# Solid-State Diffusion and NMR

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Diffusion Fundamentals, Leipzig, 23 Sept. 2005

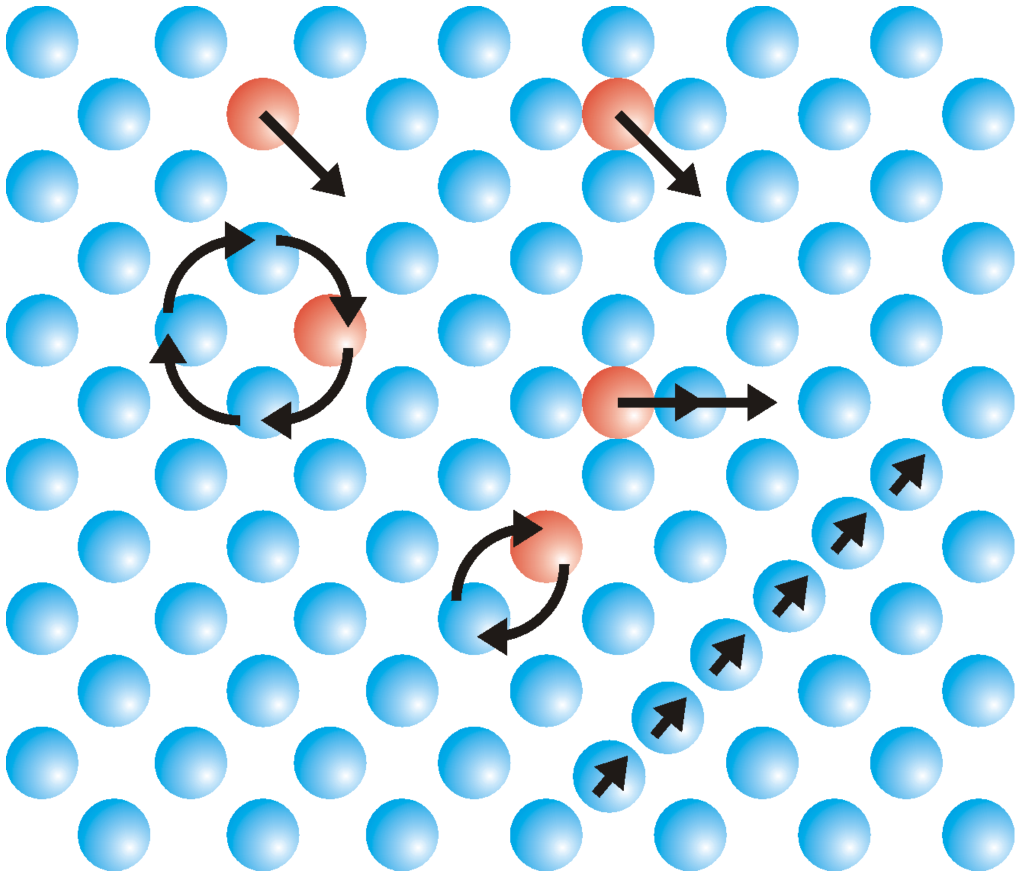
# Introduction

- Diffusivity in Solids as Compared to Liquids and Gases

| | $D$ / m$^2$ s$^{-1}$ | *time* for 1 cm | |
|---|---|---|---|
| • Gases | $10^{-4}$ | 1 s | RT |
| • Liquids | $10^{-9}$ | 1 d | RT |
| • Solids | $< 10^{-13}$ | > 30 a | $< T_m$ |
| • Interfaces/ Surfaces | $< 10^{-9}$ | > 1 d | $< T_m$ |

- Reason for Slow Diffusion in Solids:

  Formation of Defects is needed



Activation Energy

$$D \sim e^{-\overbrace{(E_F+E_M)}/k_B T}$$

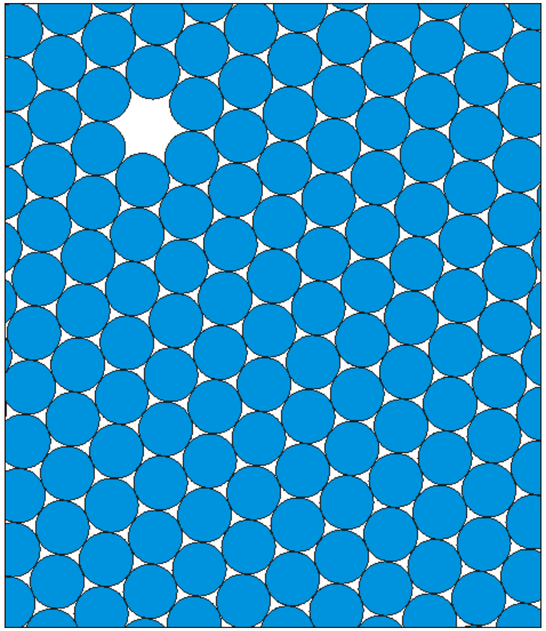
$E_F > 0$ for Solids

$E_F \approx 0$ for Liquids, Gases

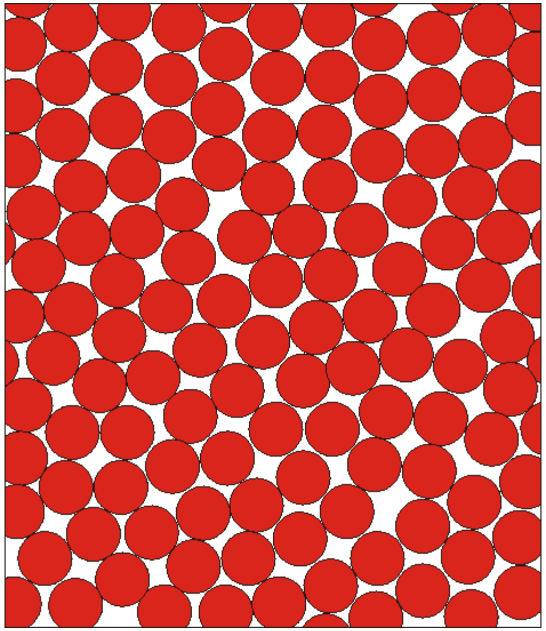
after Philibert: „Diffusion et Transport de Matière dans les Solides“ (1985)

• Overview:  Defective Solids

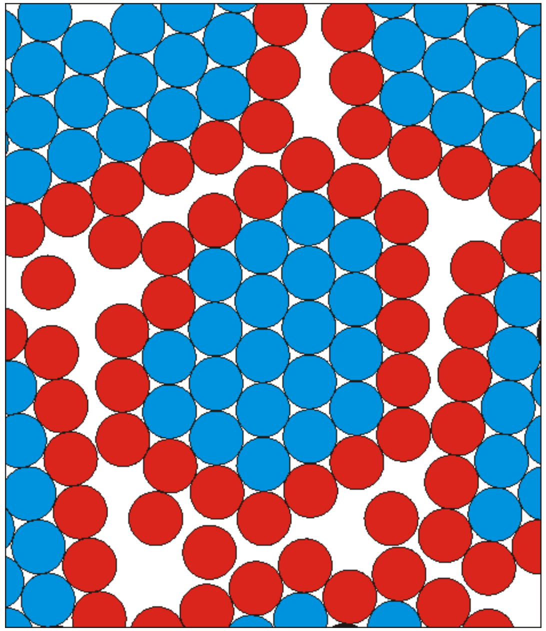
single
crystalline



amorphous

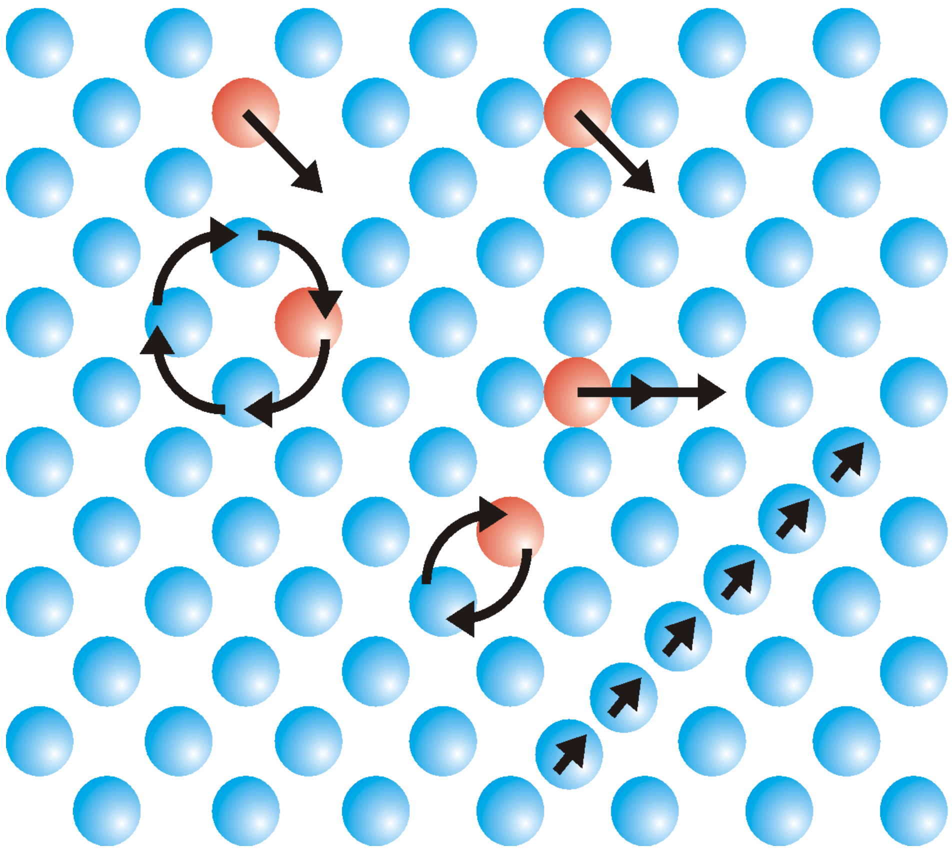


nano-
crystalline

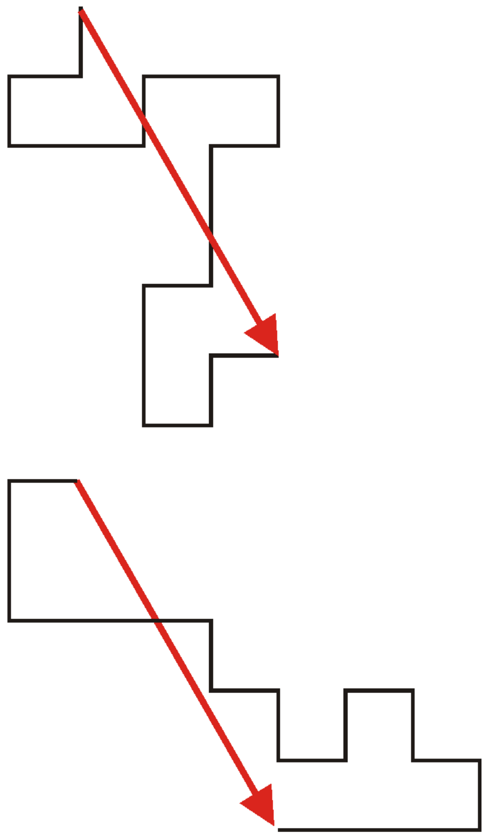


(see Talk: Chadwick)

• Microscopic and Macroscopic Aspects of Diffusion



elementary jumps



macroscopic transport

• Microscopic and Macroscopic Diffusion Quantities

Jump rate $$\tau^{-1} \cdot \frac{r^2}{6} \cdot f = D^{\mathrm{T}}$$ Tracer diffusivity

Correlation factor $f \leq 1 \Rightarrow$ Diff.mechanism (see Talk: Murch)

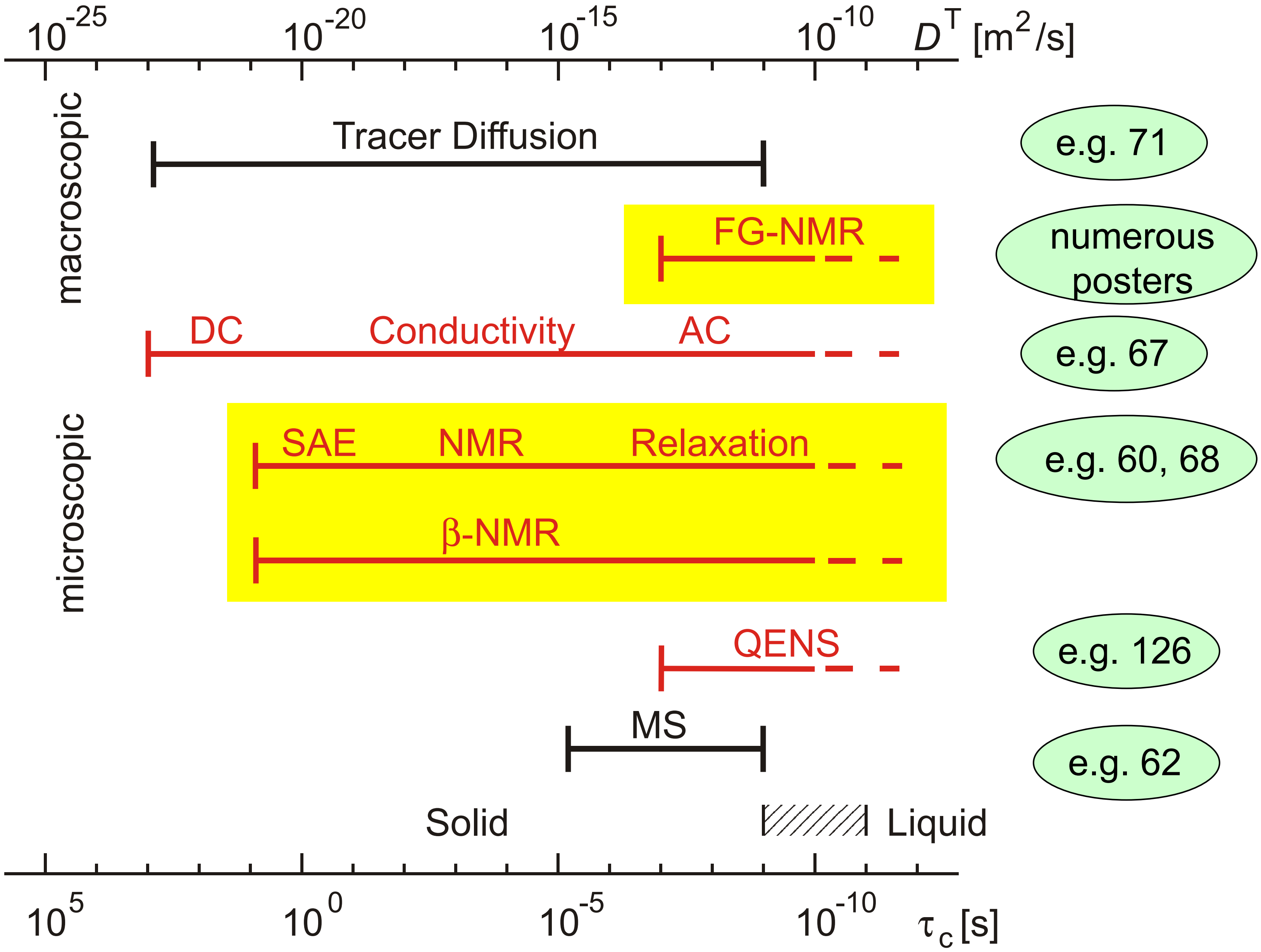
$\tau^{-1} \approx 10^6\,\mathrm{s}^{-1}$ at RT

Temperature dep. $\Rightarrow$ $E_A$ (depends on time window)

# Experimental Methods

| *Microscopic* | *Macroscopic* |
| --- | --- |
| • NMR<br>Relaxation / Lineshape<br>Spin alignment echo | • Field gradient NMR<br>Pulsed / Static |
| • β-radiation detected NMR | Radioactive tracer |
| • Quasielastic neutron scattering | Ion beam analysis |
| • AC conductivity | • DC conductivity |

# • Ranges of Diffusivities and Correlation Times

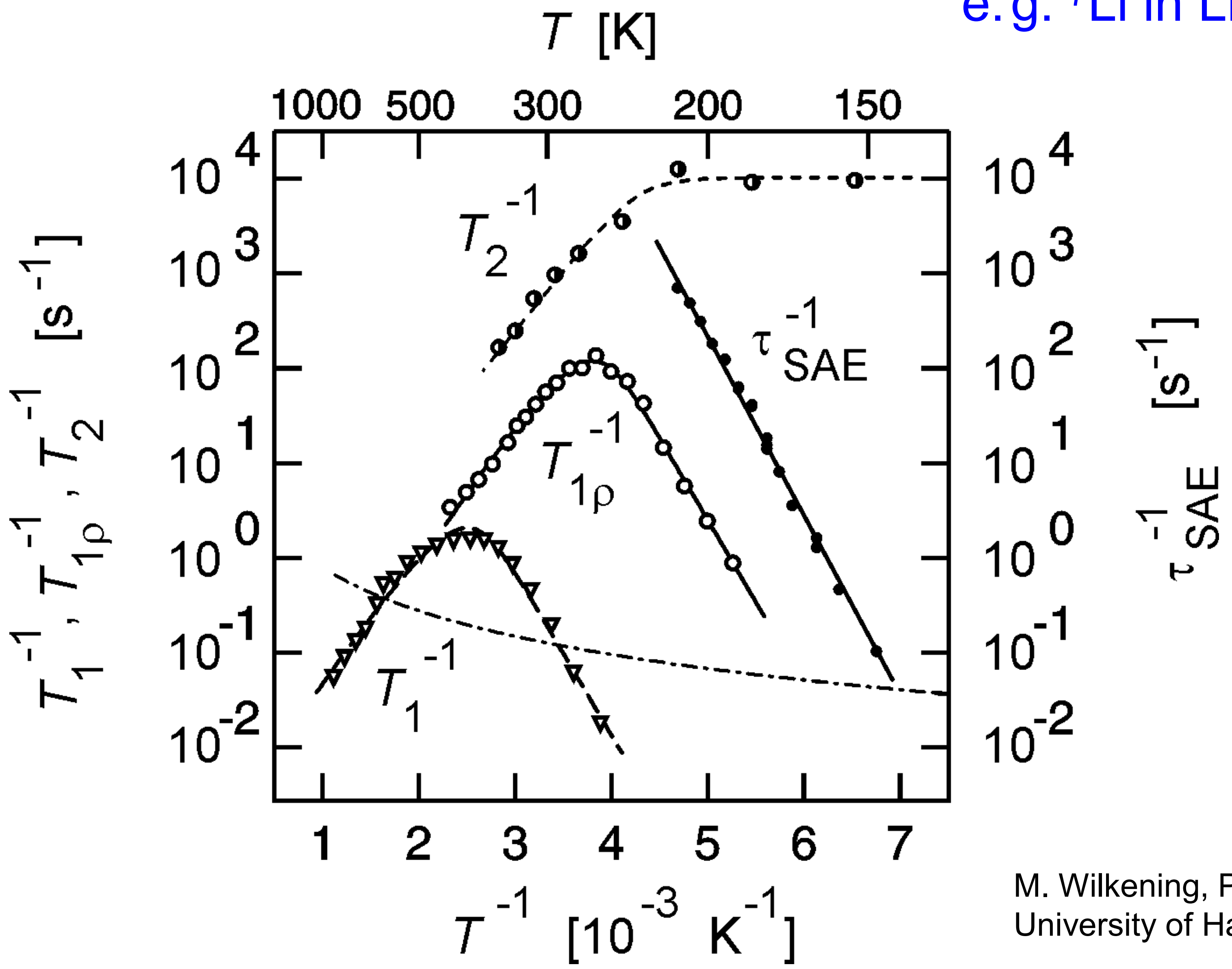



P. Heitjans, S. Indris, J. Phys.: Condens. Matter 15 (2003) R1257

• Overview NMR

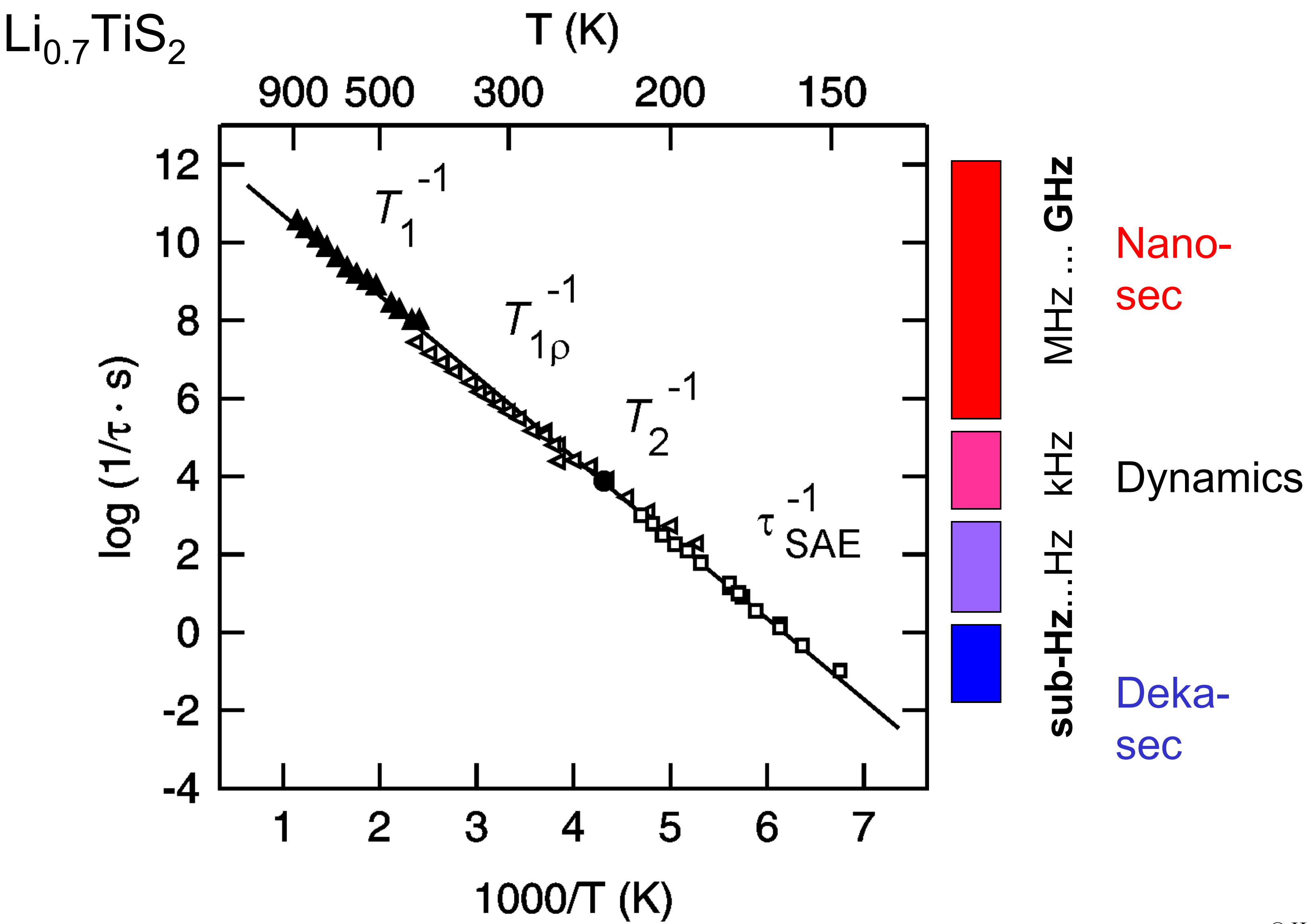
Spin-Lattice Relaxation, Spin-Spin Relaxation; Spin-Alignment Echo

e.g. $^{7}$Li in $Li_{0.7}TiS_2$




M. Wilkening, PhD thesis, University of Hannover, 2005.

- Motional Correlation Rates



# Beta-NMR: Principle (1)

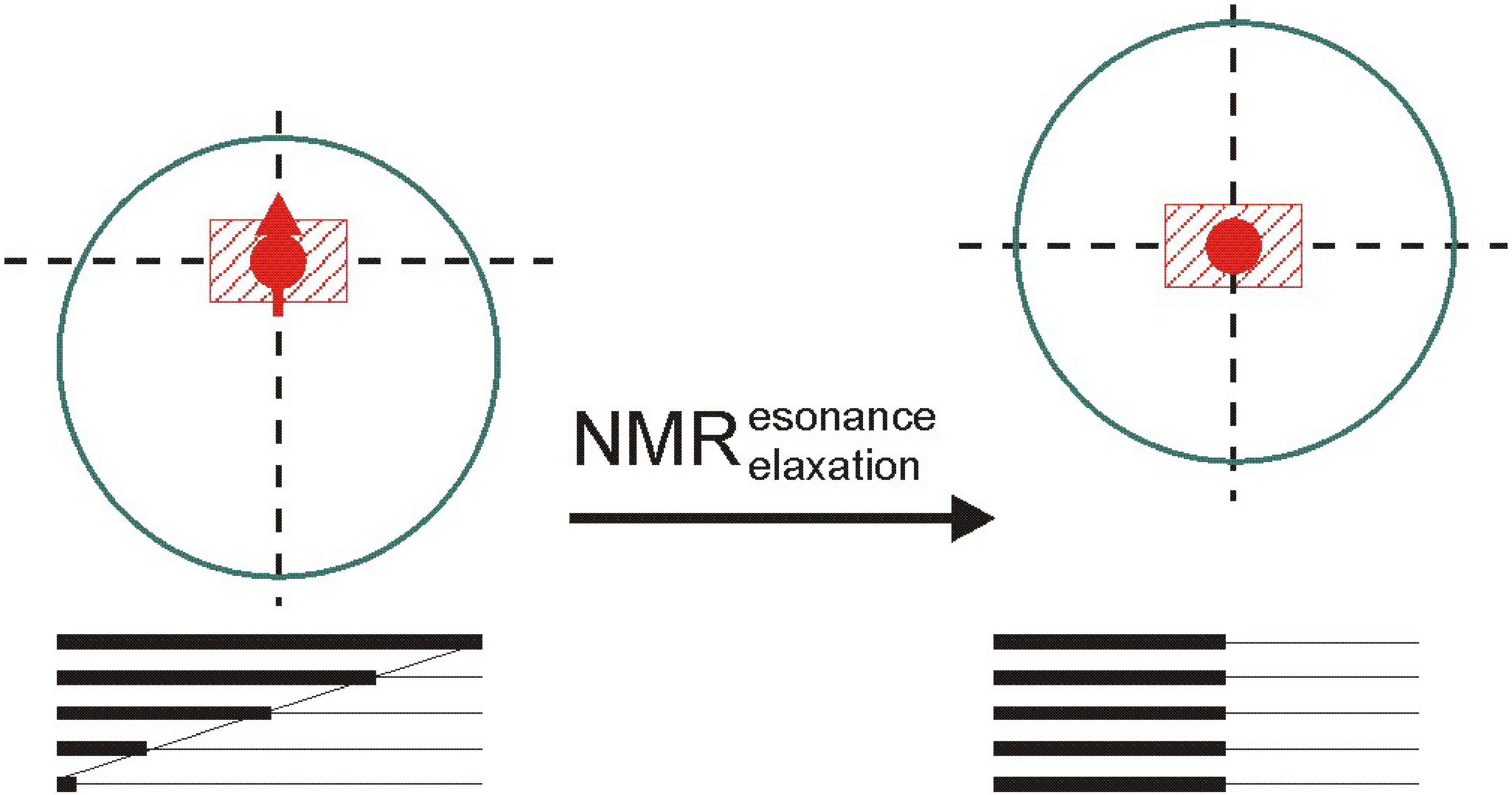
e.g. $^{11}B + \vec{n} \longrightarrow {}^{12}\vec{B} \xrightarrow[\tau_\beta = 29\text{ ms}]{\beta^-} {}^{12}C$

Probes used so far:

$^{8}$Li (1.2s, I=2), $^{12}$B(29ms, 1), $^{20}$F(16s, 2),
$^{23}$Ne(57s, 5/2), $^{24}$Na$^{*}$(29ms, 1), $^{28}$Al(3.2min, 3),
$^{38}$Cl(54min, 2), $^{108}$Ag(3.5min, 1), $^{110}$Ag(36s, 1),
$^{116}$In(20s, 1)

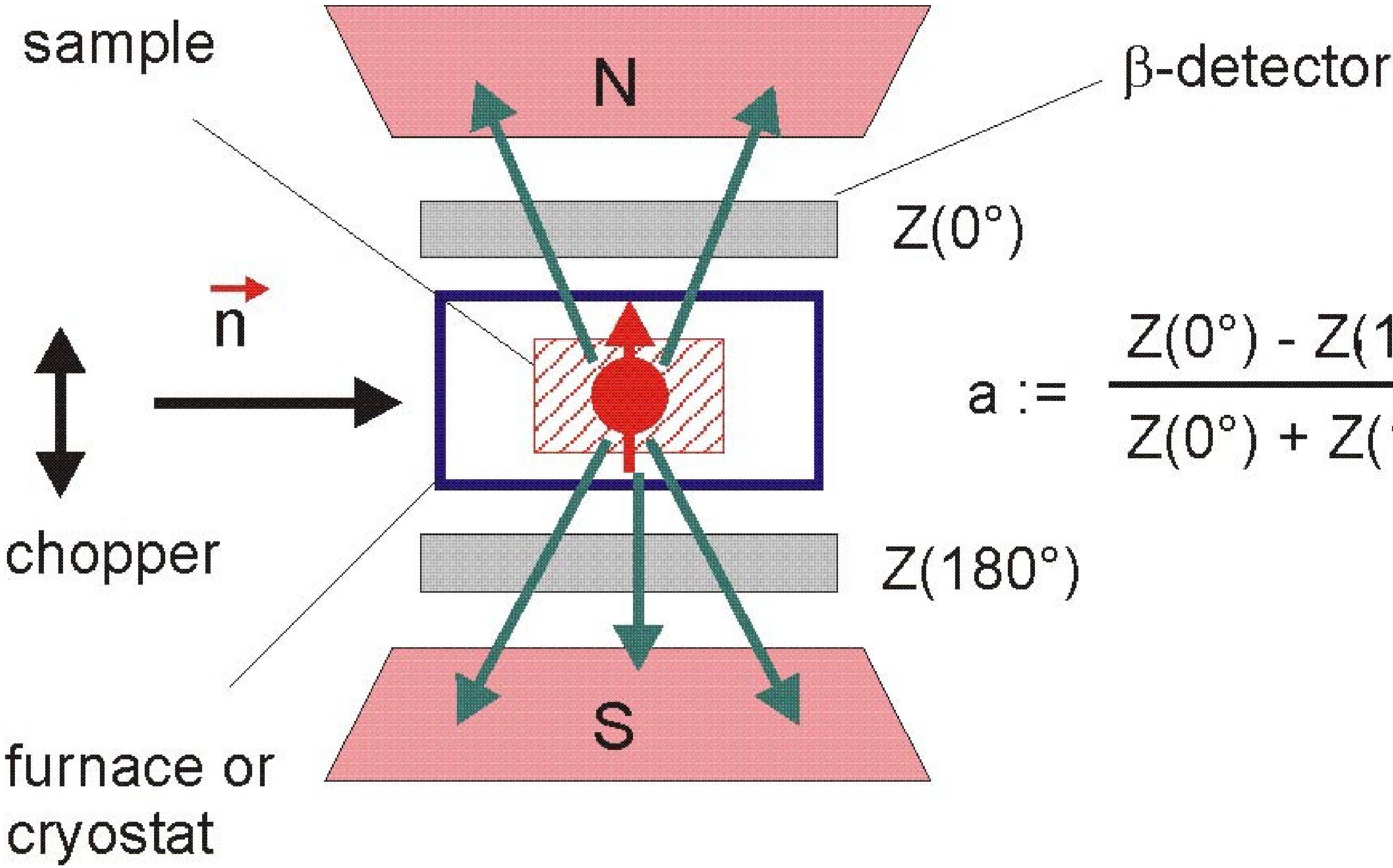
# Beta-NMR: Principle (2)

Angular distribution of β-radiation
asymmetric as long as nuclei are polarized




Population of Zeeman levels

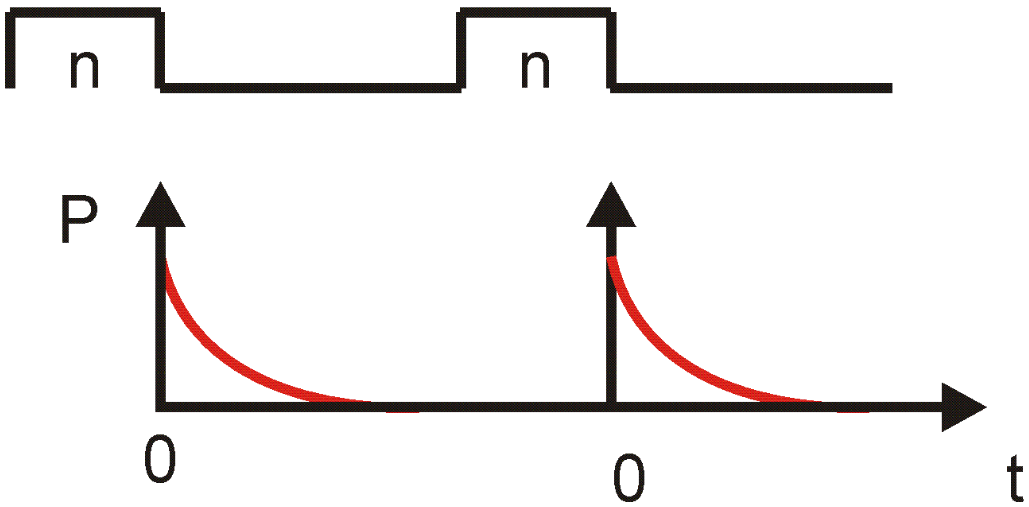
# Beta-NMR:  Setup




$$a := \frac{Z(0°) - Z(180°)}{Z(0°) + Z(180°)} \sim P$$

# Beta-NMR: Operating Modes

- transients $P(t)$ after n-activation pulses : spin-lattice relaxation (SLR)

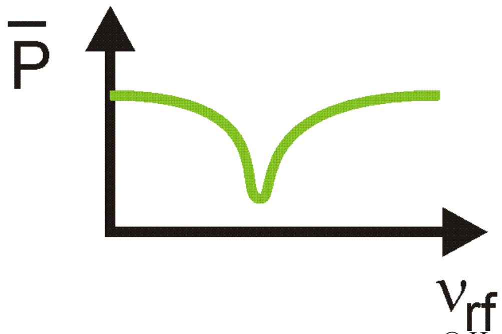



$$P = P_0 \cdot e^{-t/T_1}$$

$T_1$ = SLR time

- stationary $\overline{P}(\nu_{rf})$ : resonance spectra

$$\overline{P} \sim \overline{a} = \frac{a_0}{1 + \tau_\beta / T_1}$$



# Beta-NMR: Some Features and Implications (1)

- P ($\approx$ 10%) independent of Boltzmann factor

  $\rightarrow$ low B, high T accessible

- SLR measurements do *not* require rf fields

  $\rightarrow$ B easily variable

  $\rightarrow$ no skin effect: metallic samples/containers

- SLR time window: $0.01\ \tau_\beta < T_1 < 100\ \tau_\beta$

# <u>Beta-NMR:</u> Some Features and Implications (2)

- Concentration of probes extremely small (1:$10^{18}$)

  $\rightarrow$ probes surrounded only by *unlike* nuclei

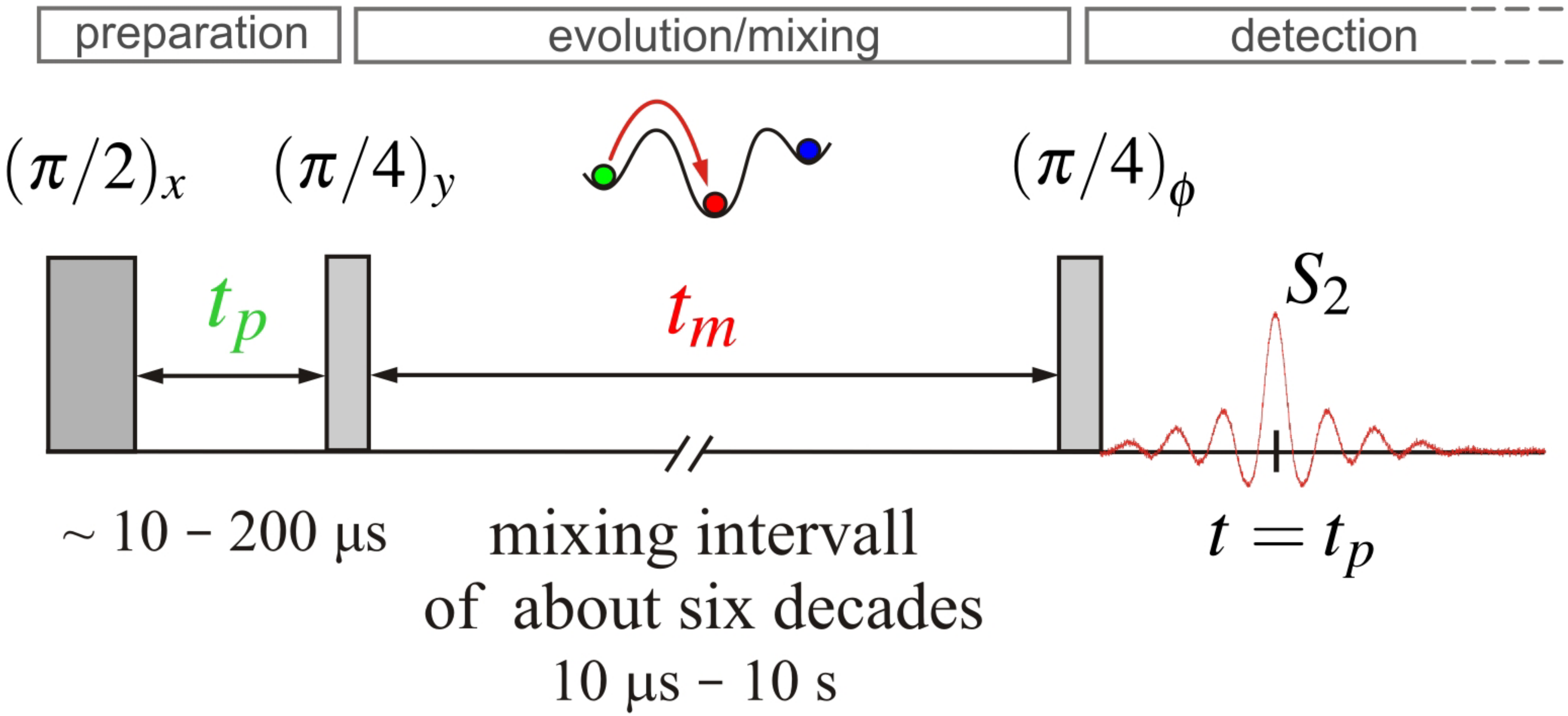
  $\rightarrow$ no spin diffusion

  - no SLR by distant paramagnetic impurities
  - inequivalent sites: inhomogeneous SLR

- Complementary probes

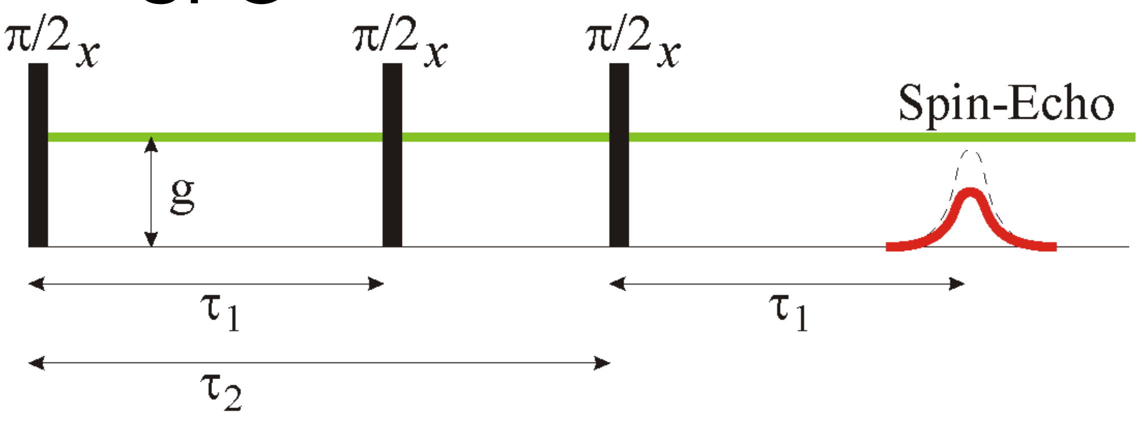
| e.g. | Q=0 for NMR | $Q \neq 0$ for β-NMR probe |
|---|---|---|
| | $^{19}$F (100%) | $^{20}$F |
| | $^{107}$Ag, $^{109}$Ag (52%+48%) | $^{108}$Ag, $^{110}$Ag |

# Multiple Time NMR: Spin-Alignment Echo (SAE)



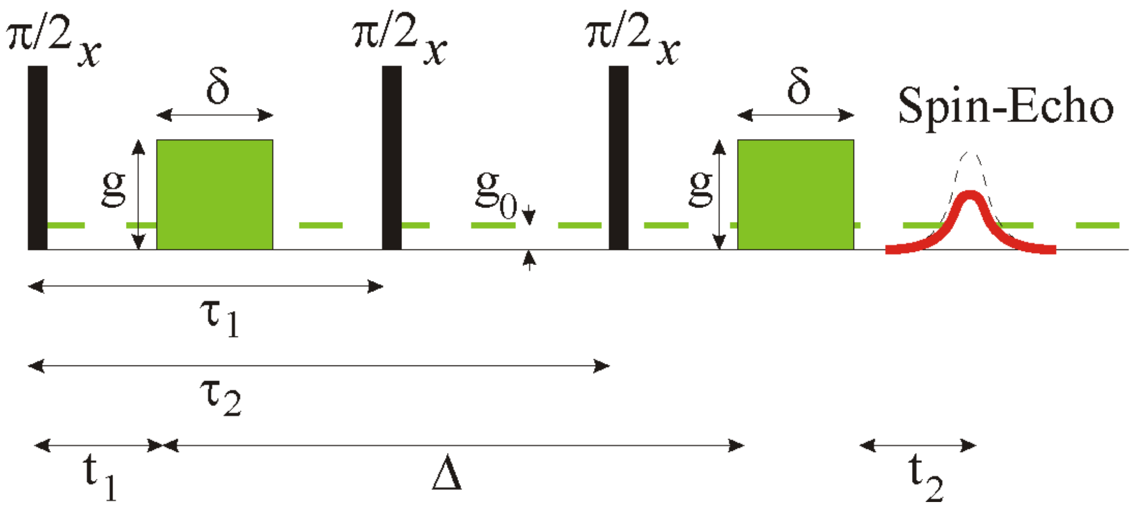
# Macroscopic Diffusion Measurem. in a Field Gradient

## SFG




$$\frac{M(\tau_1+\tau_2)}{M(0)/2} = \exp\left(-\frac{\tau_2-\tau_1}{T_1}-\frac{2\tau_1}{T_2}\right) \cdot \exp\left(-D^{\mathrm{T}}\gamma^2 g^2 \tau_1^2\left(\tau_2-\frac{\tau_1}{3}\right)\right)$$

## PFG

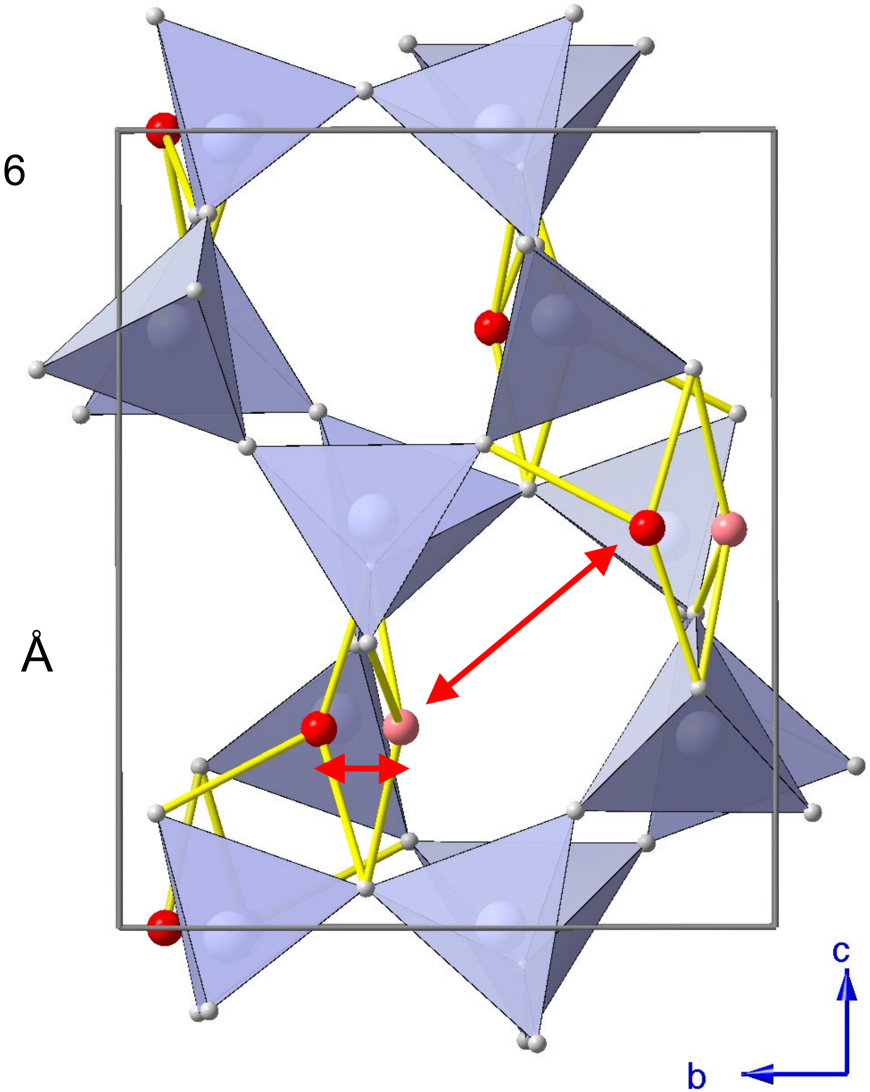



$$\frac{M(\tau_1+\tau_2)}{M(0)/2} = \exp\left(-\frac{\tau_2-\tau_1}{T_1}-\frac{2\tau_1}{T_2}\right) \cdot \exp\left(-D^{\mathrm{T}}\gamma^2 g^2 \delta^2\left(\Delta-\frac{\delta}{3}\right)\right)$$

# Case Studies:

- Glassy and Crystalline Spodumene $LiAlSi_2O_6$

$\beta$-$LiAlSi_2O_6$




$P4_32_12$

$a = b = 7.541$ Å

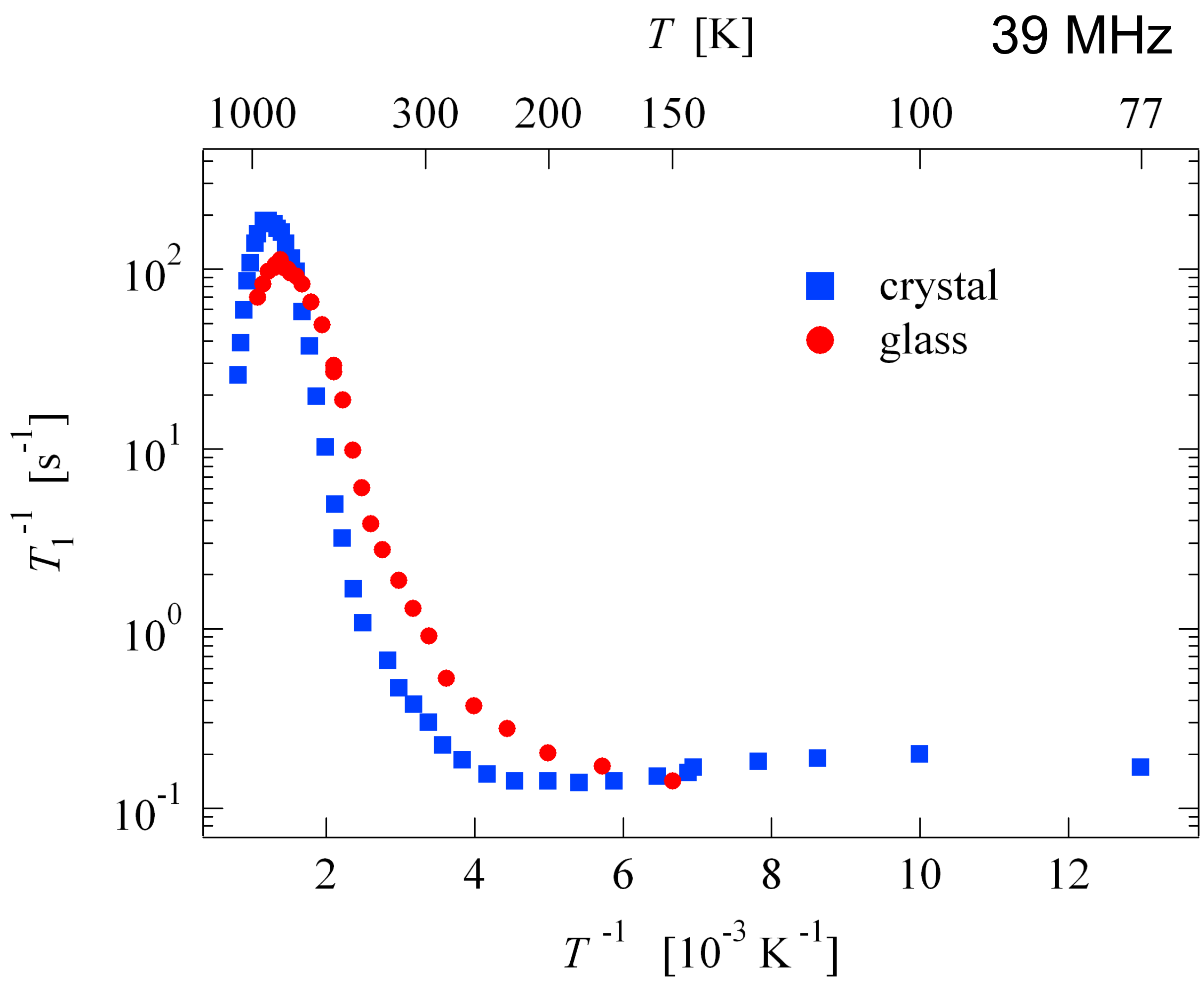
$c = 9.159$ Å

4 pairs of Li sites per unit cell (distance of neighbored paires: 4.5Å):

only one site of each pair occupied (distance only 1.3Å)

→ long-range and short-range jumps of Li ions ?

• $^7$Li Spin-Lattice Relaxation in Glassy and Crystalline Spodumene $LiAlSi_2O_6$




<u>high-*T* peak:</u>

long-range Li diffusion

faster in the glass

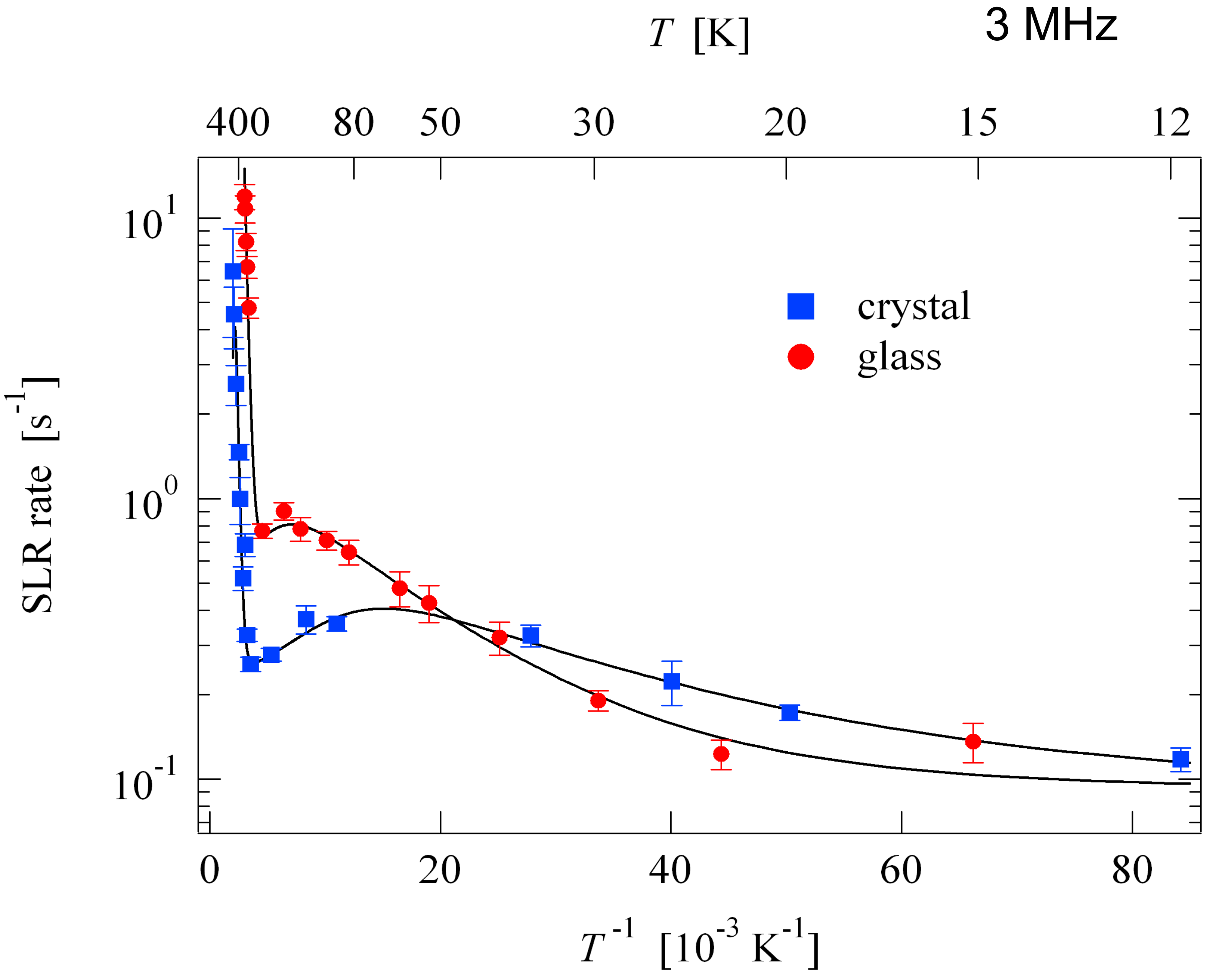
$E_A$(glass) = 0.34eV
$E_A$(cryst.) = 0.50eV

<u>low-T peak:</u>

short-range (local) jumps

F. Qi et al., Phys. Rev. B72 (2005) 104301

# $^8$Li β-NMR Spin-Lattice Relaxation in Glassy and Crystalline Spodumene $LiAlSi_2O_6$



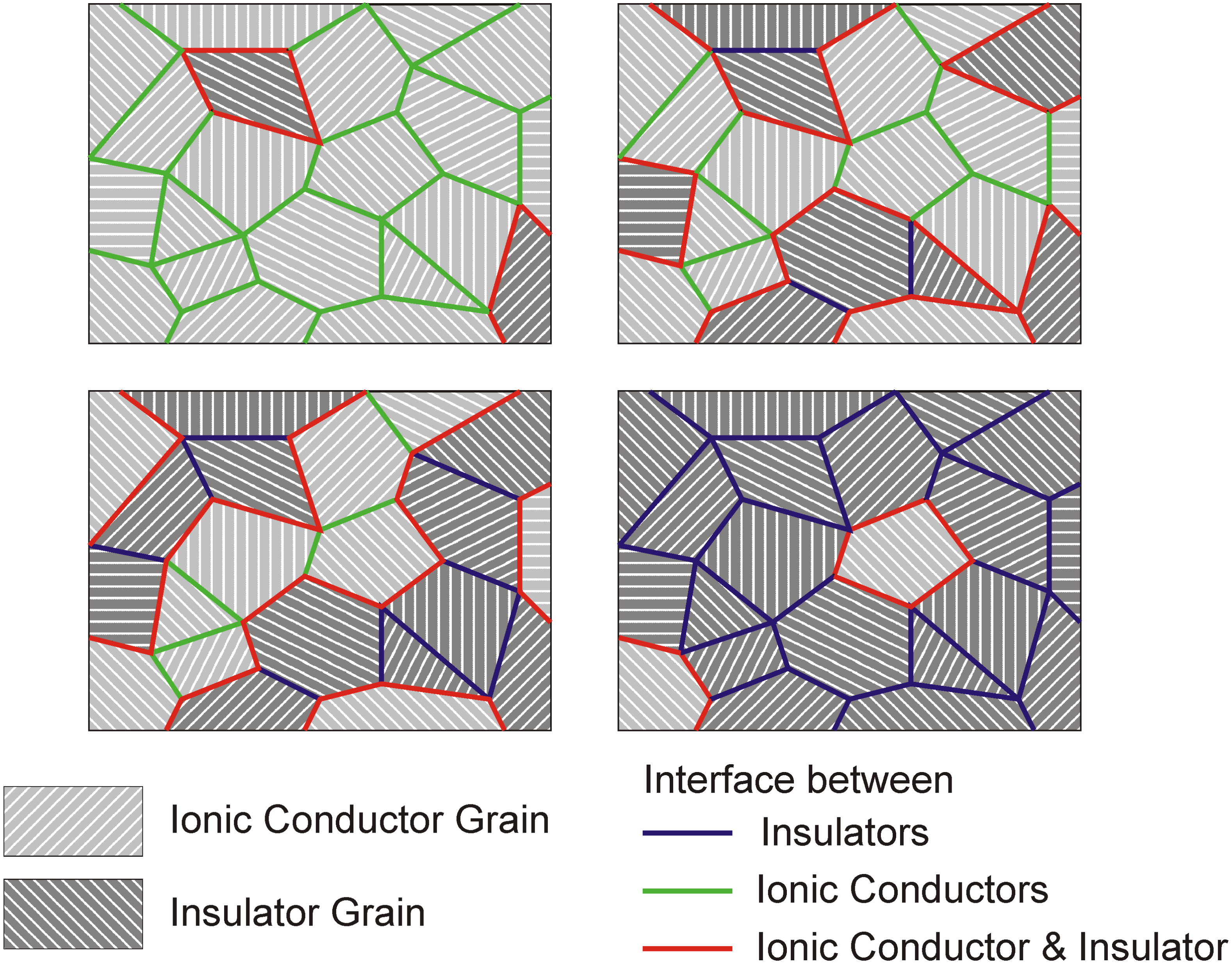

**low-*T* peak:**

localized Li motion between the pair sites in the crystal

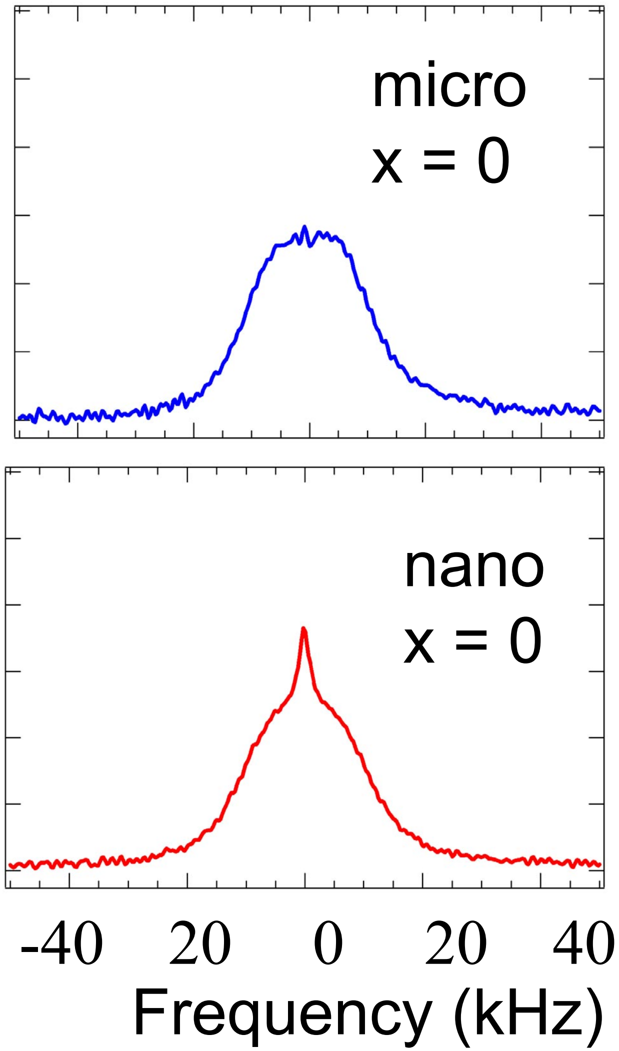
$E_A \approx 50$ meV

From:
„Diffusion in Condensed Matter - Methods, Materials, Models“, P. Heitjans, J. Kärger (Eds.), Springer, Berlin 2005

- Nanocrystalline Composites



- $^{7}$Li NMR Lineshapes: $(1\text{-}x)Li_2O{:}xB_2O_3$




T = 433 K

micro:
one-component line

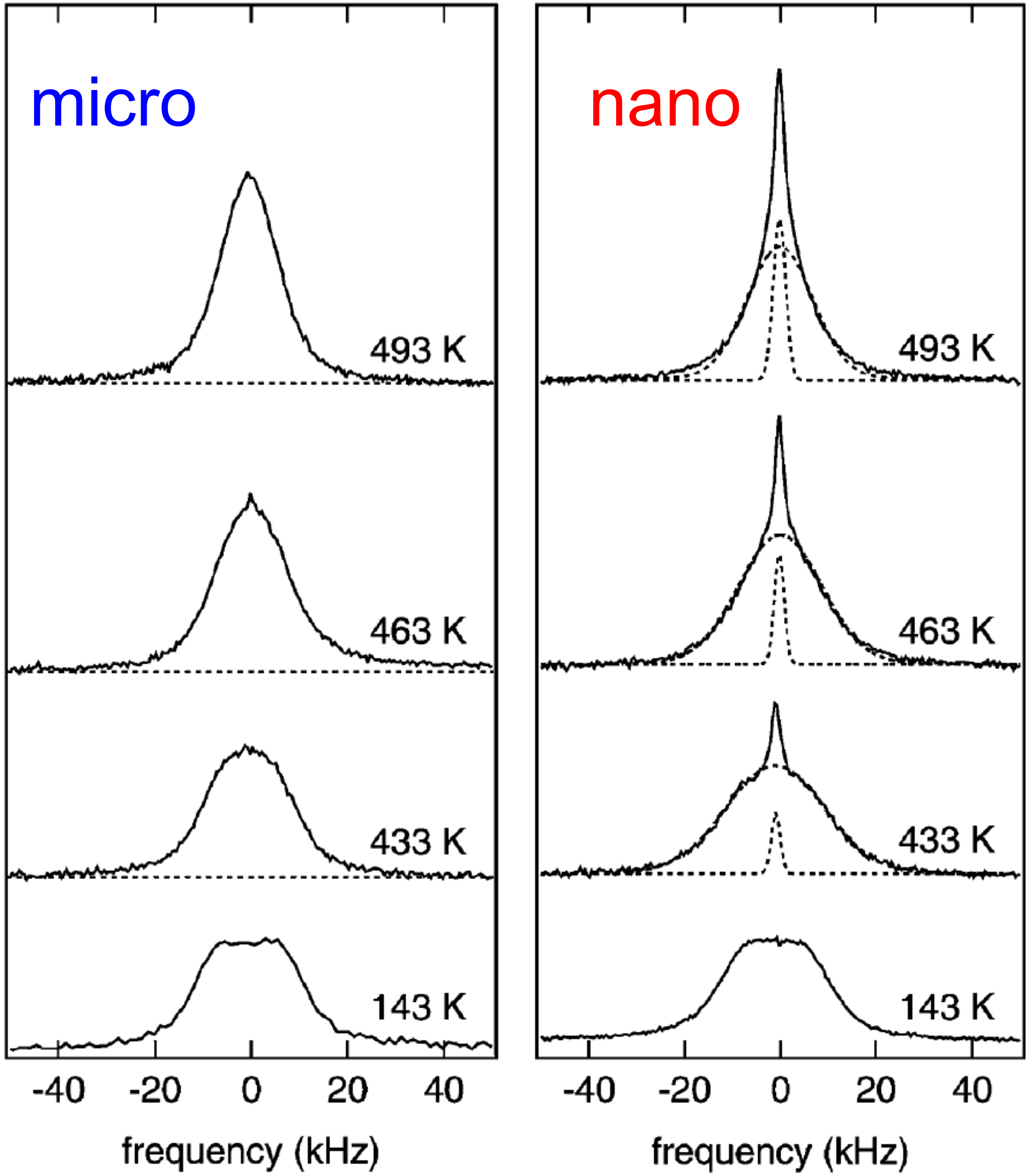
nano:
two-component line

S. Indris et al., J. Non-Cryst. Solids 307-310 (2002) 555

$^7$Li-NMR Lineshapes:

$(1\text{-}x)Li_2O:xAl_2O_3$

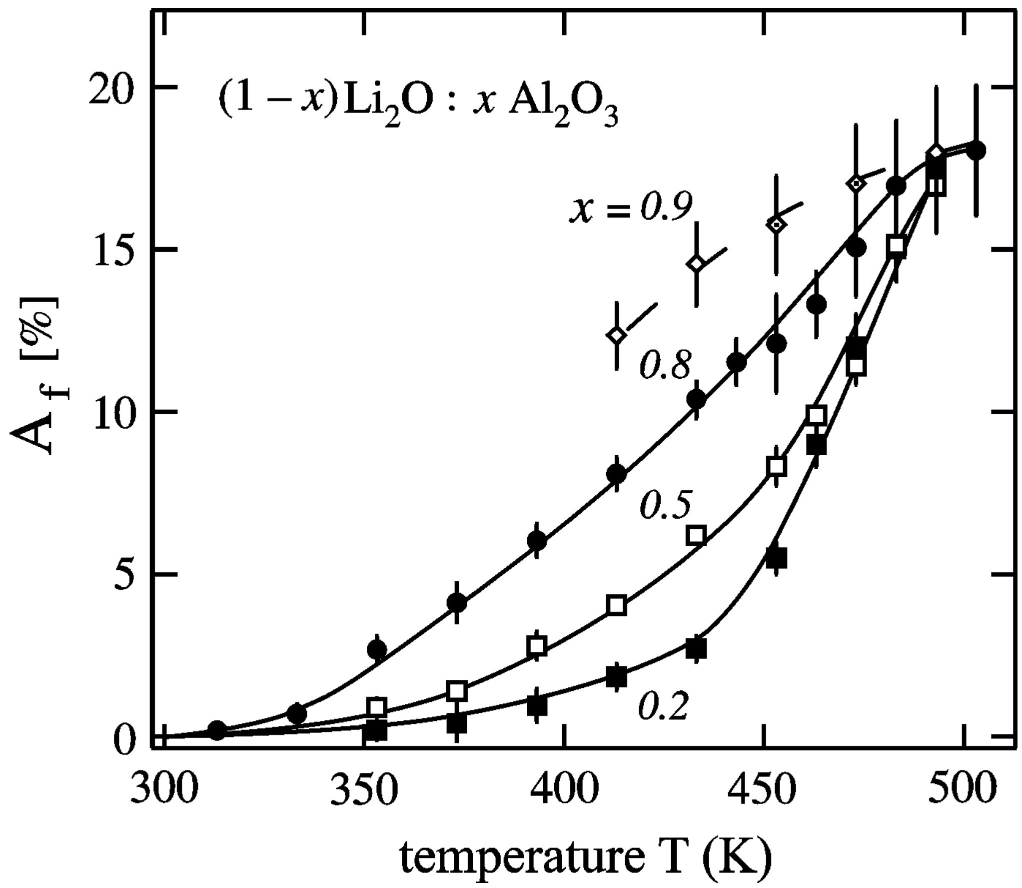
$x$=0.5




M. Wilkening et al., Phys. Chem. Chem. Phys. 5 (2003) 2225

# $^7$Li-NMR Lineshape: nanocryst. $(1\text{-}x)Li_2O{:}xAl_2O_3$

Fraction of mobile $Li^+$

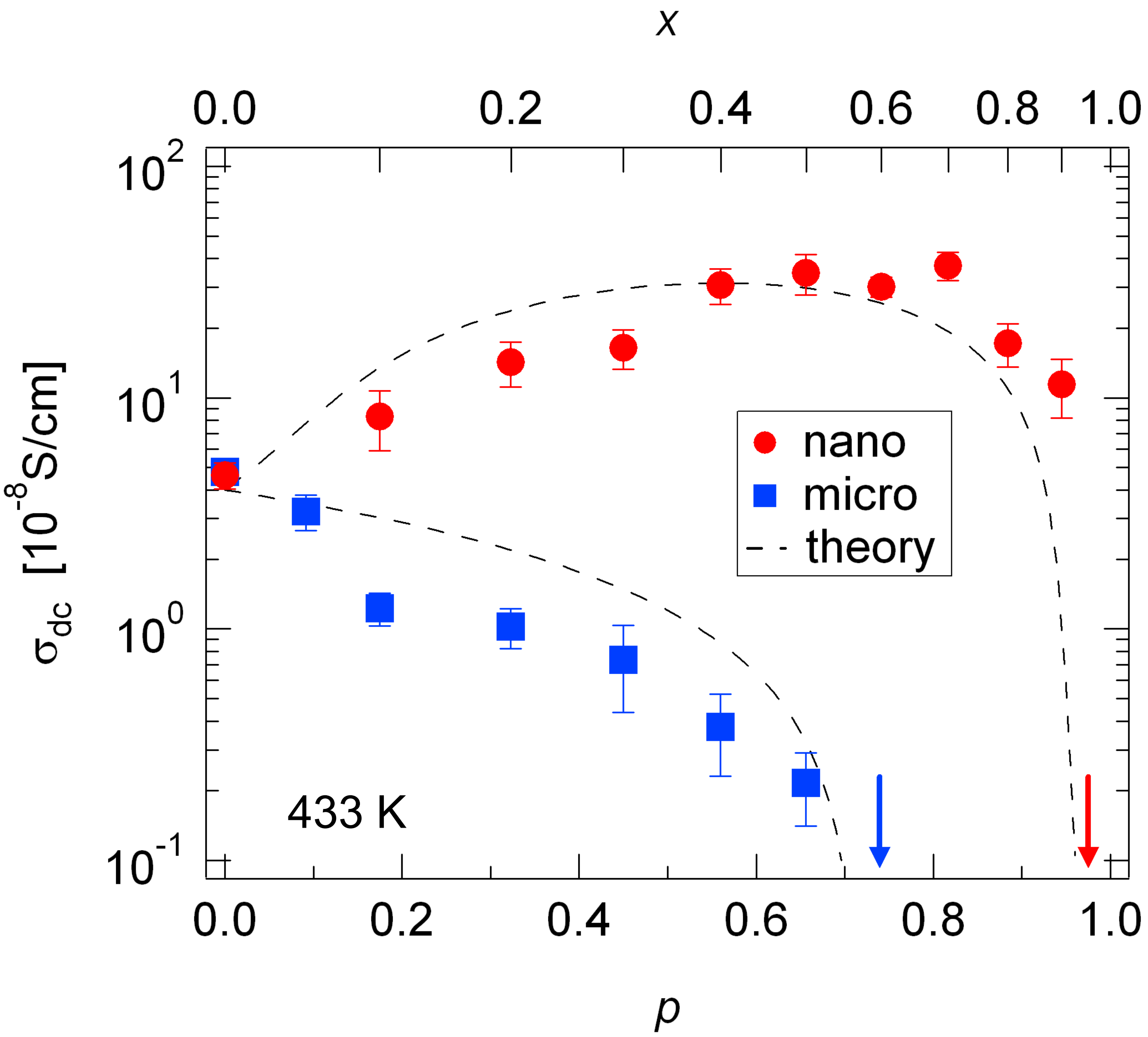



⇒ fast ions are located in the interfaces between ionic conductor and insulator

⇒ conductivity increases with insulator content x

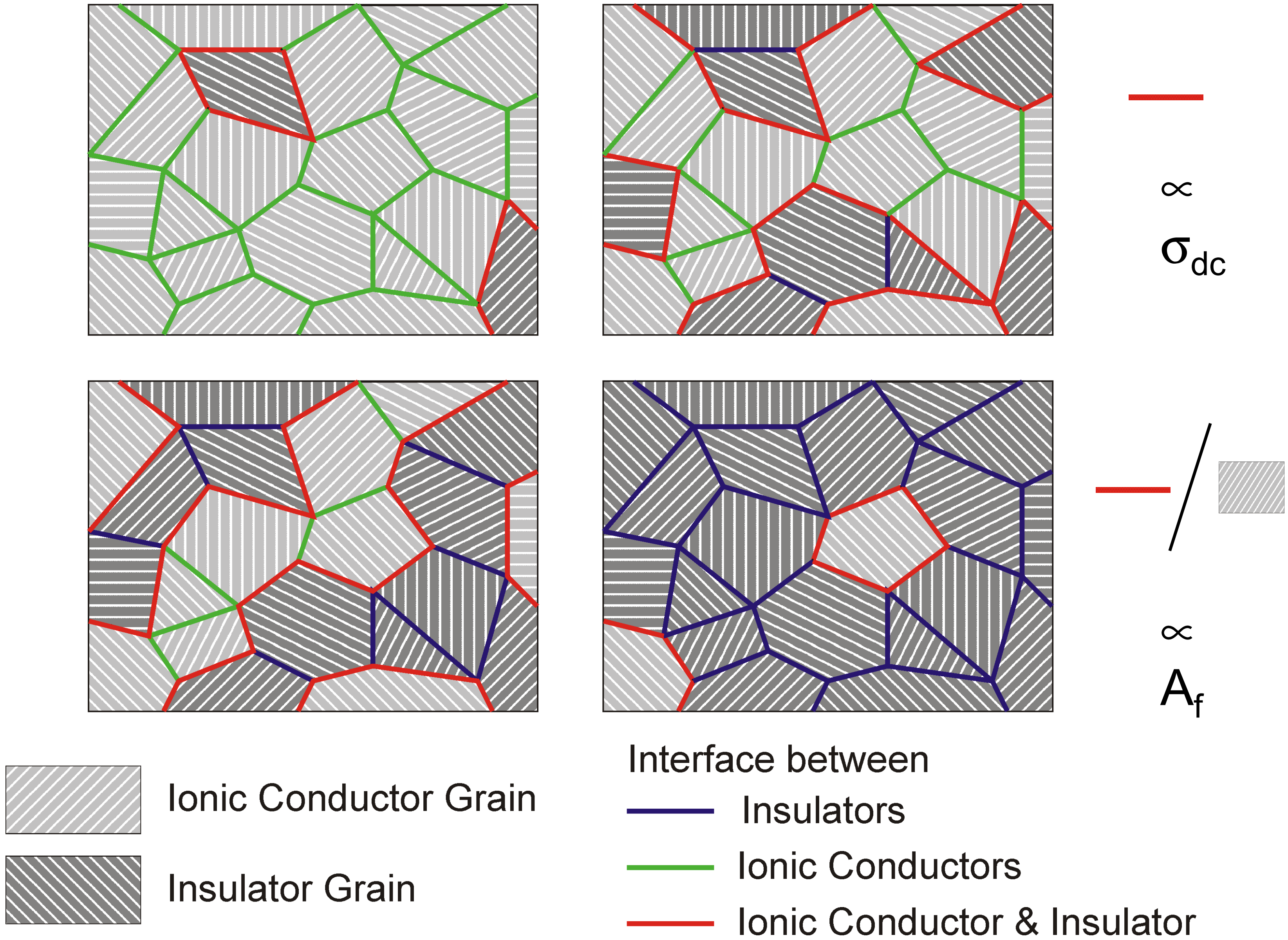
⇒ possible route to design fast solid electrolytes

# DC Conductivity: (1-$x$) $Li_2O$:$xB_2O_3$  $x$=0...1



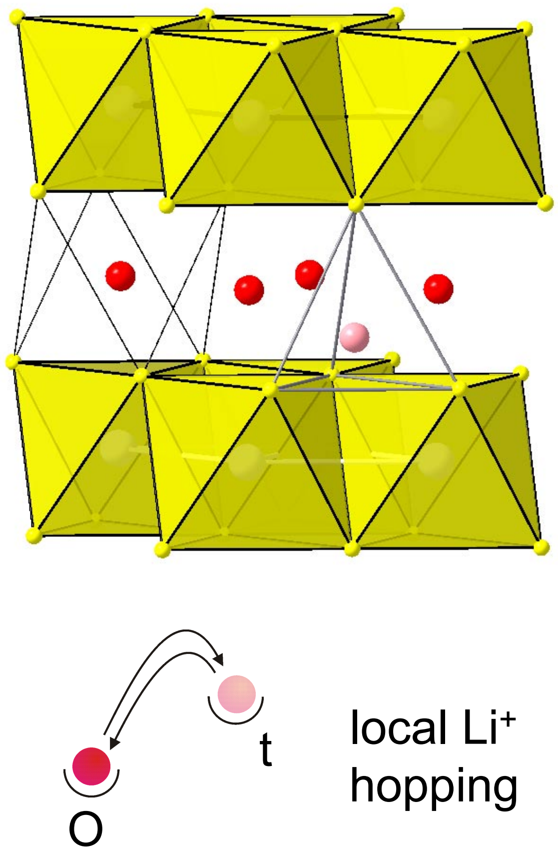

S. Indris et al.,
Phys. Rev. Lett.
87 (2000) 2889.

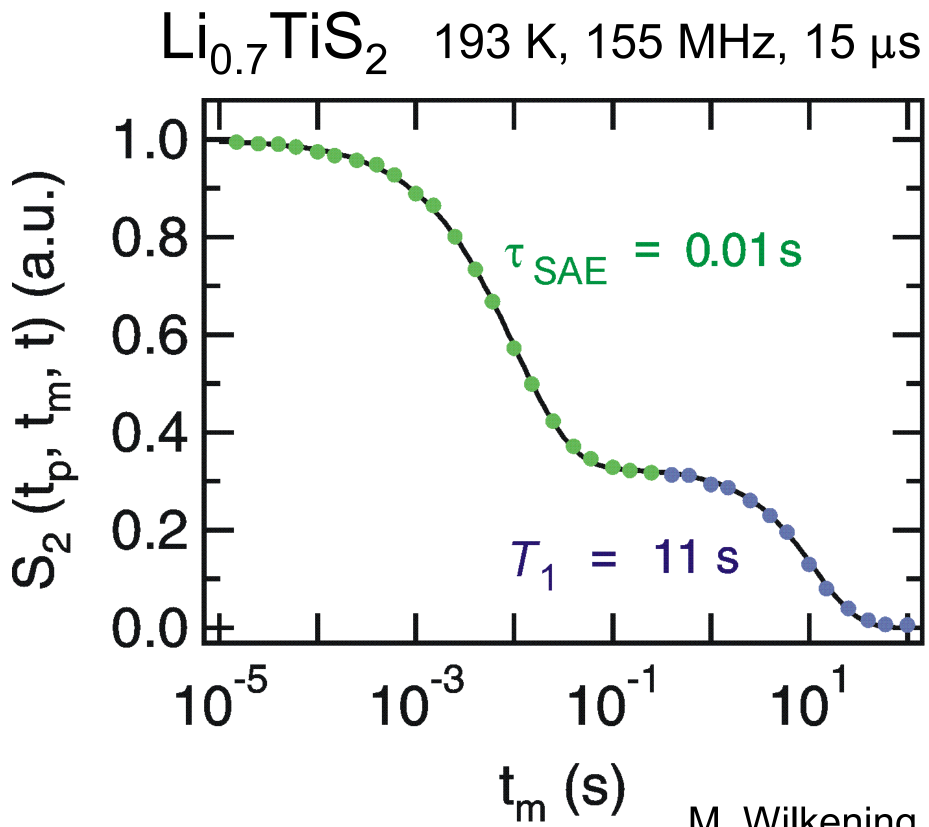
# Percolation Model



- $^{7}$Li Spin-Alignment Echo

$$S_2(t_p, t_m) \propto \left\langle \sin(\omega_Q(0)t_p)\sin(\omega_Q(t_m)t_p)\right\rangle \exp\left(-\frac{t_m}{T_{1Q}}\right)$$

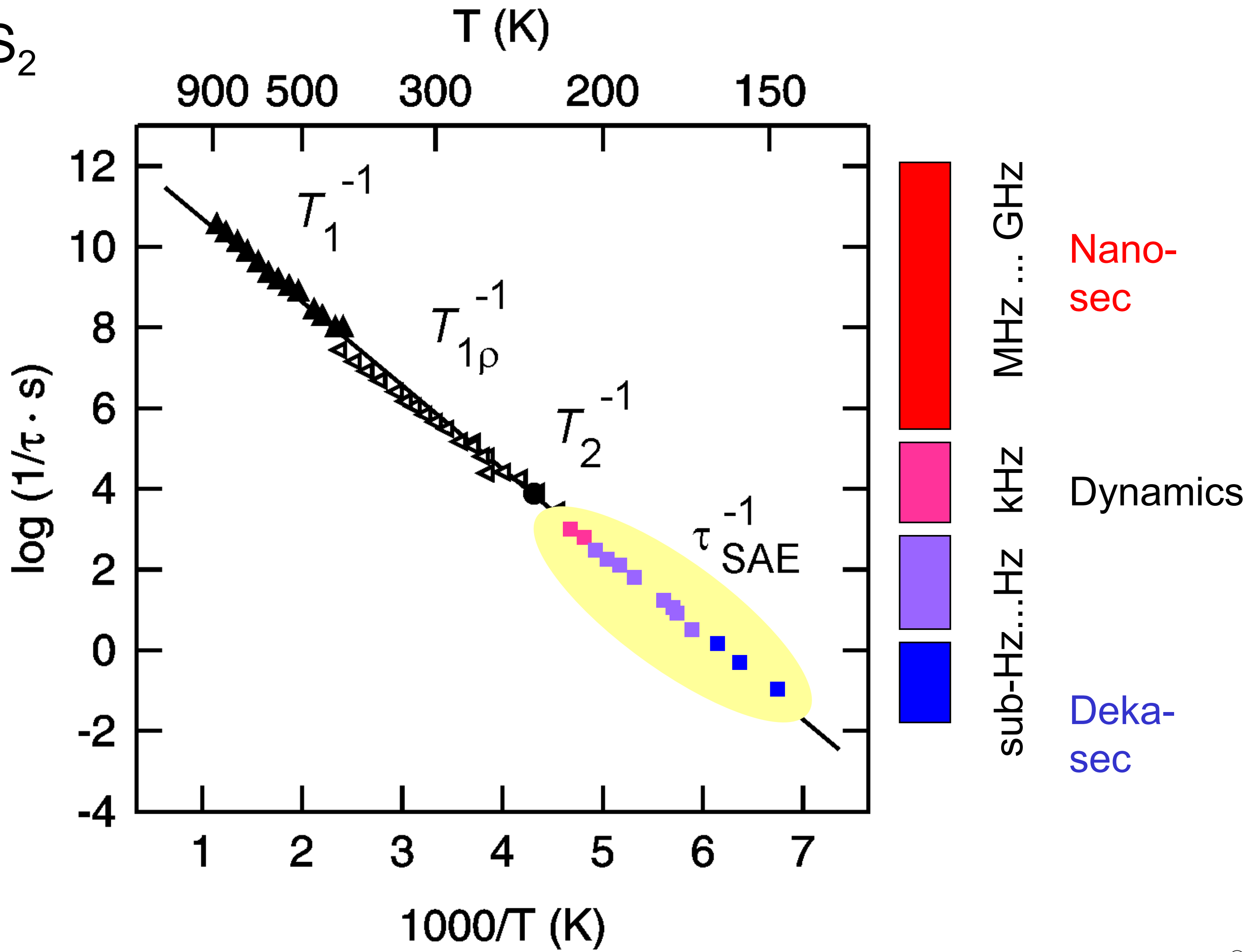


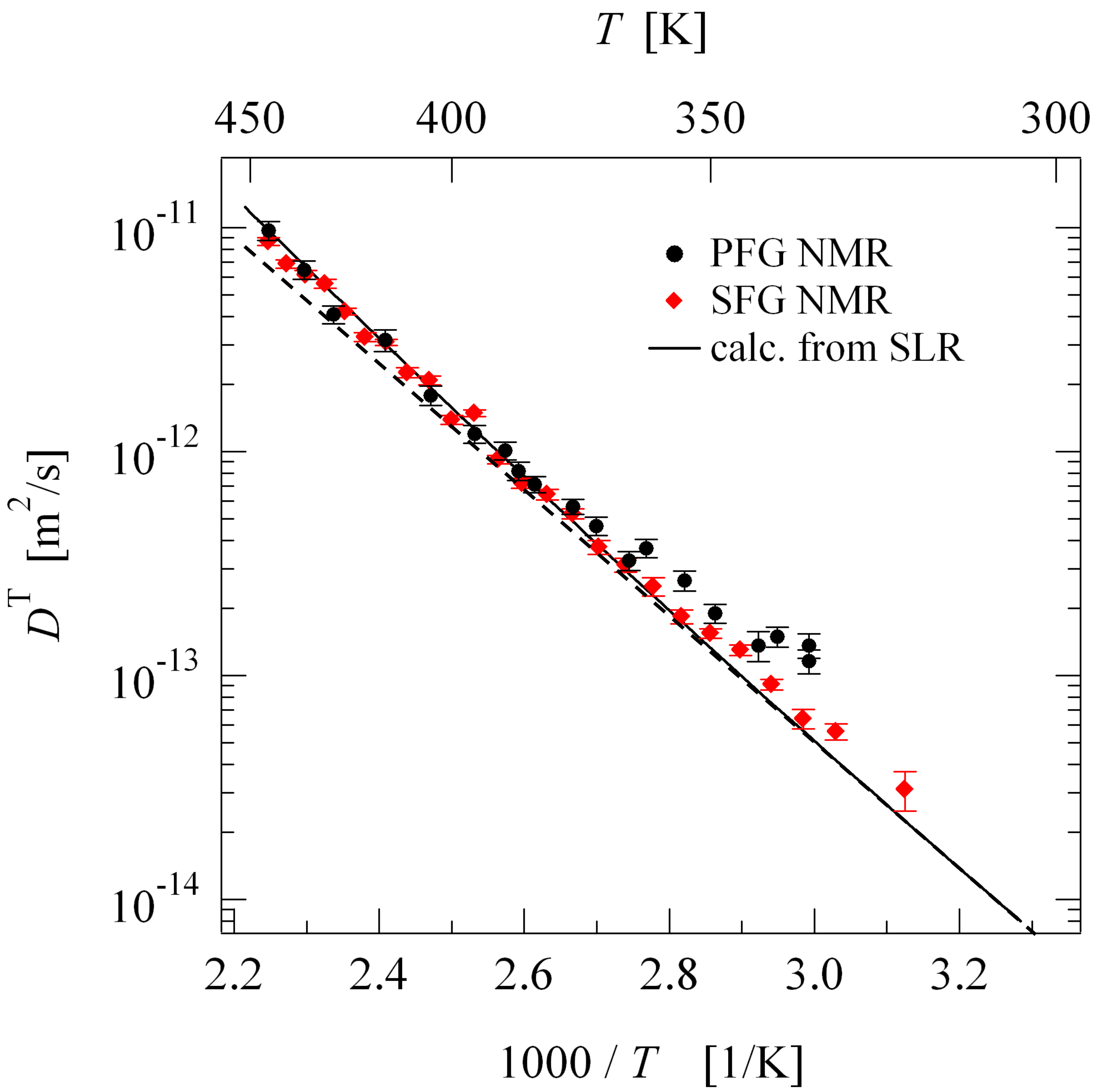

M. Wilkening, PhD thesis, University of Hannover, 2005.

# Motional Correlation Rates

$Li_{0.7}TiS_2$



# • $^{7}Li$ SFG and PFG NMR
# on Solid Lithium as Simple Test Case




$D^T$ measured down to about $10^{-14}$ $m^2/s$

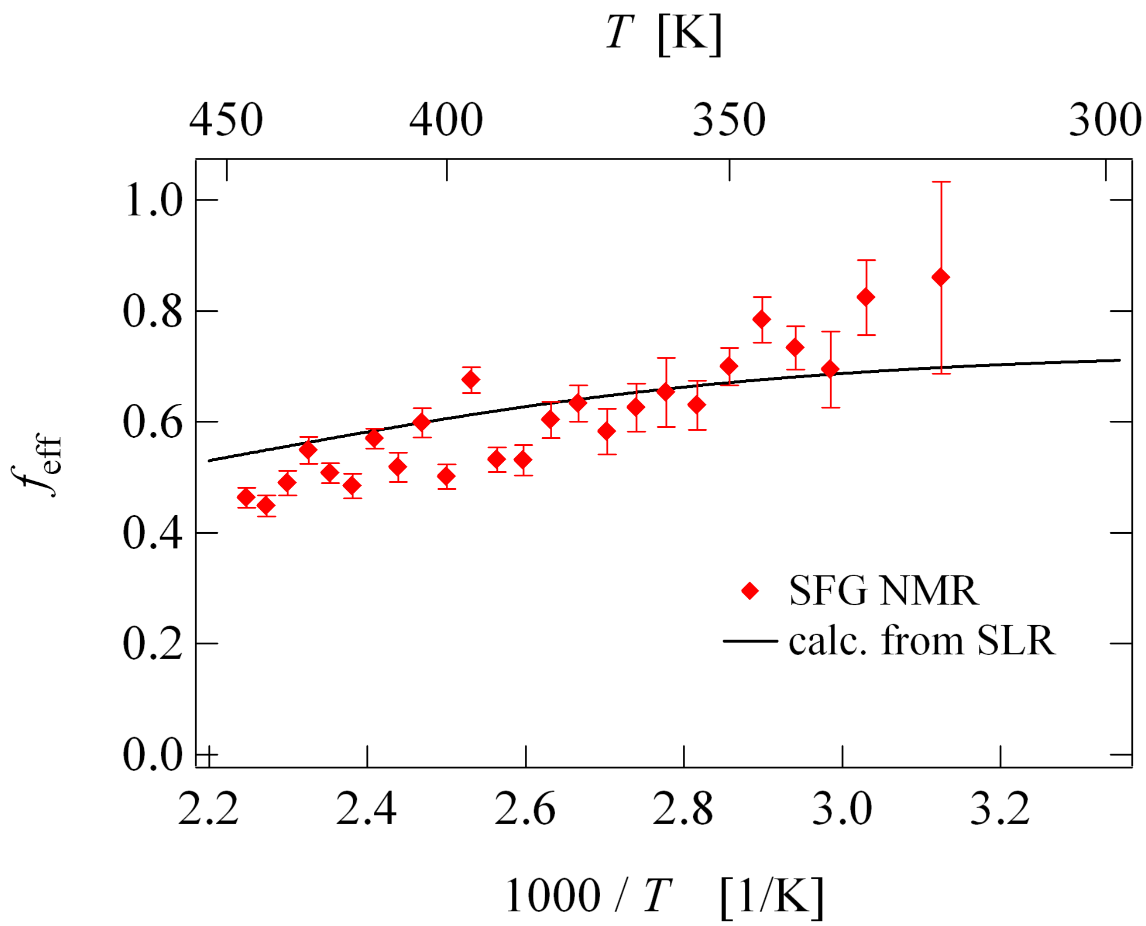
Comparison with $T_1$:

$D^T$ calculated from $^{8}Li$ SLR data assuming Monovacancy-Divacancy-Mechanism

D. M. Fischer et al.,
Solid State NMR, 26 (2004) 74

# $^7$Li SFG NMR on Solid Lithium

effective correlation factor $f_{eff} = \dfrac{D^T}{r^2 / 6\tau}$




$D^T = f_{1V} D_{1V} + f_{2V} D_{2V}$

$f_{1V} = 0.727$

$f_{2V} = 0.347$

(Mehrer 1973)

consistent with
1V-2V mechanism

# Conclusion

- NMR provides arsenal of techniques

  microscopic: $T_1$, $T_2$, $T_{1\rho}$, β-NMR, SAE

  macroscopic: SFG NMR, PFG NMR

- Used to measure jump rates ($10^9 ... 10^{-1}$ $s^{-1}$) and tracer diffusion coefficients ($10^{-11} ... 10^{-14}$ $m^2s^{-1}$) in

  metals, glasses, ceramics, nanocrystals,
  intercalation compounds, solid electrolytes ...

- Comparison of microscopic and macroscopic diffusion parameters allows determination of diffusion mechanisms

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