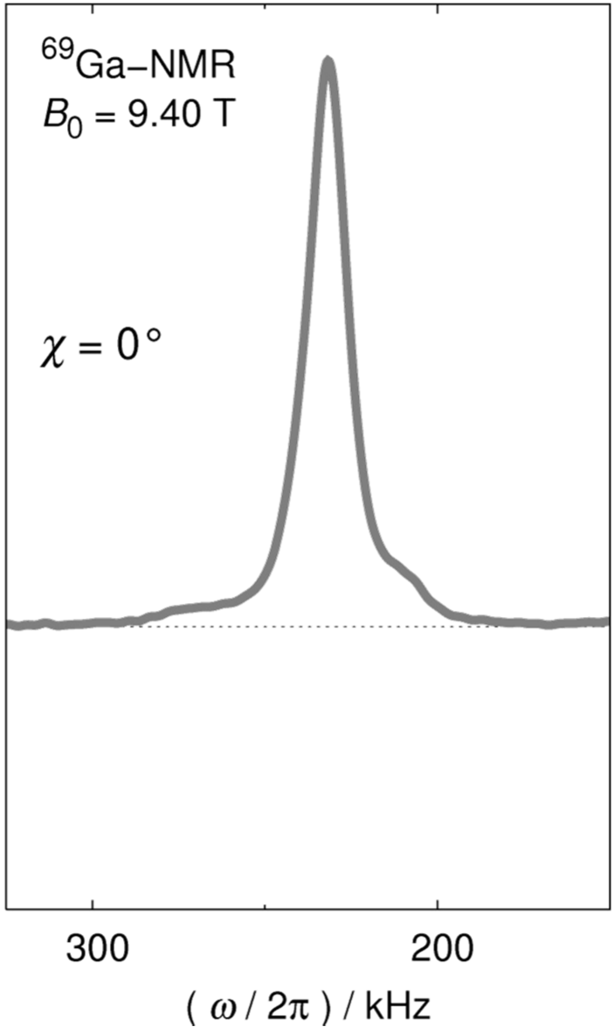
- ❐ **regular powder**
- ❐ **aligned powder**

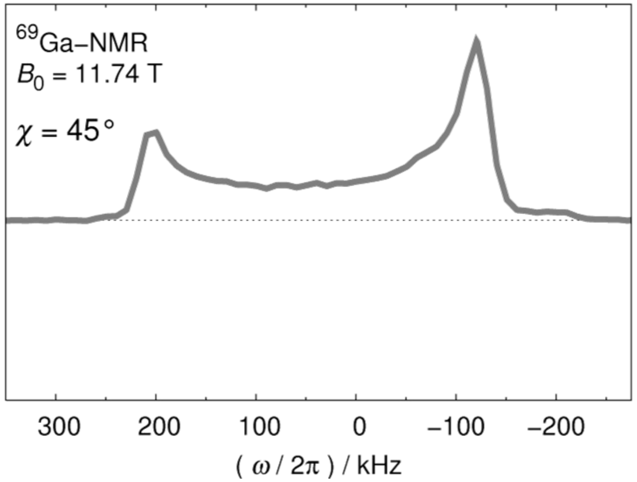
[1] F. Haarmann, M. Armbrüster, Yu. Grin *Chem. Mater.* 2007, *19*, 1147.
[2] F. Haarmann, K. Koch, D. Grüner, W. Schnelle, O. Pecher, R. Cardoso-Gil, H. Borrmann, H. Rosner, Yu. Grin *Chem. Eur. J.* 2009, *15*, 1673.
[3] F. Haarmann. Quadrupolar, Enzyclopedia of Magnetic Resonance. JohnWiley&Sons, Ltd, Chichester (2011).

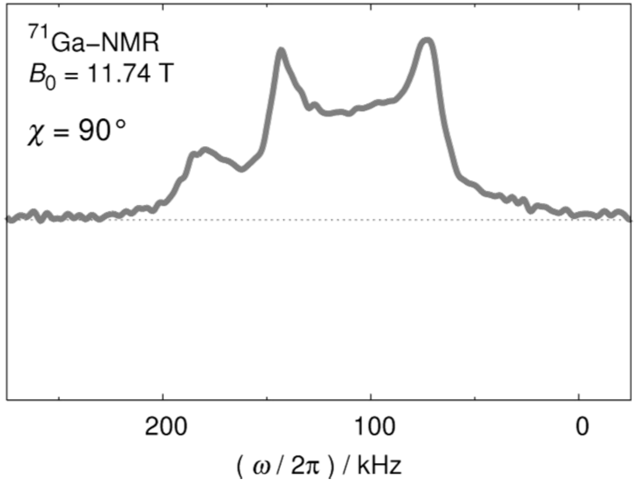
$Sr_{1-x}Ba_xGa_2$ with x = 0.975

(Orientation dependent experiments)



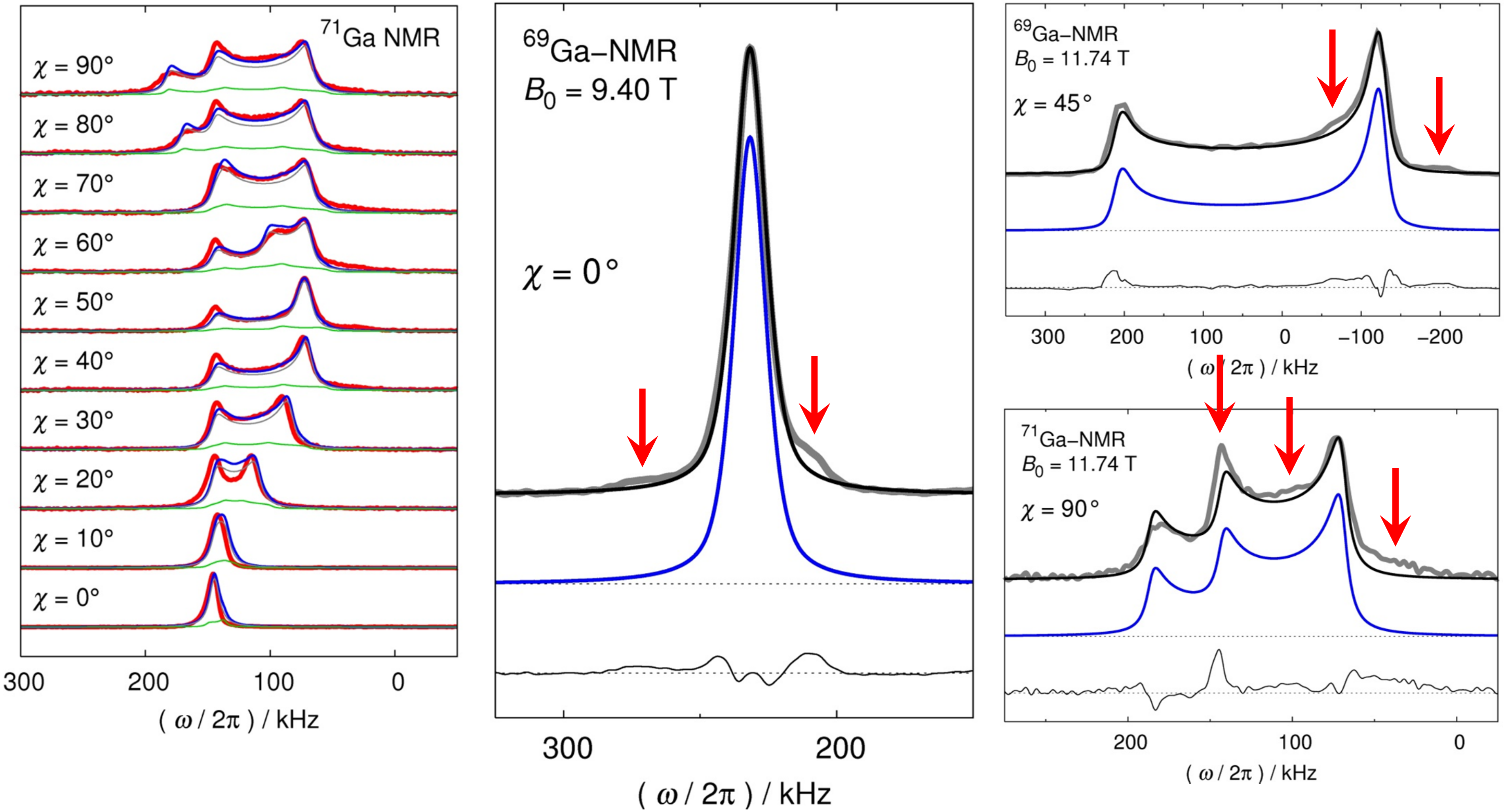






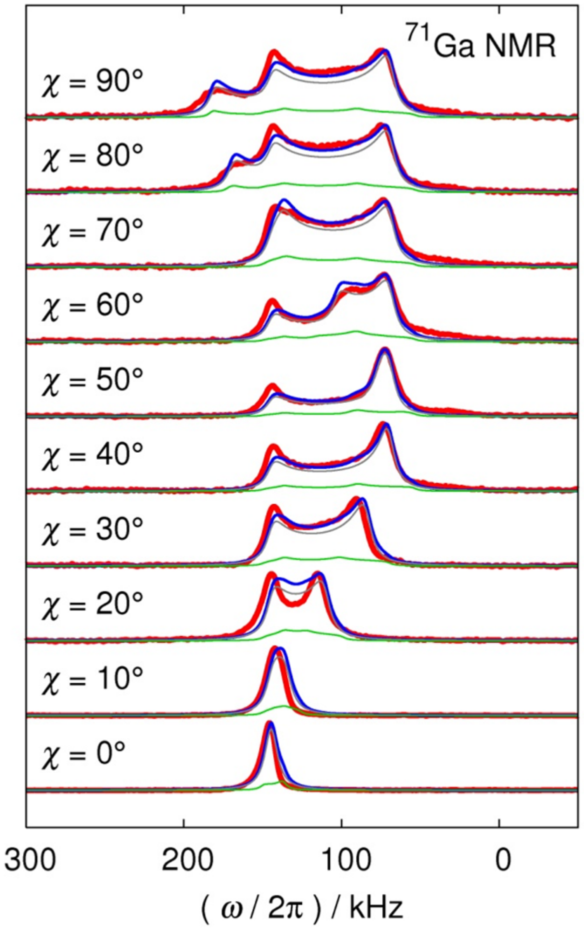
$Sr_{1-x}Ba_xGa_2$ with x = 0.975

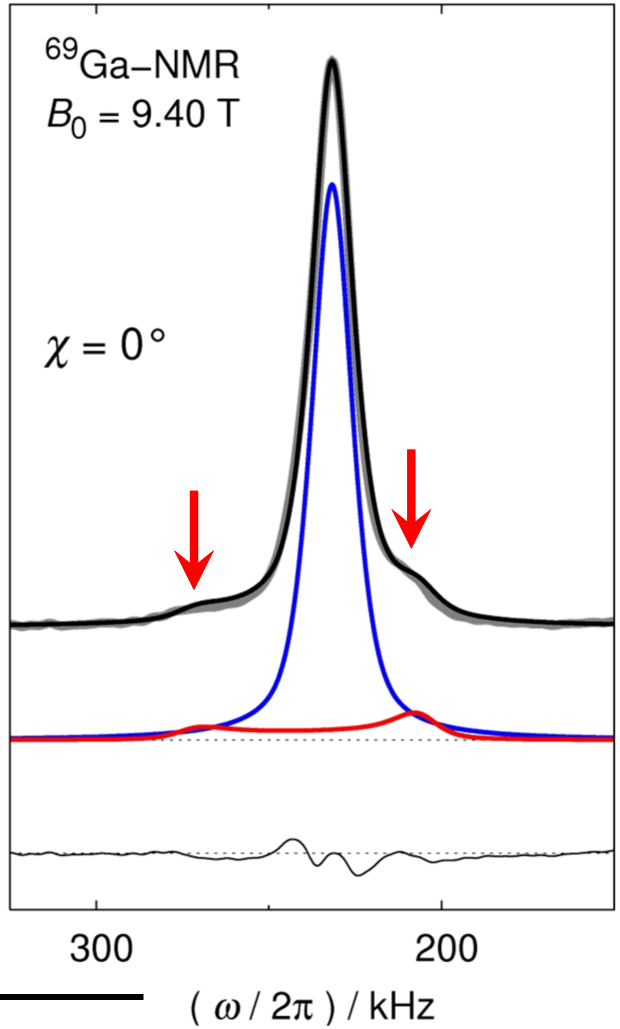
(*Orientation dependent experiments*)

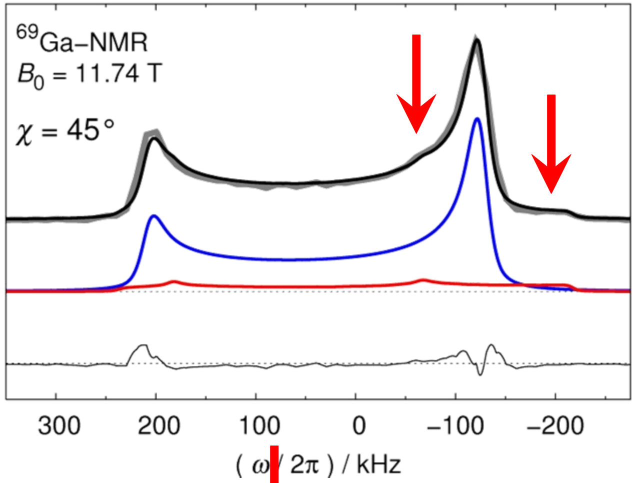


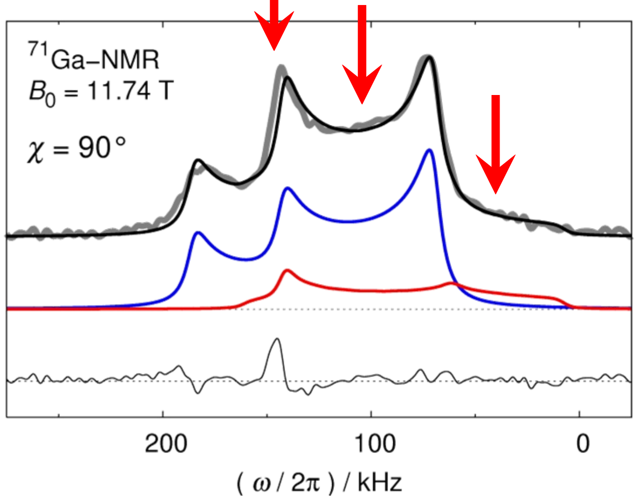
$Sr_{1-x}Ba_xGa_2$ with x = 0.975

(*Orientation dependent experiments*)







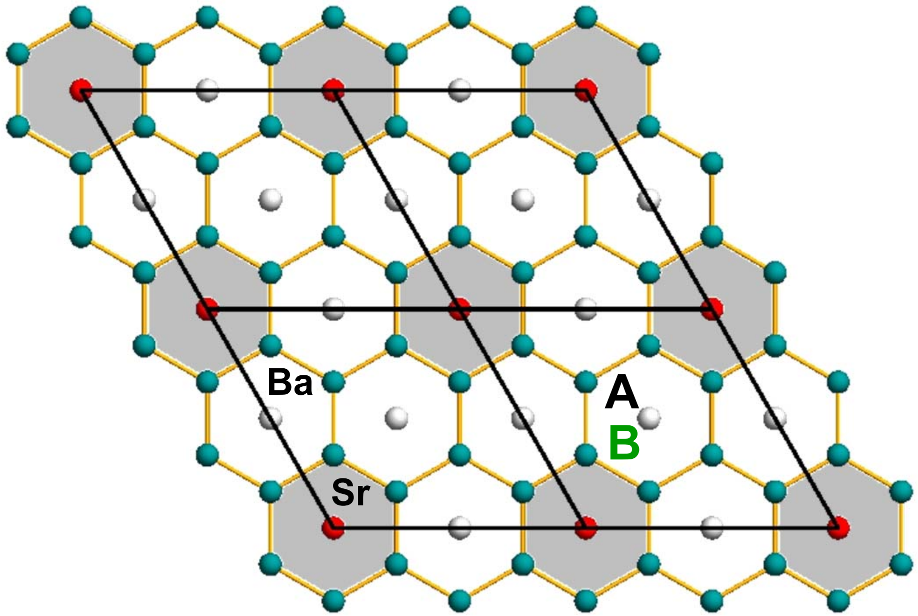


	V_{zz} / 10^{21} Vm^{-2}	η_Q
A	**4.48**	**0**
B	**4.40**	**0.25**

➔ **two Ga environments**
➔ **local reduction of symmetry**

Super lattice calculations

($Sr_{1-x}Ba_xGa_2$)



P $\overline{6}$ *m* 2
a = 8.79 Å *c* = 9.79 Å
24 atoms

Binary

QM(A)	$BaGa_2$
V_{zz} / 10^{21} Vm^{-2}	4.47
η	0

Super lattice

QM(B)	$Sr_{1-x}Ba_xGa_2$ (x = 0.875)
V_{zz} / 10^{21} Vm^{-2}	4.10
η	0.15

Solid solution

NMR	$Sr_{1-x}Ba_xGa_2$ (x = 0.975)
V_{zz} / 10^{21} Vm^{-2}	4.48 (A)
η	0
V_{zz} / 10^{21} Vm^{-2}	4.40 (B)
η	0.25

Gallides – quadrupole coupling

(Intermediate summary)

- ❒ EFG

  a) local property of the atoms

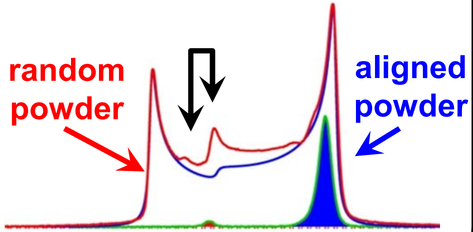
  b) sensitive link of NMR – experiment and theory

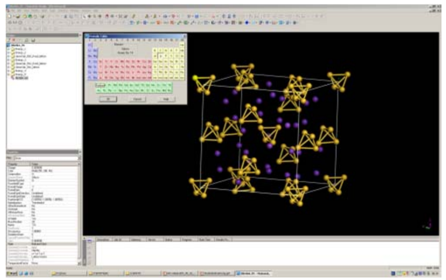
  → valuable information about chemical bonding

- ❒ Local order

  → influence of substitution on the NMR signal and chemical bonding

Summary and outlook





Diffraction

Chemical bonding in intermetallic compounds

NMR

DFT

EFG
Chemical shielding

δ_{iso} , K_{iso}
$\Delta_{\delta / K}$
$\eta_{\delta / K}$

J. C. Pickard, F. Mauri *Phys. Rev. B* 2007, 63(24) 245101-1/13.

Acknowledgment

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Prof. Jürgen Senker (Universität Bayreuth)
Prof. Rainer Niewa (Universität Stuttgart)

Dr. Marco Braun — NMR Service

Gregor Schmidt
Dr. Stefan Steuernagel — BRUKER

Excellence Initiative of the German federal and state governments.

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