

# Atomic Tunneling Systems in Solids



real crystals

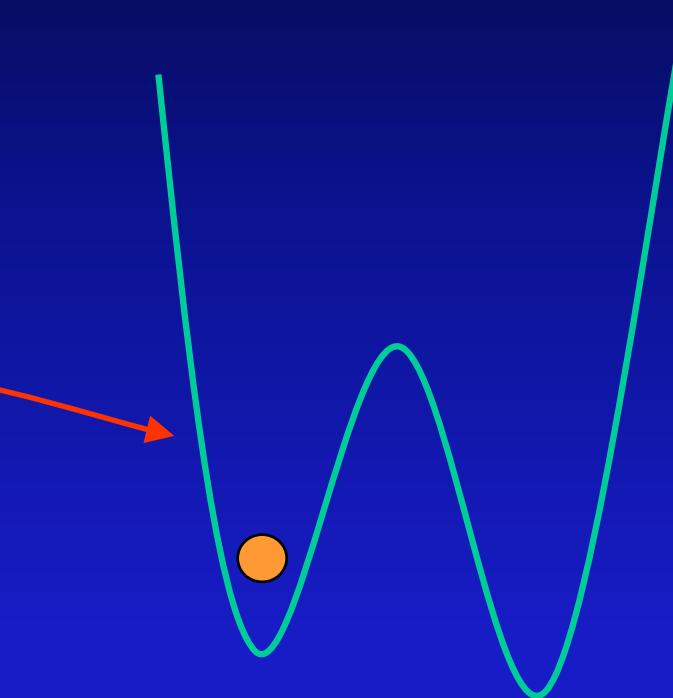
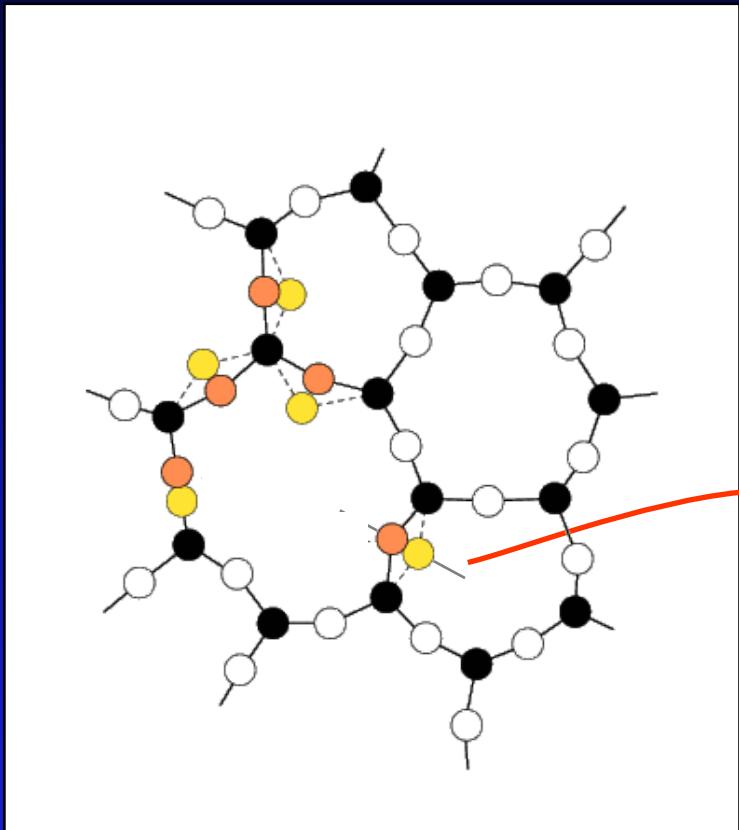


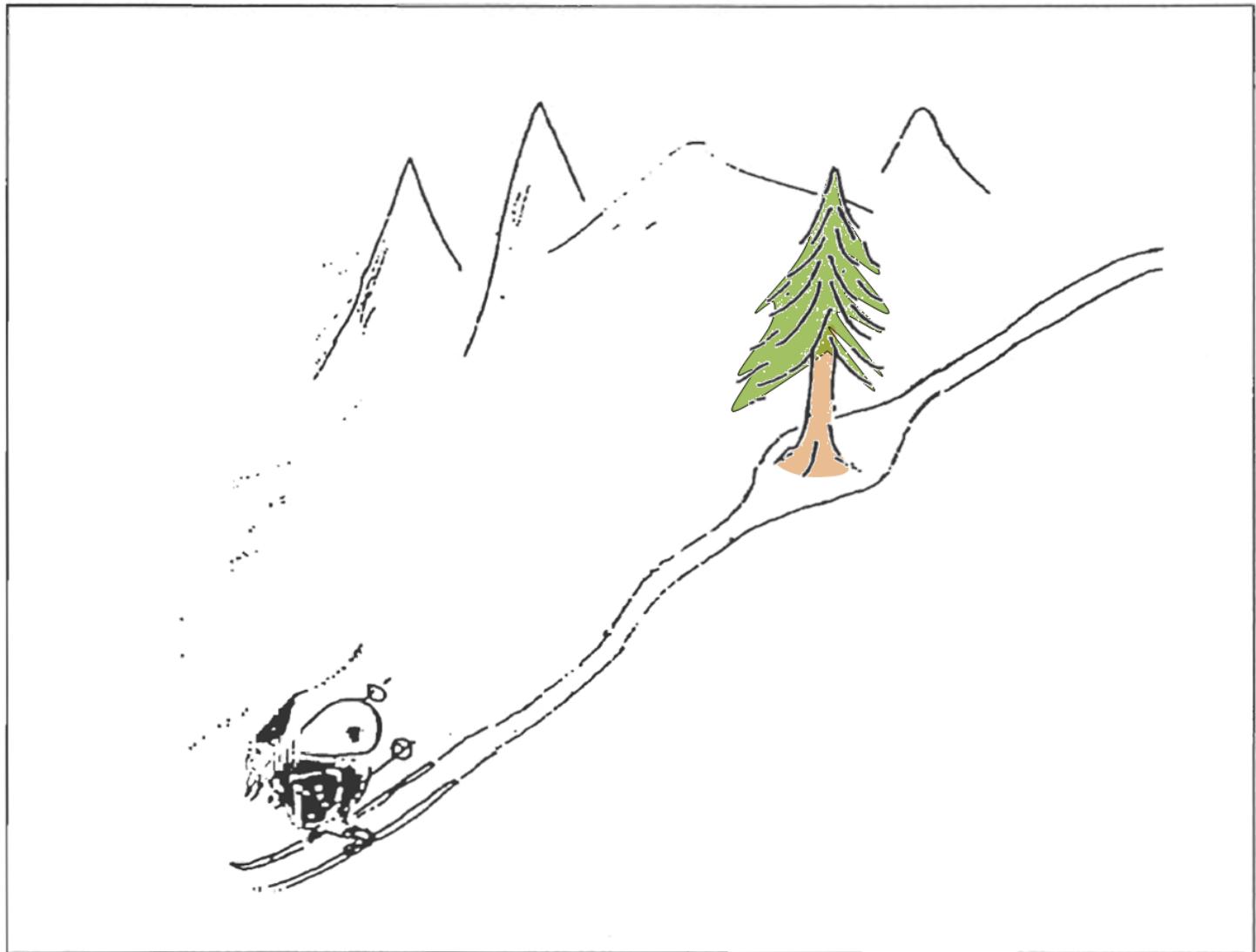
glasses



Christian Enss  
Kirchhoff-Institut of Physics  
Heidelberg University

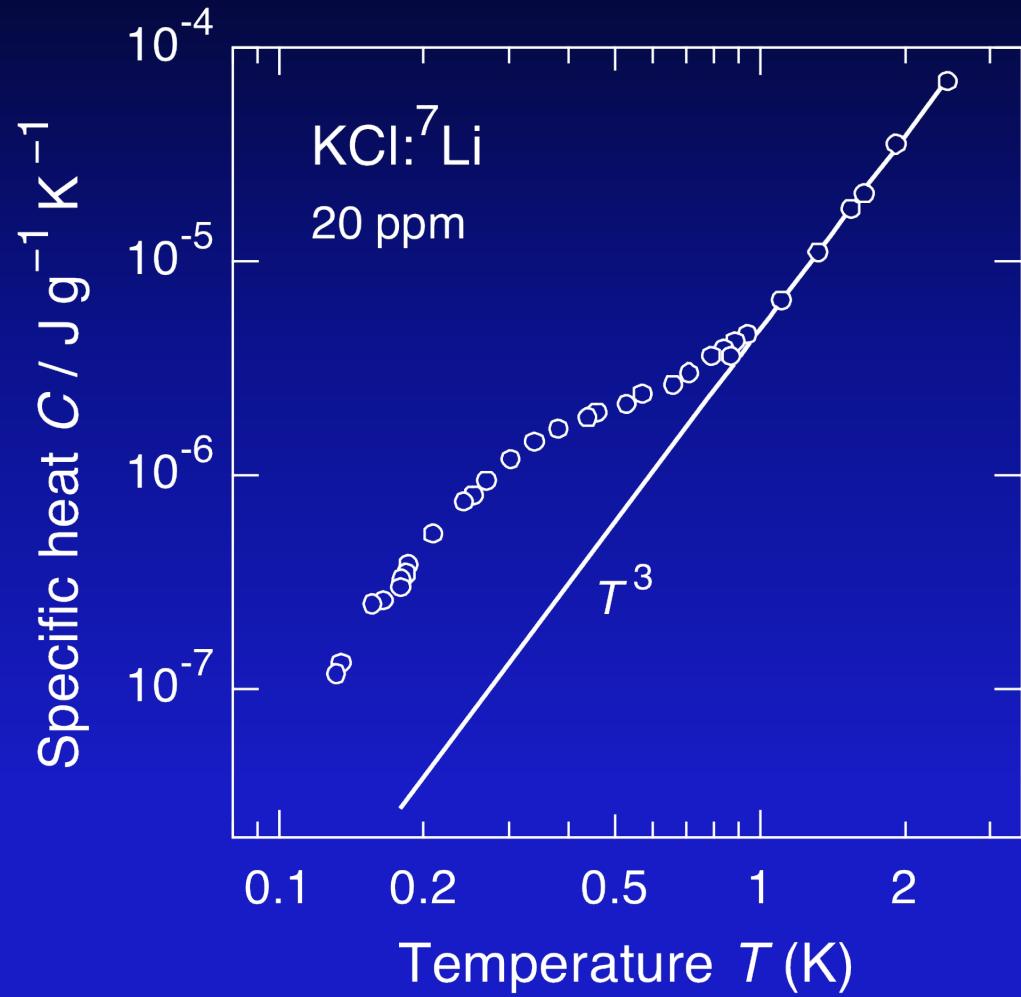
# Tunneling of Atoms in Solids





# KCl:Li Specific Heat

specific heat roughly a  
factor of 10 higher at 0.5 K



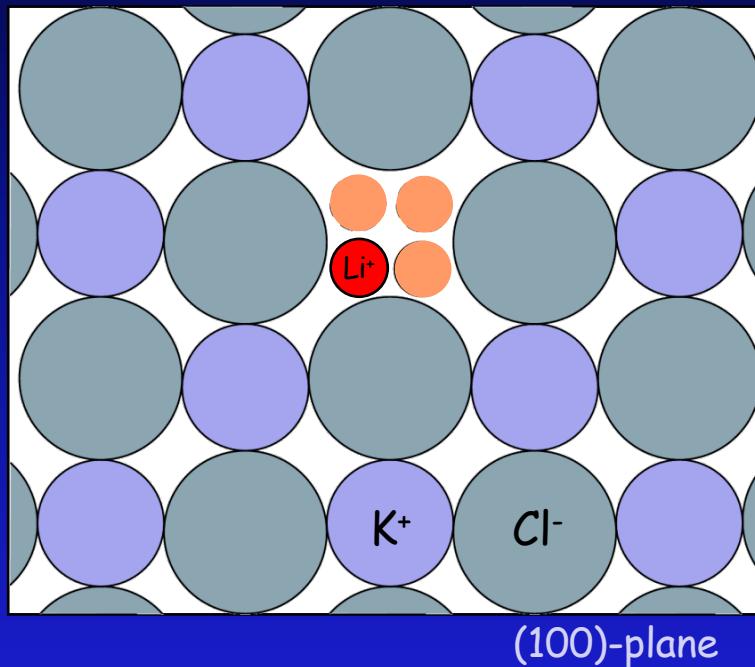
J.P. Harrison, Phys. Rev. 171, 1037 (1968)

# Li-Tunneling Systems in KCl-Crystals

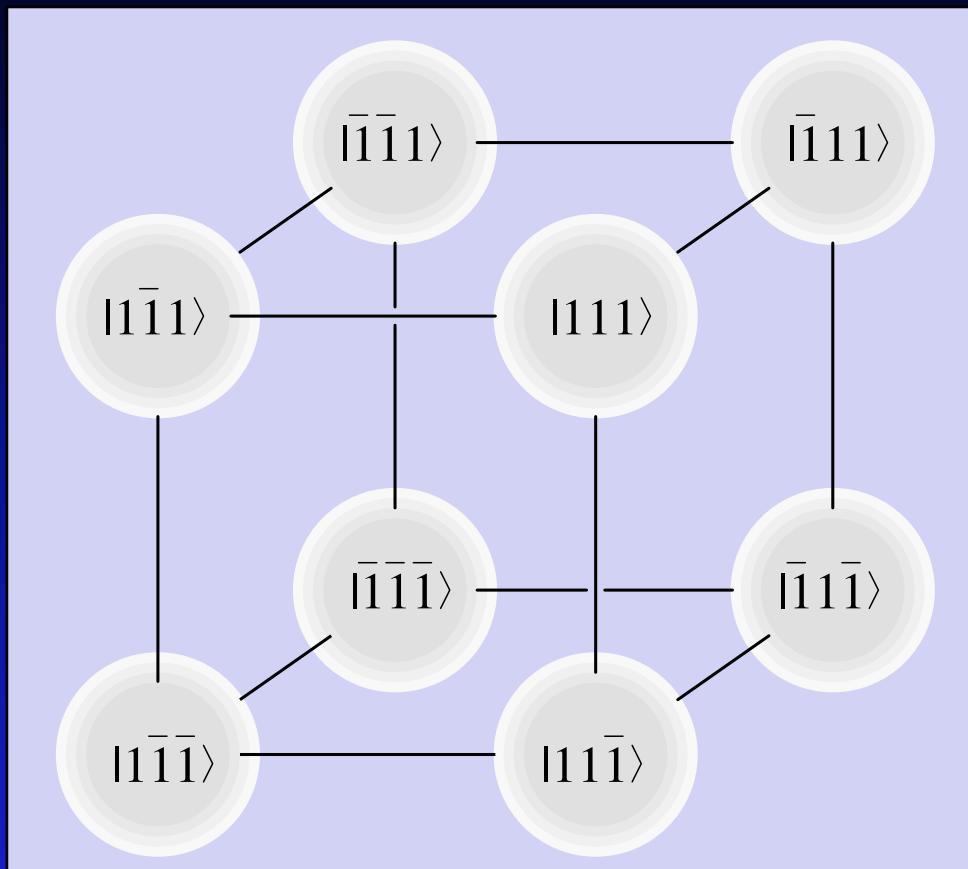
$\text{Li}^+$  substitutes  $\text{K}^+$

ionic radius:  $r_{\text{Li}^+} < r_{\text{K}^+}$

→ 8 off-center positions  
in  $\langle 111 \rangle$  direction



# Quantum States of <111> Systems

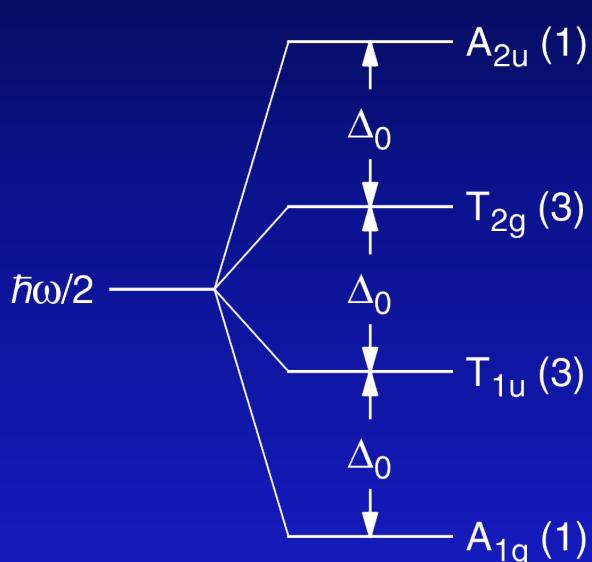


$$\eta' = \langle 111 | \mathbf{H} | 11\bar{1} \rangle = \langle \bar{1}11 | \mathbf{H} | \bar{1}\bar{1}1 \rangle = \dots \quad \text{edge tunneling}$$

$$\mu' = \langle 111 | \mathbf{H} | 1\bar{1}\bar{1} \rangle = \langle 1\bar{1}1 | \mathbf{H} | 11\bar{1} \rangle = \dots \quad \text{face diagonal tunneling}$$

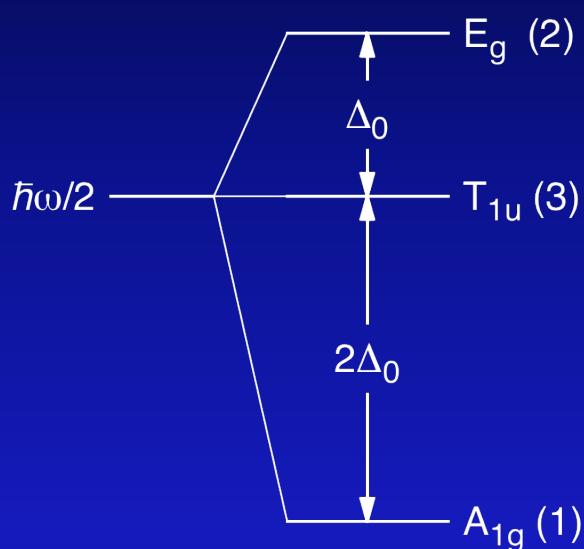
$$\nu' = \langle 111 | \mathbf{H} | \bar{1}\bar{1}\bar{1} \rangle = \langle 1\bar{1}1 | \mathbf{H} | \bar{1}1\bar{1} \rangle = \dots \quad \text{room diagonal tunneling}$$

# Tunneling Systems with Cubic Symmetry



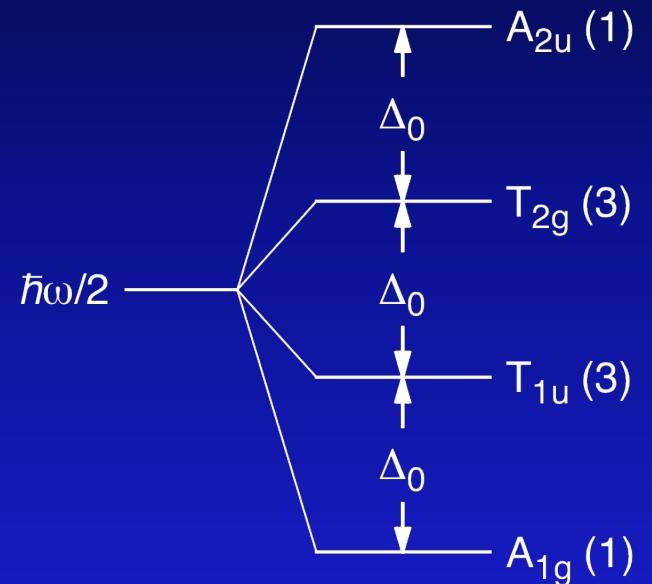
$<111>$

KCl:Li, KBr:CN



$<100>$

KCl:OH, LiF:OH



$<110>$

NaBr:F

# Li-Tunneling Systems in KCl-Crystals

$\text{Li}^+$  substitutes  $\text{K}^+$

ionic radius:  $r_{\text{Li}^+} < r_{\text{K}^+}$

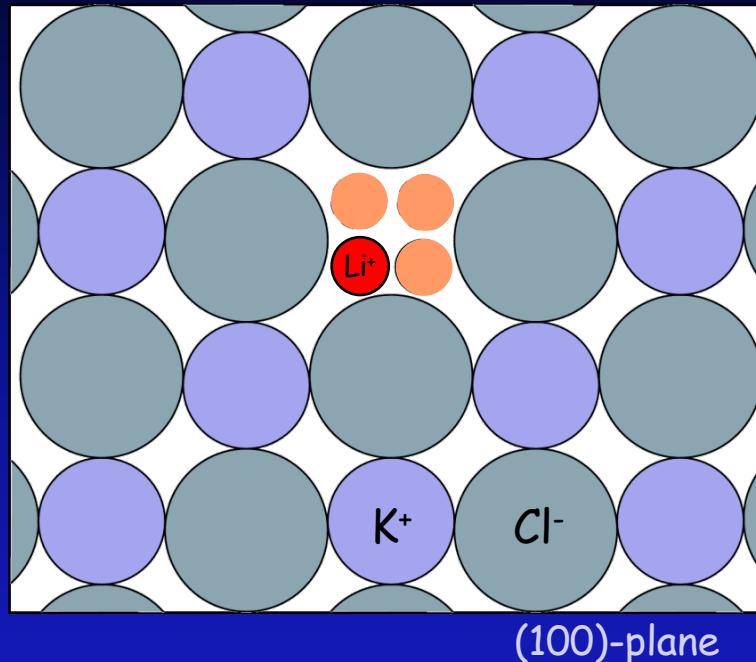
→ 8 off-center positions  
in  $\langle 111 \rangle$  direction

tunnel splitting:

$$\Delta_0 = \hbar \Omega e^{-\lambda} \quad \text{with} \quad \lambda = \frac{d}{2\hbar} \sqrt{2mV}$$

$${}^7\text{Li} : \quad {}^7\Delta_0/k_B = 1,1 \text{ K}$$

$${}^6\text{Li} : \quad {}^6\Delta_0/k_B = 1,6 \text{ K}$$



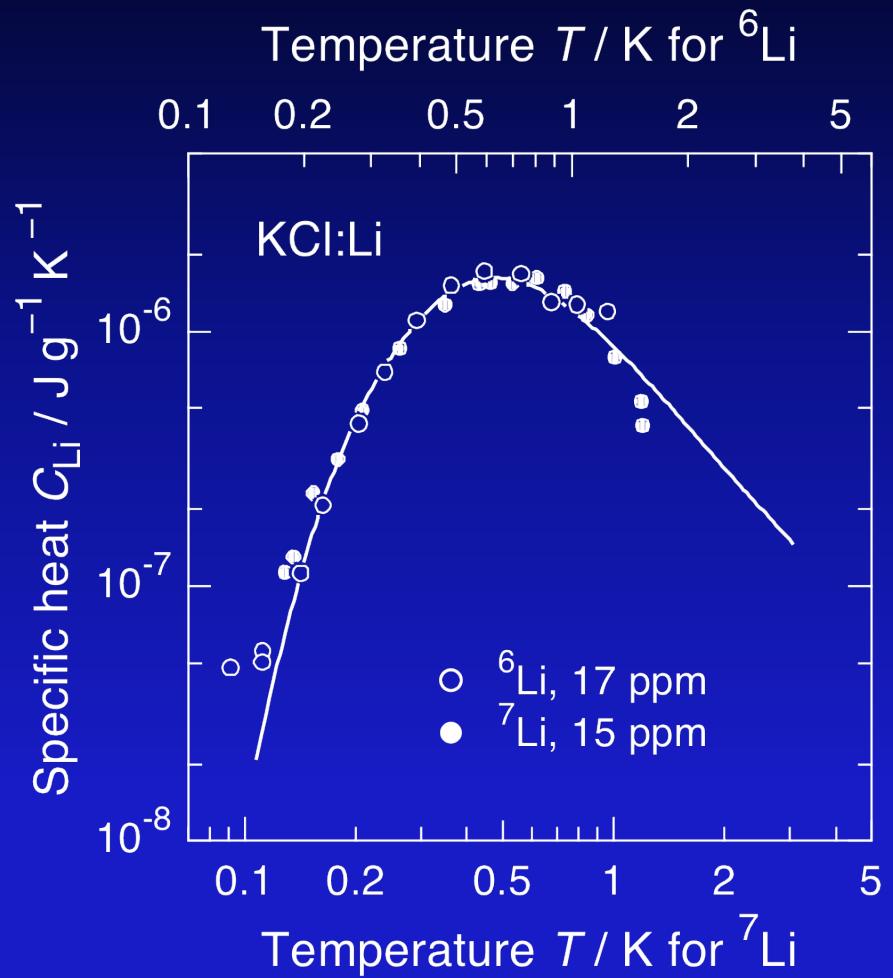
X. Wang, F. Bridges, Phys. Rev. B**46**, 5122 (1992)

# Isotope effect

Schottky-Anomaly

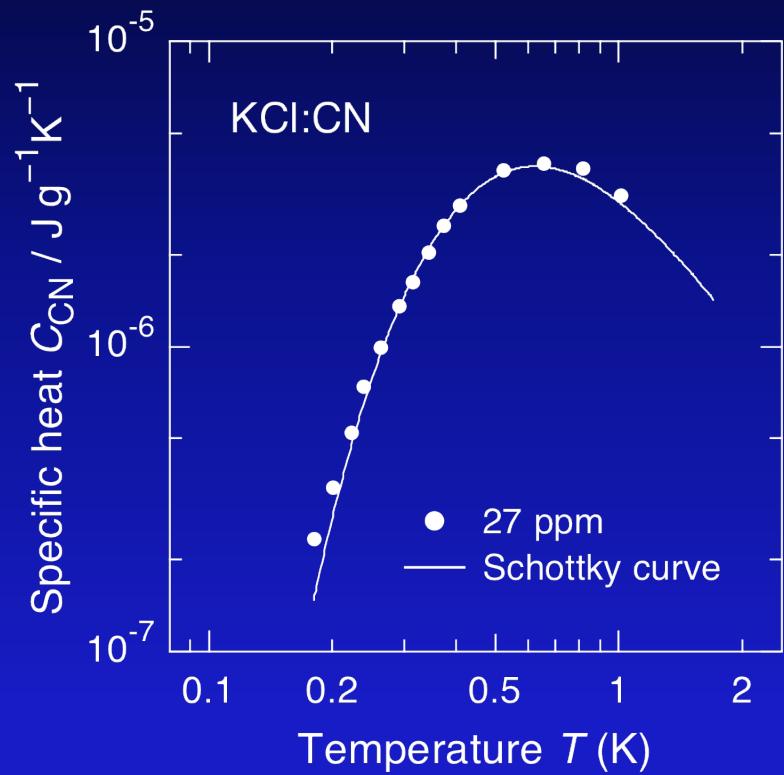
$$C_{\text{TS}} = \frac{3nk_{\text{B}}}{\varrho} \left( \frac{\Delta_0}{2k_{\text{B}}T} \right)^2 \operatorname{sech}^2 \left( \frac{\Delta_0}{2k_{\text{B}}T} \right)$$

number density       $n = N/V$

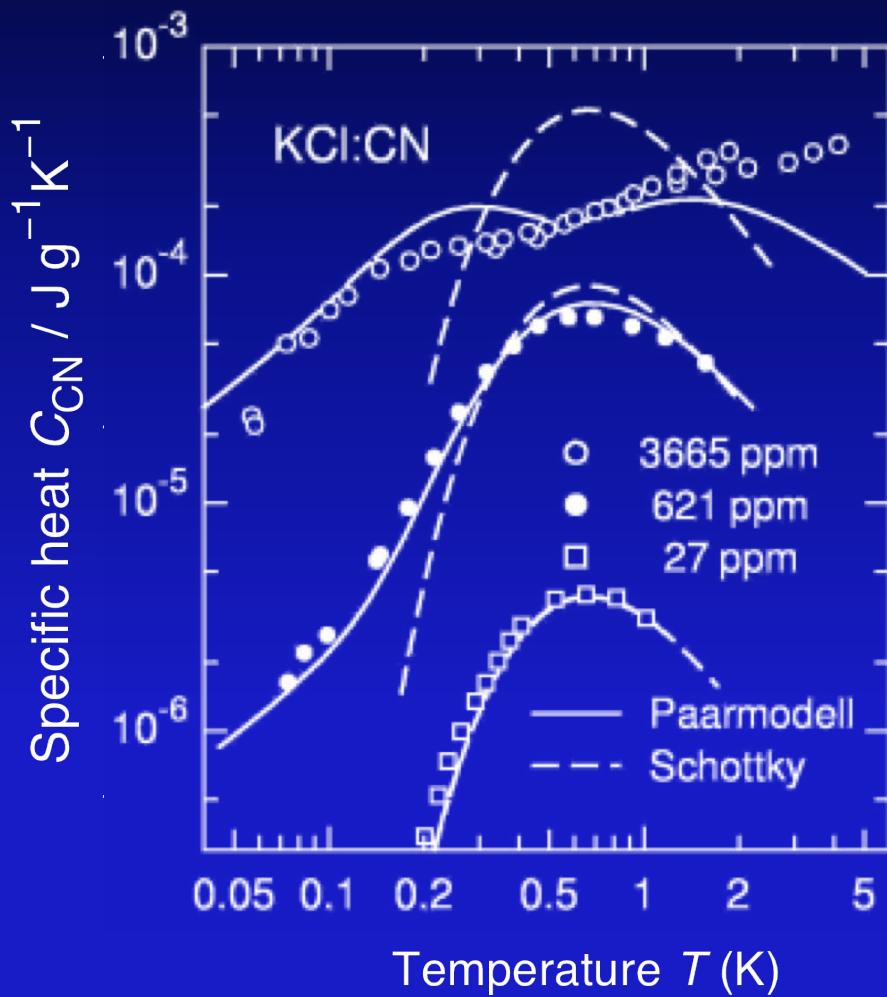


J.P. Harrison, Phys. Rev. 171, 1037 (1968)

# KCl:CN



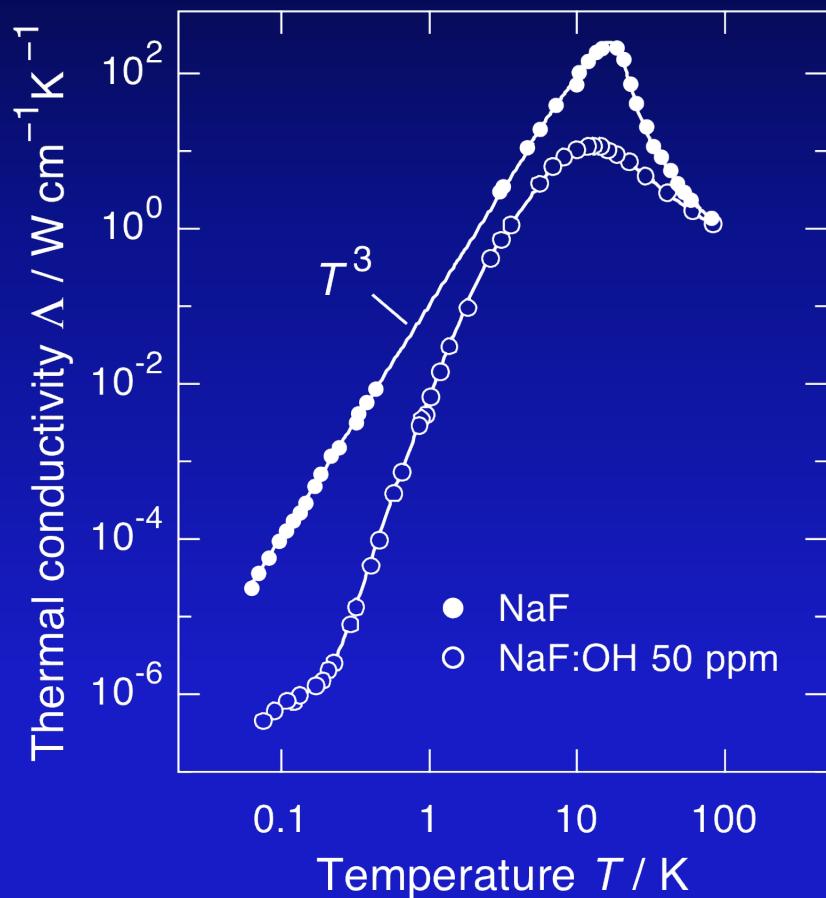
concentration dependence



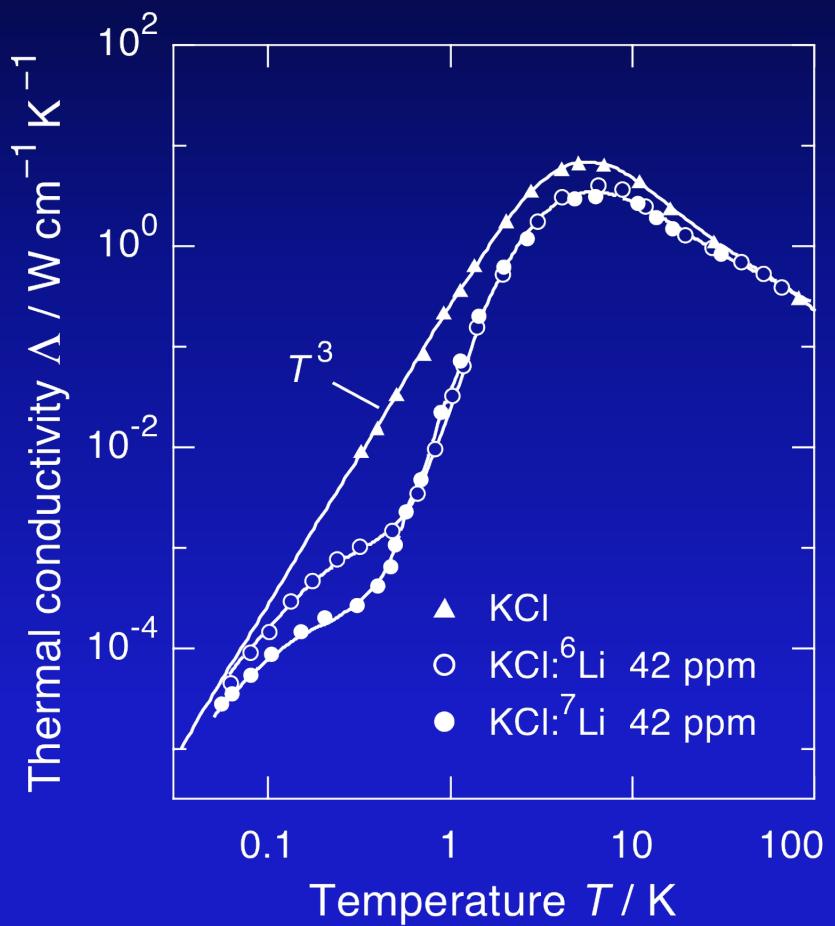
P.P. Peressini, J.P. Harrison, R.O. Pohl,  
Phys. Rev. **182**, 939 (1969)

# Thermal Conductivity

$\text{NaF: OH}^-$



$\text{KCl:Li}$

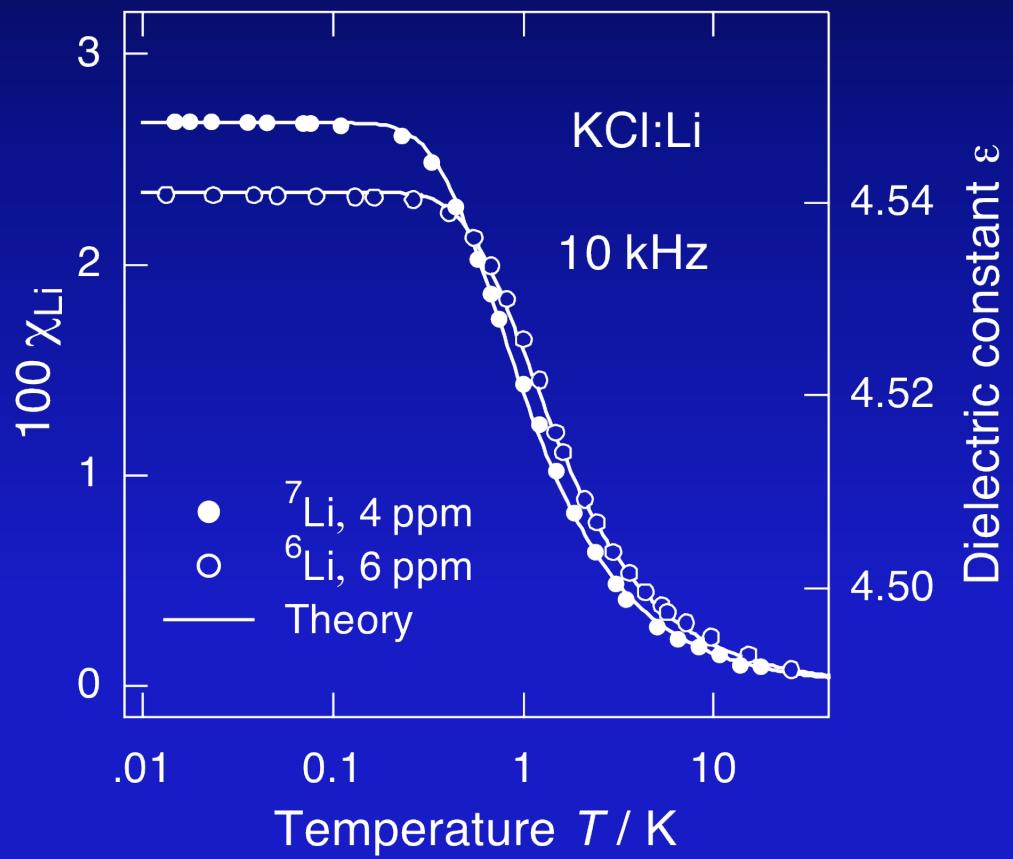


T.F. McNelly, Ph.D. thesis  
(Cornell University 1974)

P.P. Peressini, J.P. Harrison, R.O. Pohl,  
Phys. Rev. 180, 926 (1969)

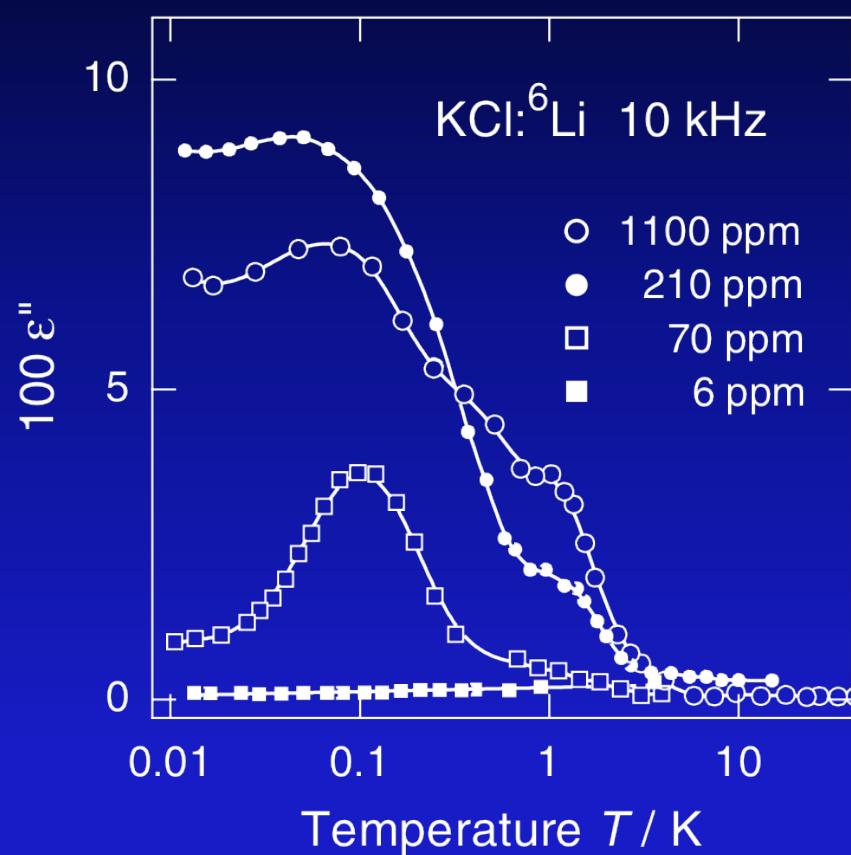
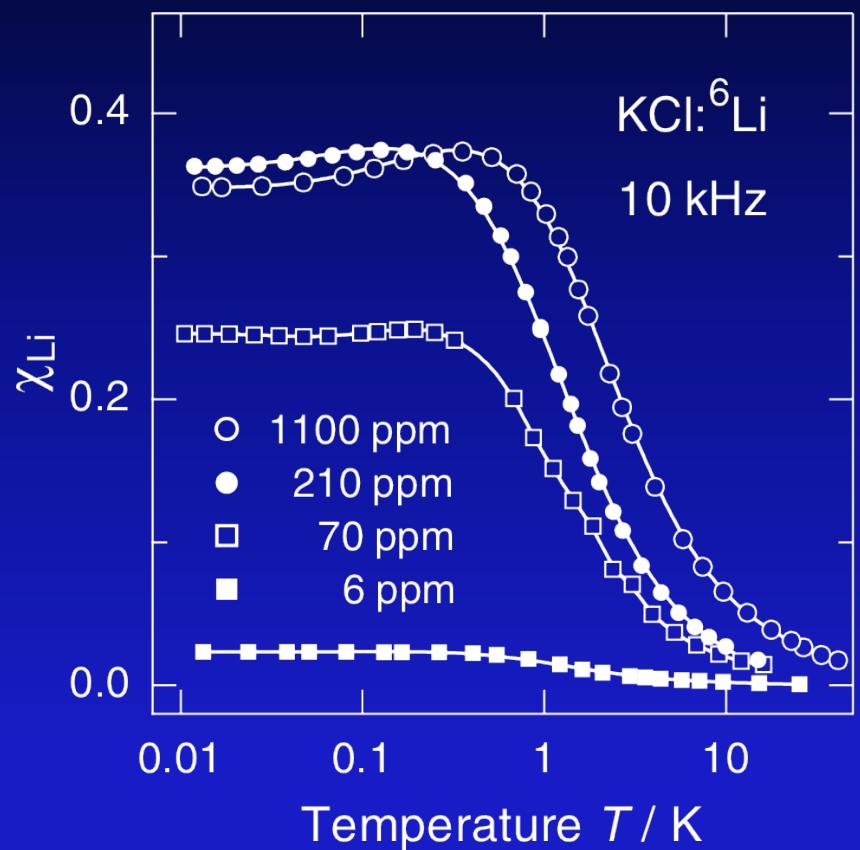
# Dielectric Susceptibility

$$\chi_{\text{iso}} = \frac{2}{3} \frac{np^2}{\varepsilon_0 \Delta_0} \tanh \left( \frac{\Delta_0}{2k_B T} \right)$$



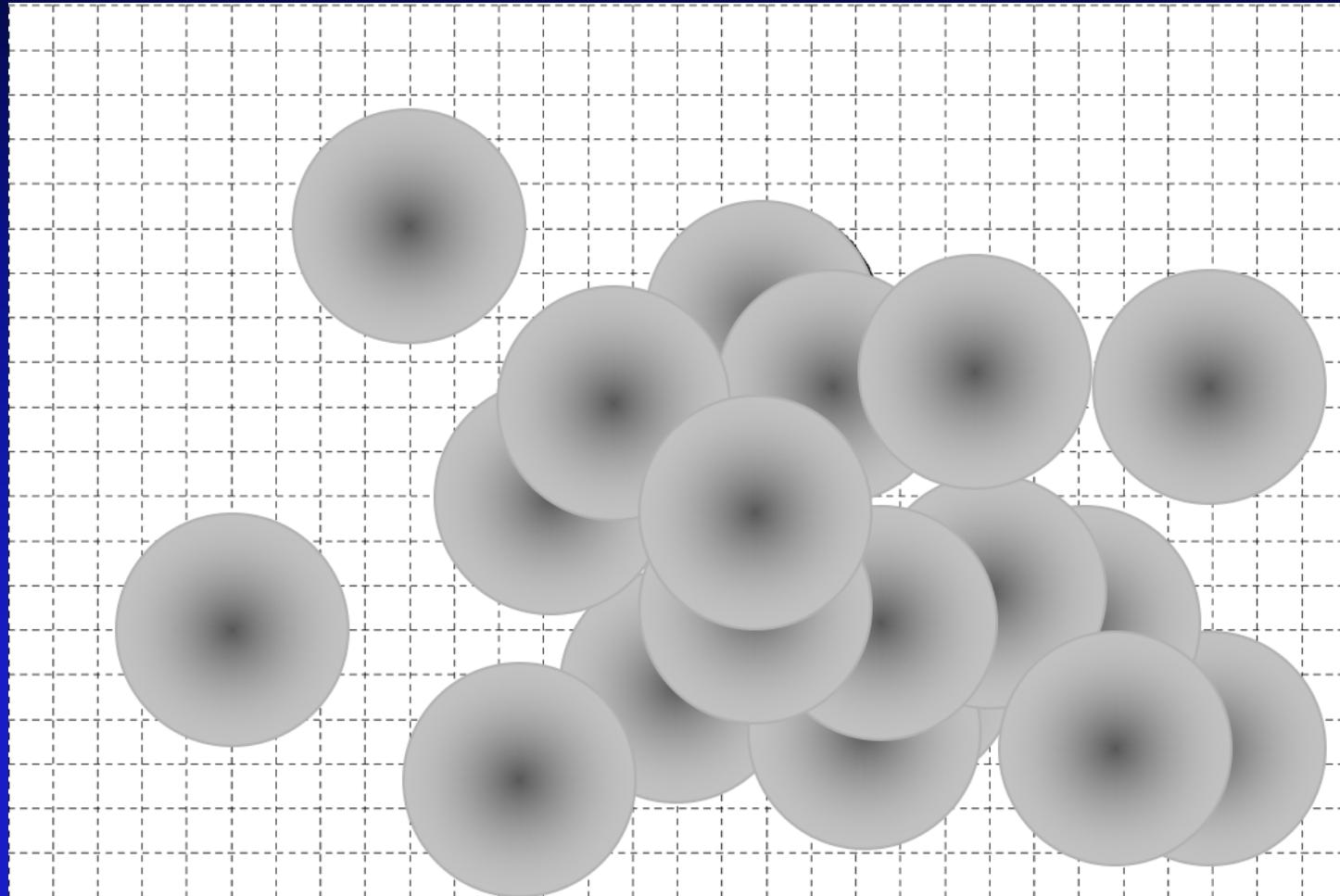
C. Enss, M. Gaukler, S. Hunklinger, M. Tornow, R. Weis, A. Würger, Phys. Rev. B 53, 12094 (1996)

# Dielectric Susceptibility: High Concentrations



C. Enss, M. Gaukler, S. Hunklinger, M. Tornow, R. Weis, A. Würger, Phys. Rev. B **53**, 12094 (1996)

# Interacting Tunneling Systems



# Transition to Incoherent Tunneling

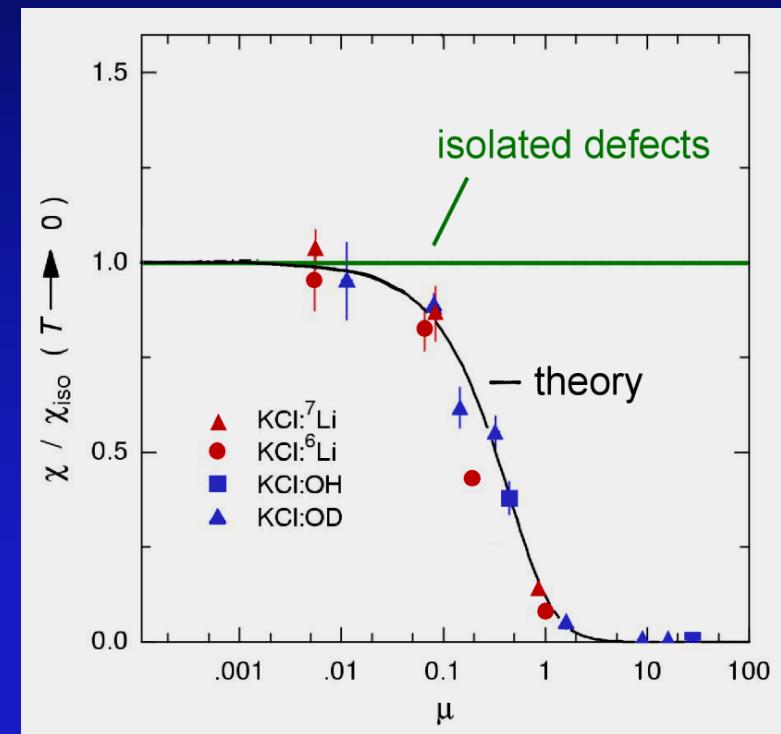
- defects in crystals:  
at high concentrations  $\longrightarrow$  cross over to incoherent tunneling

consequences:

- reduced resonant contribution
- new phononless relaxation channel

$$\mu = \frac{\bar{J}}{\Delta_0}$$

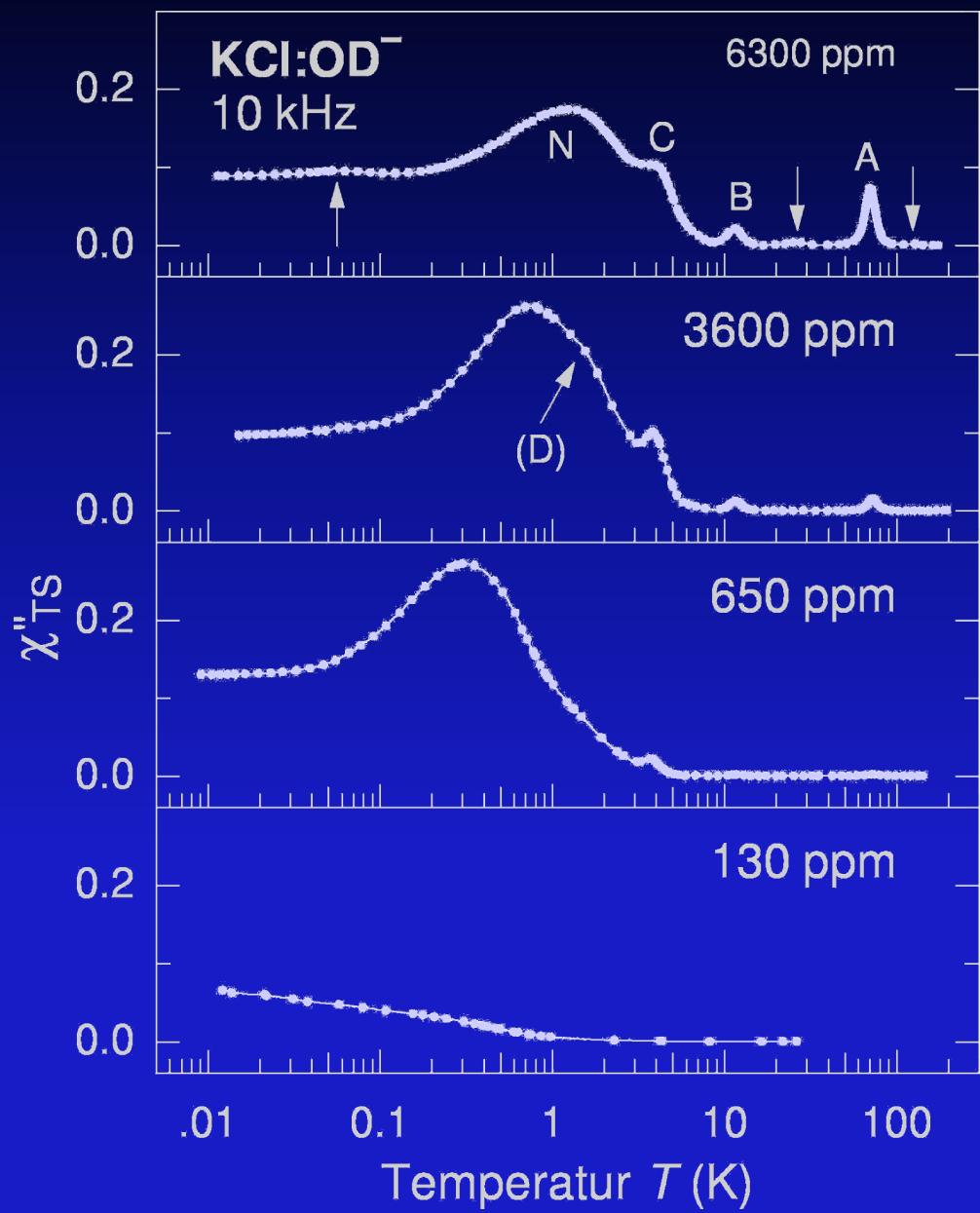
- incoherent tunneling in glasses at very low temperatures?



$$\bar{J} > \Delta_0 \approx k_B T$$

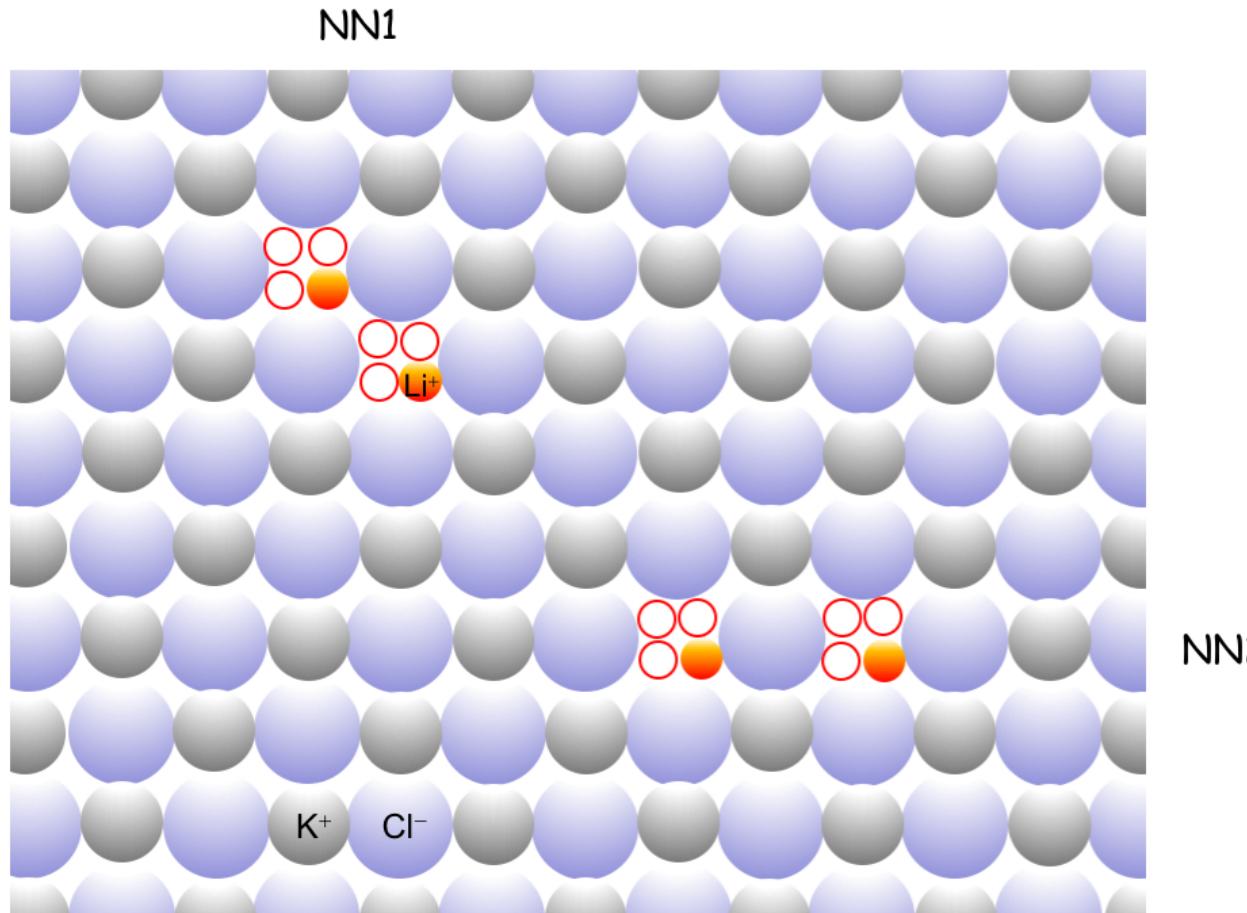
A. Würger, R. Weis, M. Gaukler, C. Enss, Europhys.  
Lett. **33**, 533 (1996)

# Thermally Activated Pairs



S. Ludwig, C. Enss, J. Low Temp. Phys. 137,  
371 (2004)

# Tunneling of Li Pairs



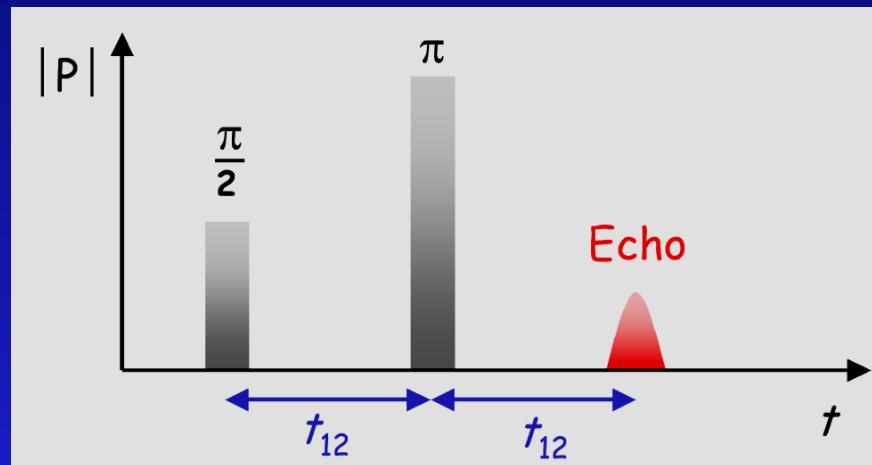
# Coherent Properties

$$t \ll \tau_1, \tau_2 \rightarrow \infty$$



coherent regime

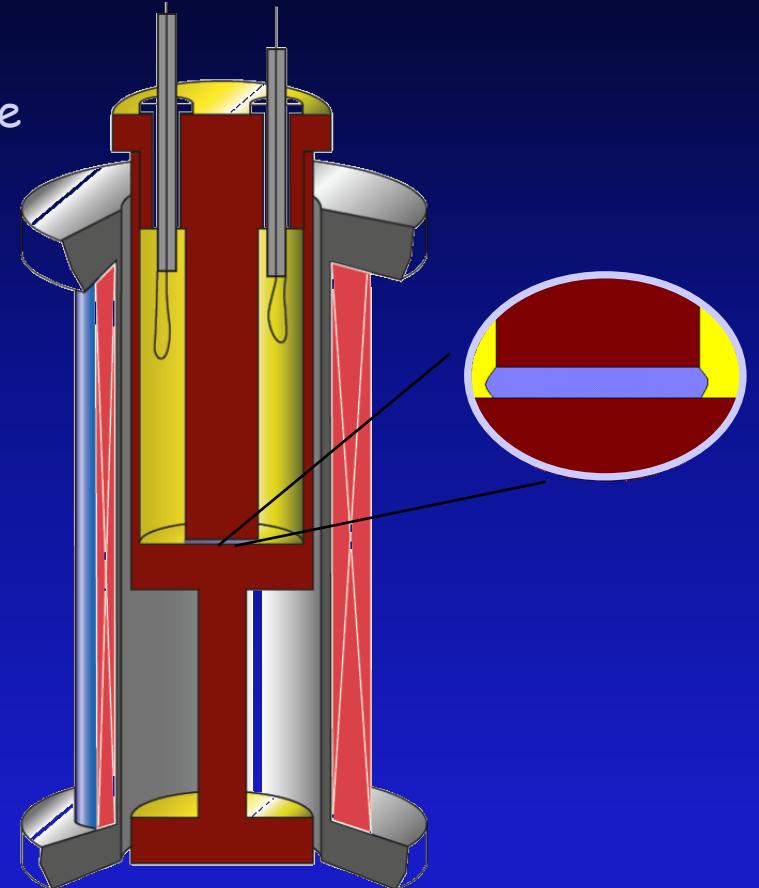
two-pulse polarization echoes:



$$\Theta_p = \Omega_R t_p$$

Rabi frequency

$$\Omega_R = \frac{1}{\hbar} \frac{\Delta_0}{E} \mathbf{p} \cdot \mathbf{F}$$



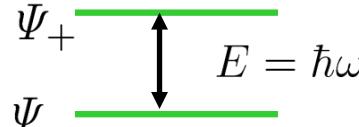
microwave cavity

$$1 \text{ GHz} \rightarrow 50 \text{ mK}$$

# Echo – Theoretical Background I

coherent regime:  $t \ll \tau_1, \tau_2 \rightarrow \infty$

two level approximation:


$$E = \hbar\omega$$

applied field:  $\mathbf{F} = \mathbf{F}_0 (\mathrm{e}^{\mathrm{i}\omega_r t} + \mathrm{e}^{-\mathrm{i}\omega_r t})$

Schrödinger equation:  $i\hbar \frac{\partial \Psi}{\partial t} = [H_0 + H_S] \Psi$  mit  $H_S = 2 \frac{\Delta_0}{E} \mathbf{p} \cdot \mathbf{F}$

ansatz:  $\Psi(t) = a_1(t) \Psi_- + a_2(t) \Psi_+$   $\left. \right\} \begin{aligned} a_1(t) &= \cos(\Omega_R t) \mathrm{e}^{-\mathrm{i}\omega_r t} \\ a_2(t) &= -\mathrm{i} \sin(\Omega_R t) \mathrm{e}^{-\mathrm{i}\omega_r t} \end{aligned}$

Rabi frequency:  $\Omega_R = \frac{1}{\hbar} \frac{\Delta_0}{E} \mathbf{p} \cdot \mathbf{F}_0$

# Phase Jump Rotary Echoes

coherent regime:

$$t \ll \tau_1, \tau_2 \rightarrow \infty$$

applied field:

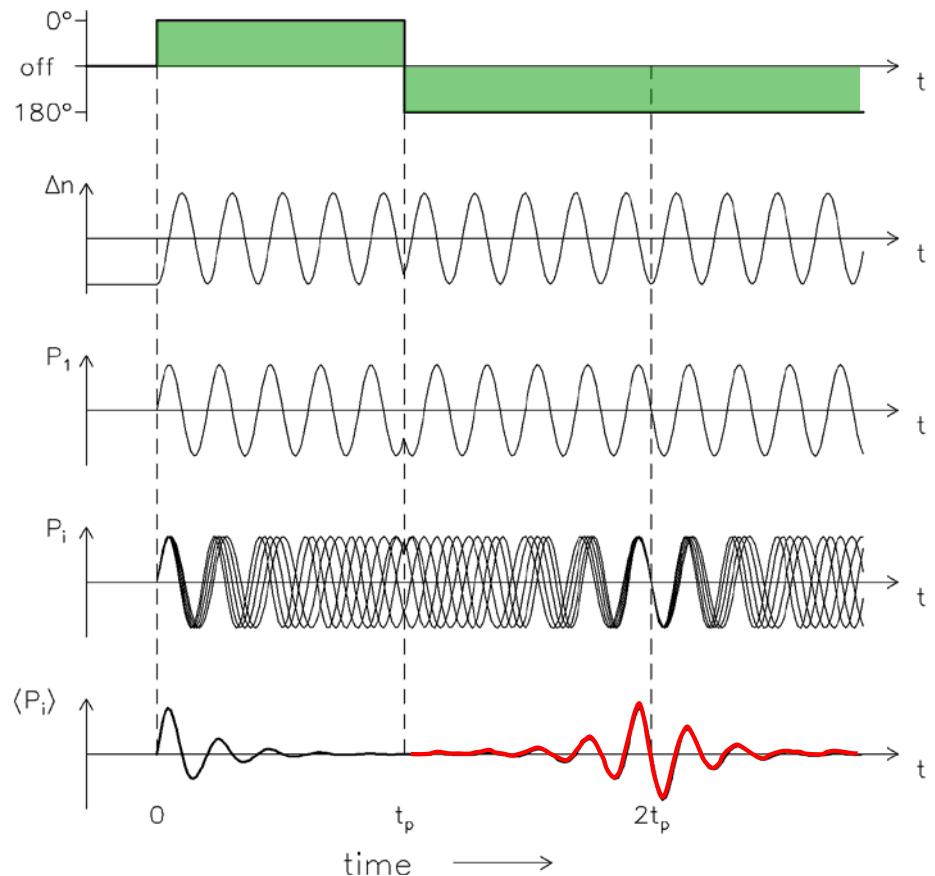
$$\mathbf{F} = 2\mathbf{F}_0 \cos(\omega t)$$

occupation number difference

$$\Delta n = \cos(\Omega_R t)$$



periodic change of polarisation



$$A_r(t) \propto \int_0^{+\infty} \int_0^E P(E, \Delta_0) \frac{\Delta_0}{E} \frac{\mathbf{p} \cdot \mathbf{F}_0}{|\mathbf{F}_0|} \left[ \frac{\Omega_R}{\Omega} \right]^3 e^{-\beta} \sin [\Omega (t - 2t_p)] d\Delta_0 dE$$

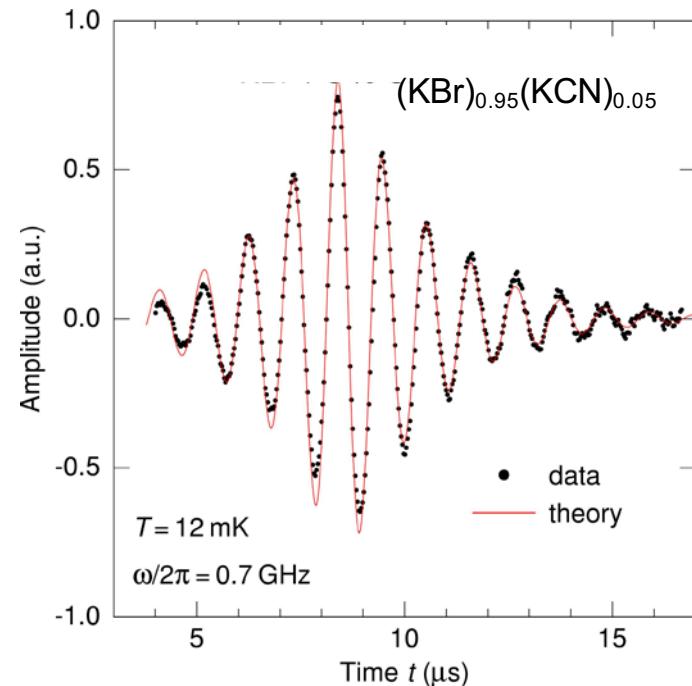
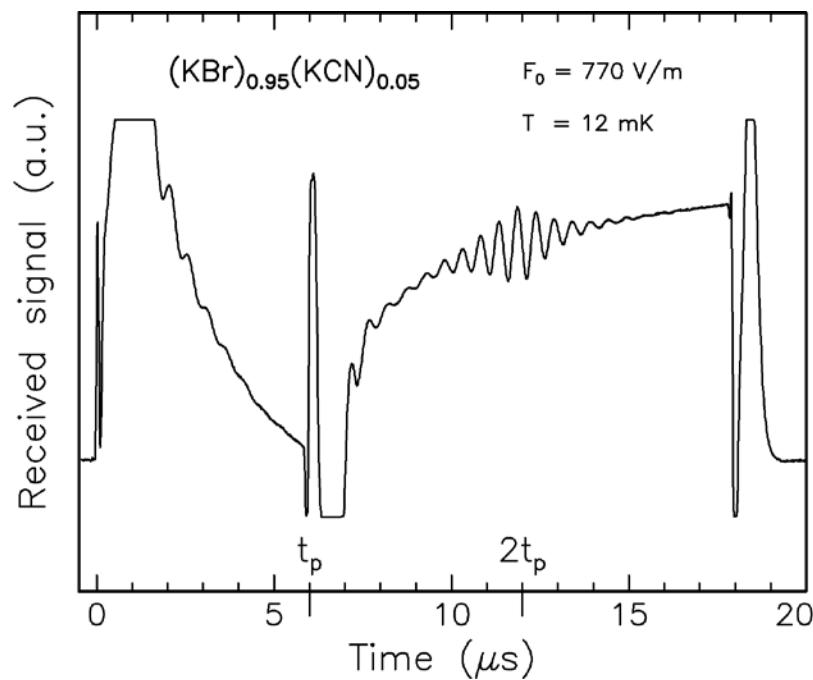
with  $\Omega = \sqrt{\Omega_R^2 - \omega_d^2}$

$$\omega_d = \omega_r - \omega$$

$$\beta = \frac{1}{\Omega^2} \left( \frac{\omega_d^2}{\tau_2} + \frac{\Omega_R^2}{2\tau_1} + \frac{\Omega_R^2}{2\tau_2} \right)$$

# Phase Jump Rotary Echoes

$(\text{KBr})_{1-x}(\text{KCN})_x$



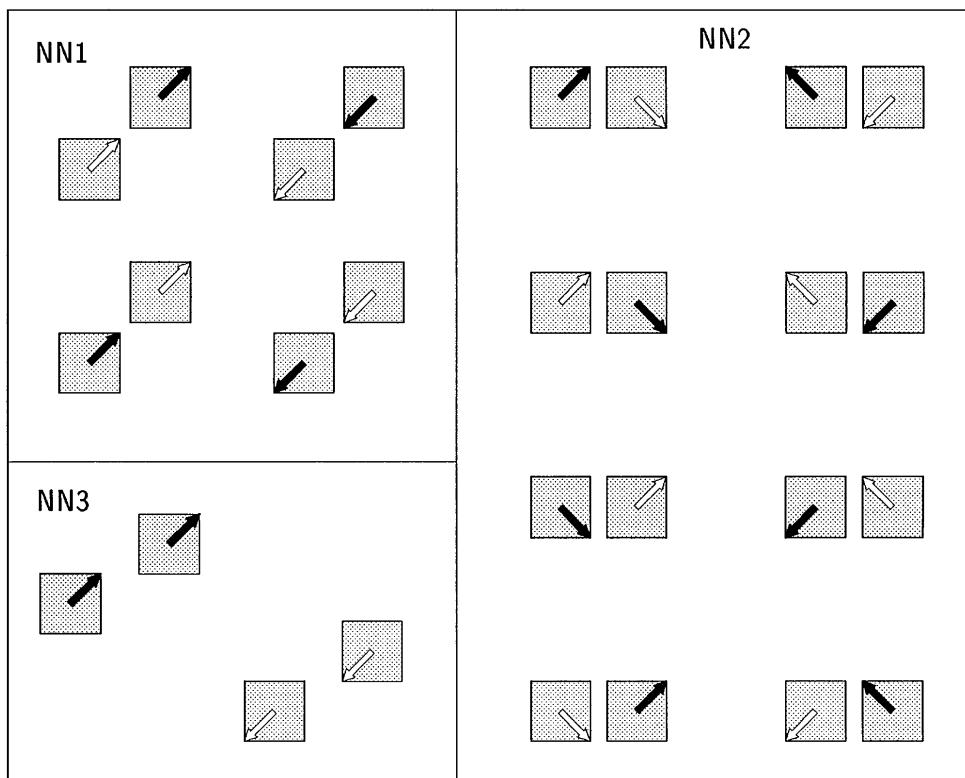
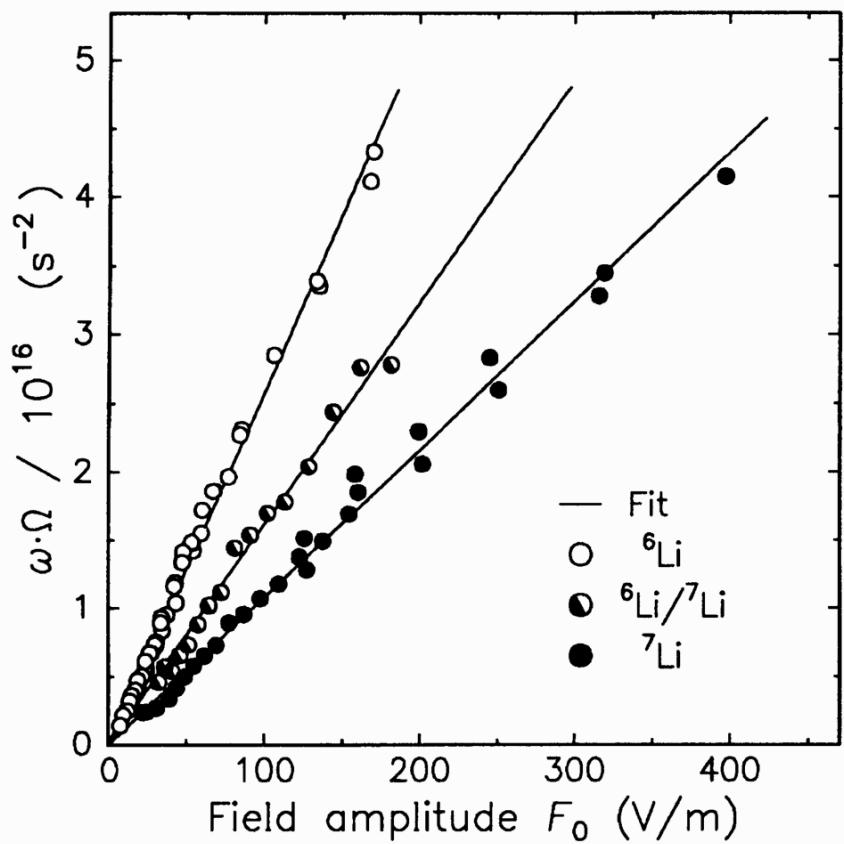
many oscillations  $\longrightarrow$  well defined  $\Omega_R$

fit: fixed values of  $E, p$   
Lorentz distribution of  $\Delta_0$  width 10%

G. Baier, M.v. Schickfus, C. Enss,  
Europhys. Lett. 8, 487 (1989)

# Coherent Pair Tunneling

Rabi-Frequency of NN2 pairs of different isotopes



only NN2 pairs contribute

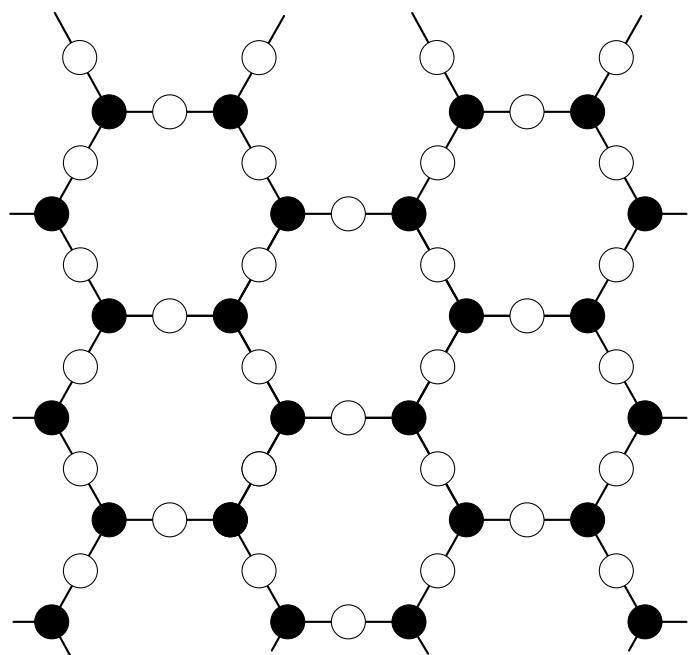
R. Weis, C. Enss, A. Würger, F. Lüty, Ann. Phys. 6, 263 (1956)

# Atomic Tunneling Systems in Amorphous Solids

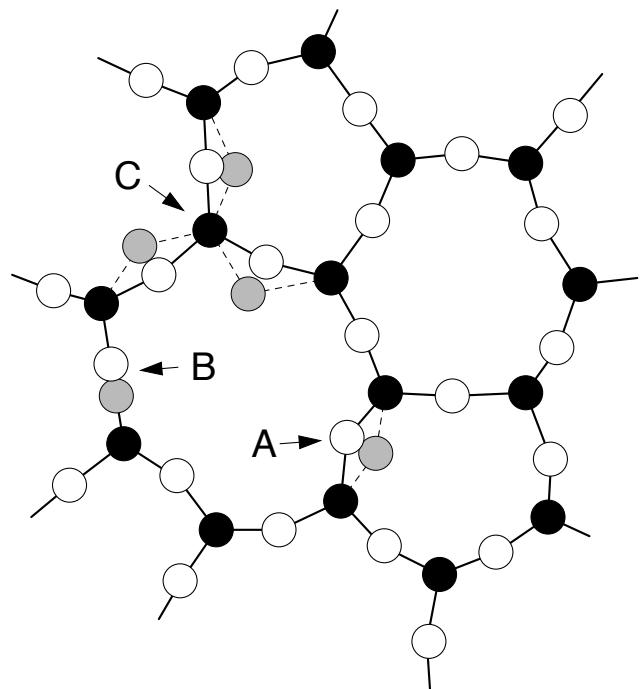


*glasses*

# Structure of Crystalline and Amorphous Materials

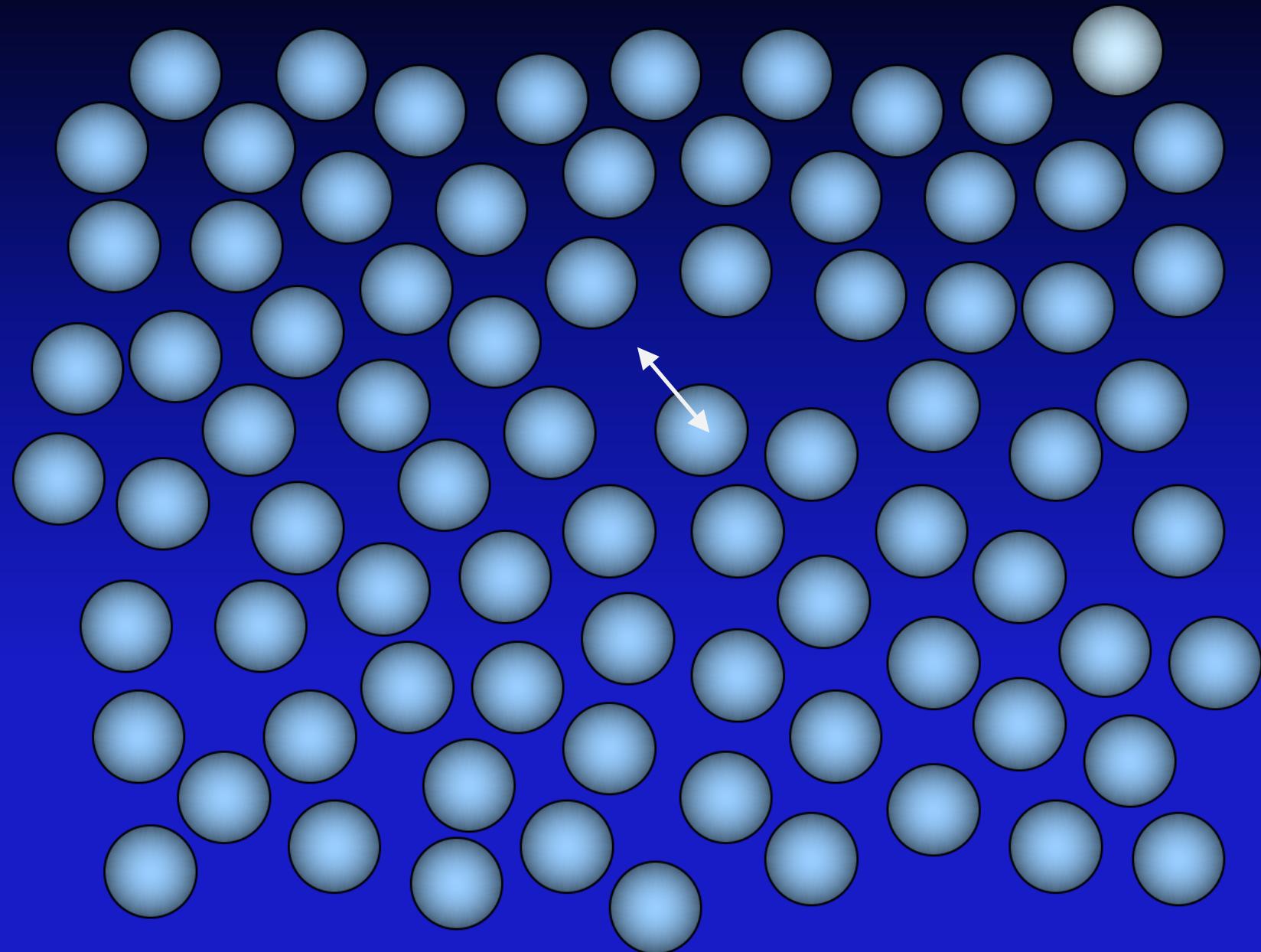


Crystal

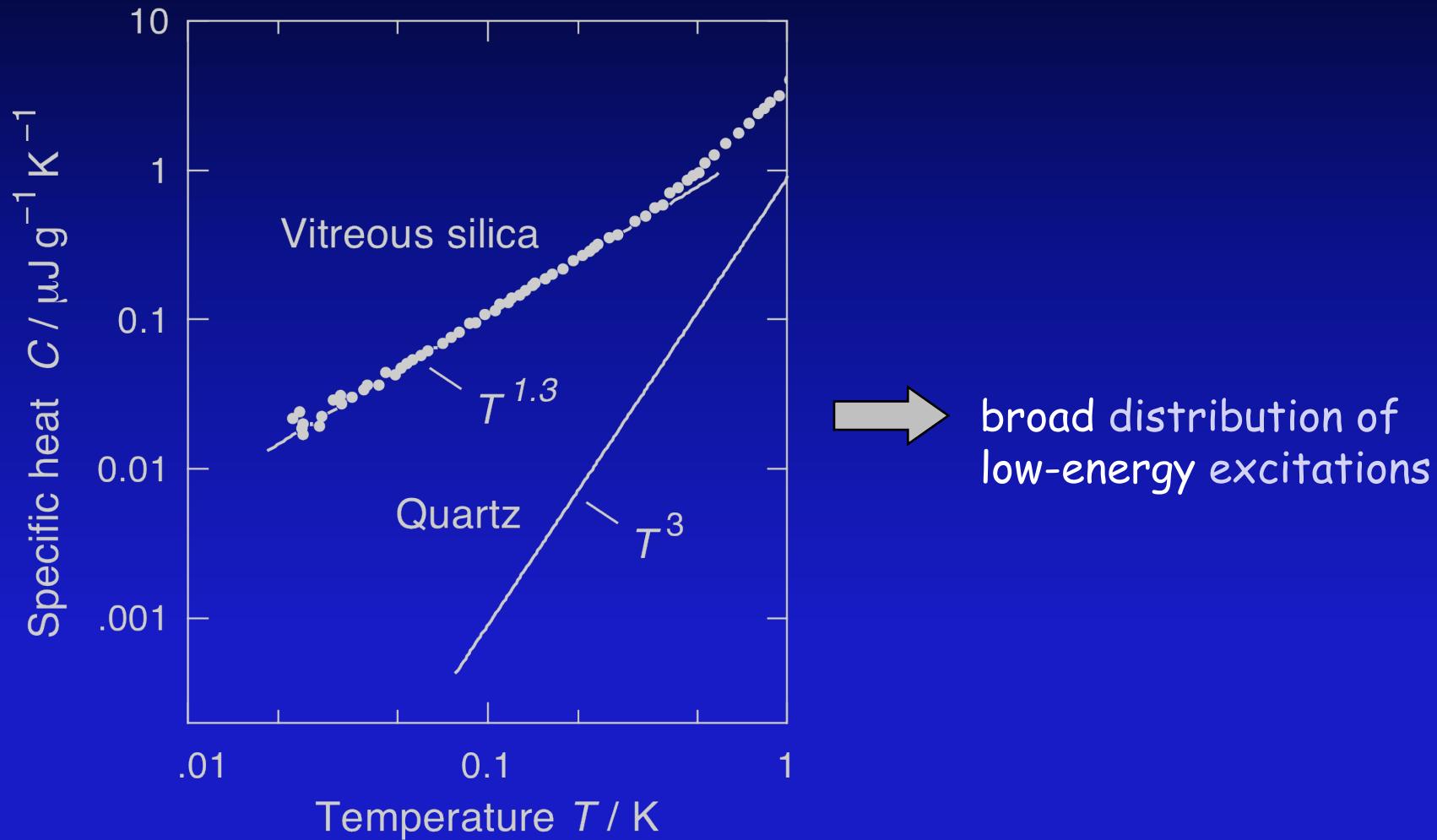


Glass

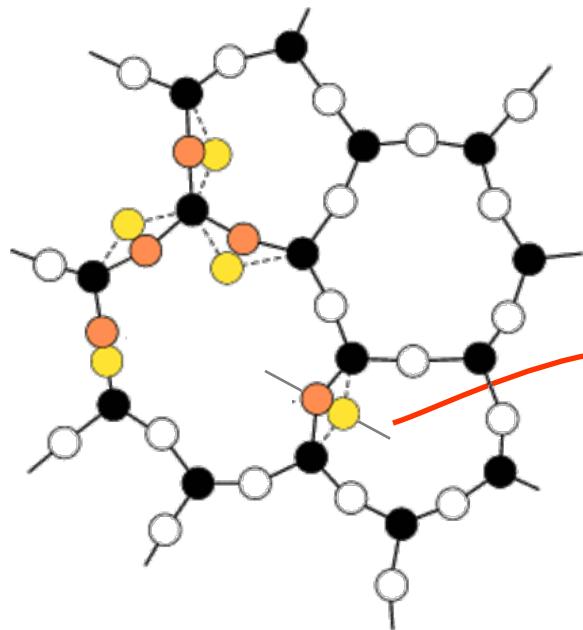
# Atomic Tunneling Systems in Glasses



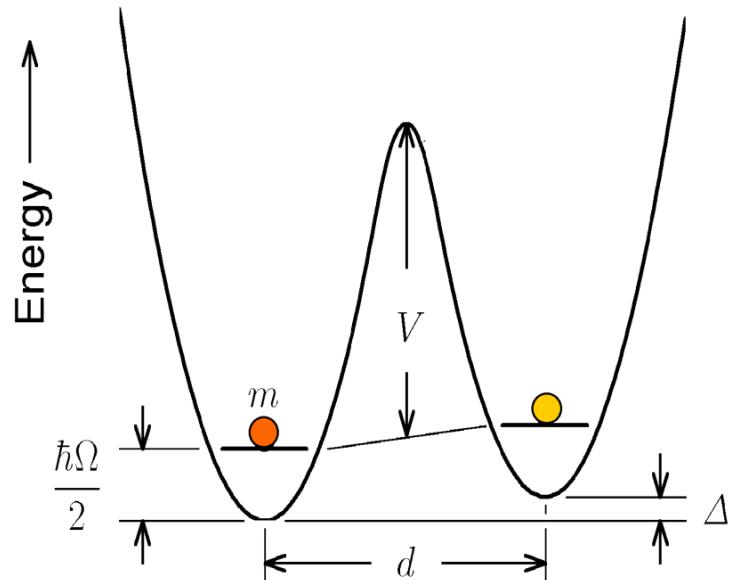
# Specific Heat



# Atomic Tunneling Systems in Glasses



W.A. Phillips, J. Low. Temp. Phys. 7, 351 (1972)  
P.W. Anderson et al., Philos. Mag. 25, 1 (1972)



energy splitting

$$E = \sqrt{\Delta_0^2 + \Delta^2} \quad \begin{array}{c} \text{---} \\ E \\ \text{---} \end{array}$$

distribution function

$$P(\lambda, \Delta) d\lambda d\Delta = \bar{P} d\lambda d\Delta$$

tunnel splitting

$$\Delta_0 = \hbar\Omega e^{-\lambda} \quad \lambda = \frac{d}{2\hbar} \sqrt{2mV}$$

elastic, dielectric und thermal properties

# Thermal Properties in the Tunneling Modell

Specific heat:

$$D(E) = \int_0^{\lambda_{\max}} P(E, \lambda) d\lambda = \overline{P} \lambda_{\max} \ln \frac{2E}{\hbar\Omega} \approx D_0 = \text{const.}$$
$$P(E, \lambda) dE d\lambda = P(\Delta, \lambda) \frac{\partial \Delta}{\partial E} dE d\lambda$$

$$C_V = \frac{1}{6} D_0 \pi^2 k_B^2 T \propto T$$

Thermal Conductivity:

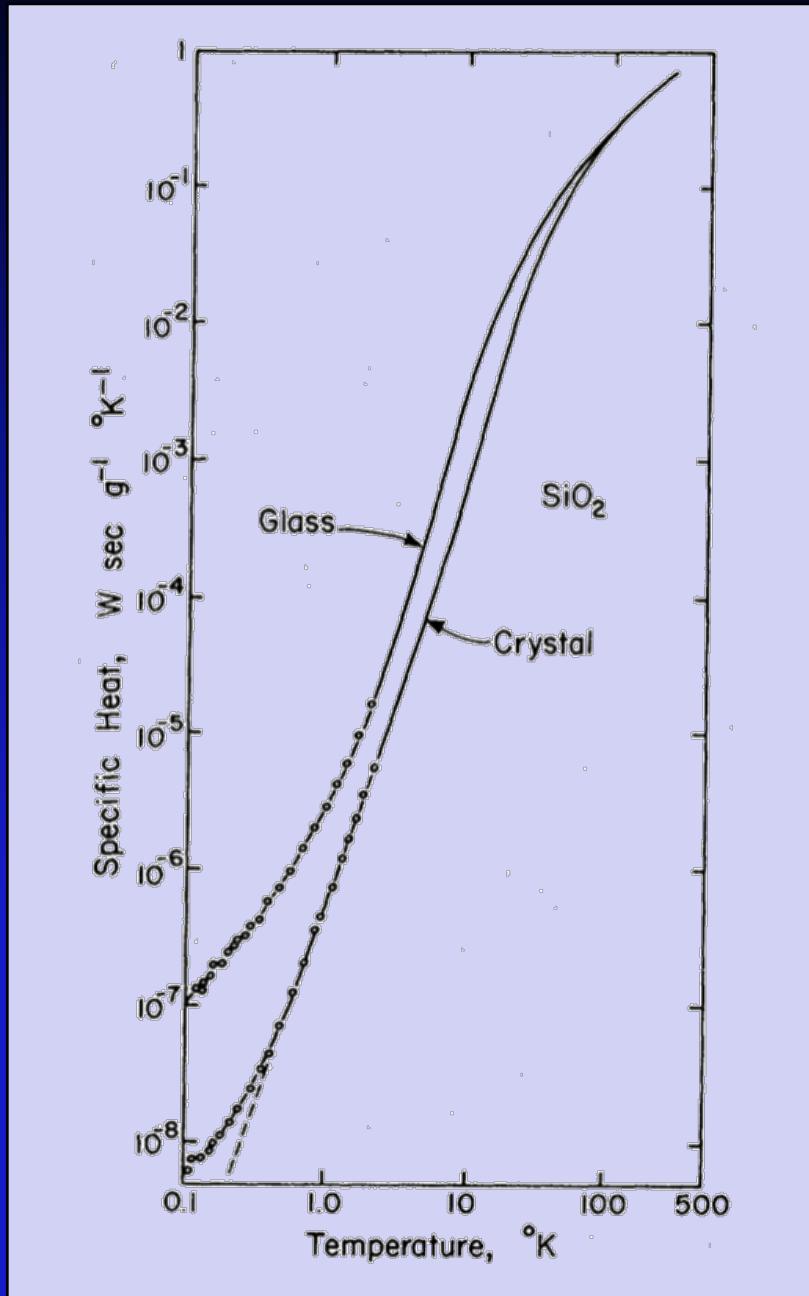
$$\Lambda = \frac{1}{3} C_V v \ell \propto T^3$$
$$\ell^{-1} \propto E \tanh \left( \frac{E}{2k_B T} \right) \propto \overline{\omega} \propto T$$
$$E = \hbar \overline{\omega} = k_B T$$

$$\Lambda \propto T^2$$

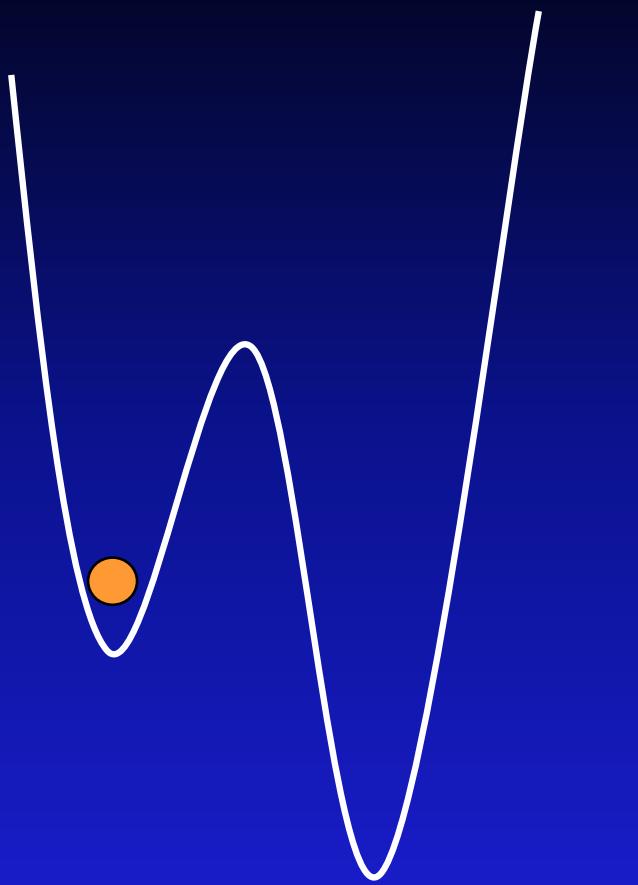
# Specific Heat

$$C = aT + bT^3 + C_{\text{Debye}}$$

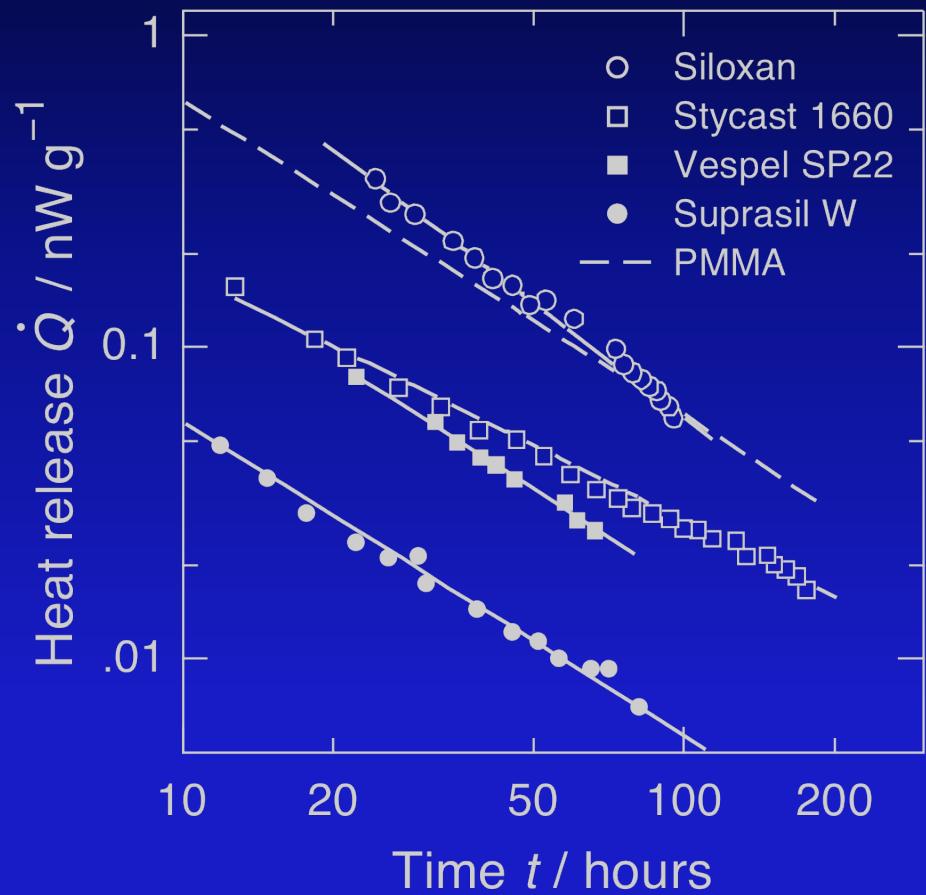
R. C. Zeller and R. O. Pohl. Phys. Rev. B 4, 2029 (1971)



# Heat Release of Amorphous Solids

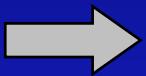
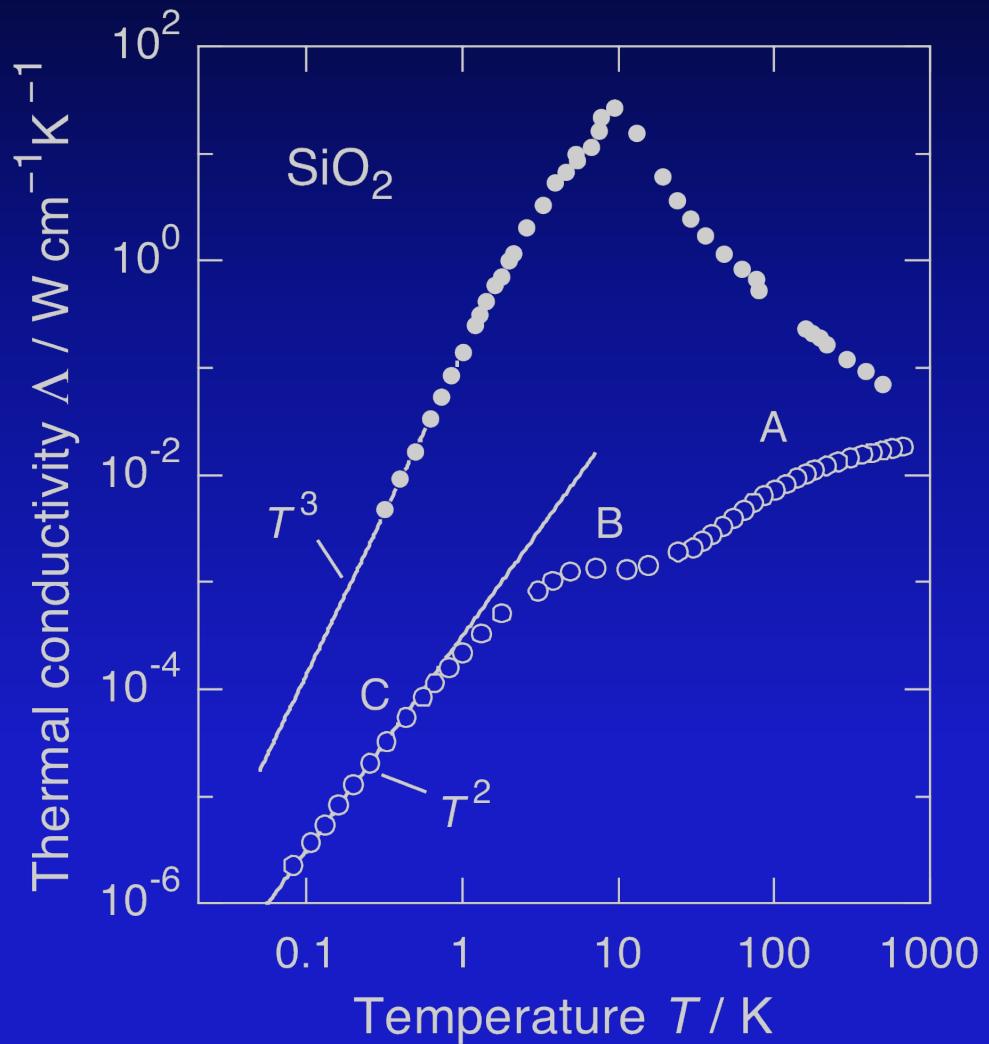


$$\dot{Q} = \frac{\pi^2 k_B^2}{24} P_0 (T_1^2 - T_0^2) \frac{1}{t}$$



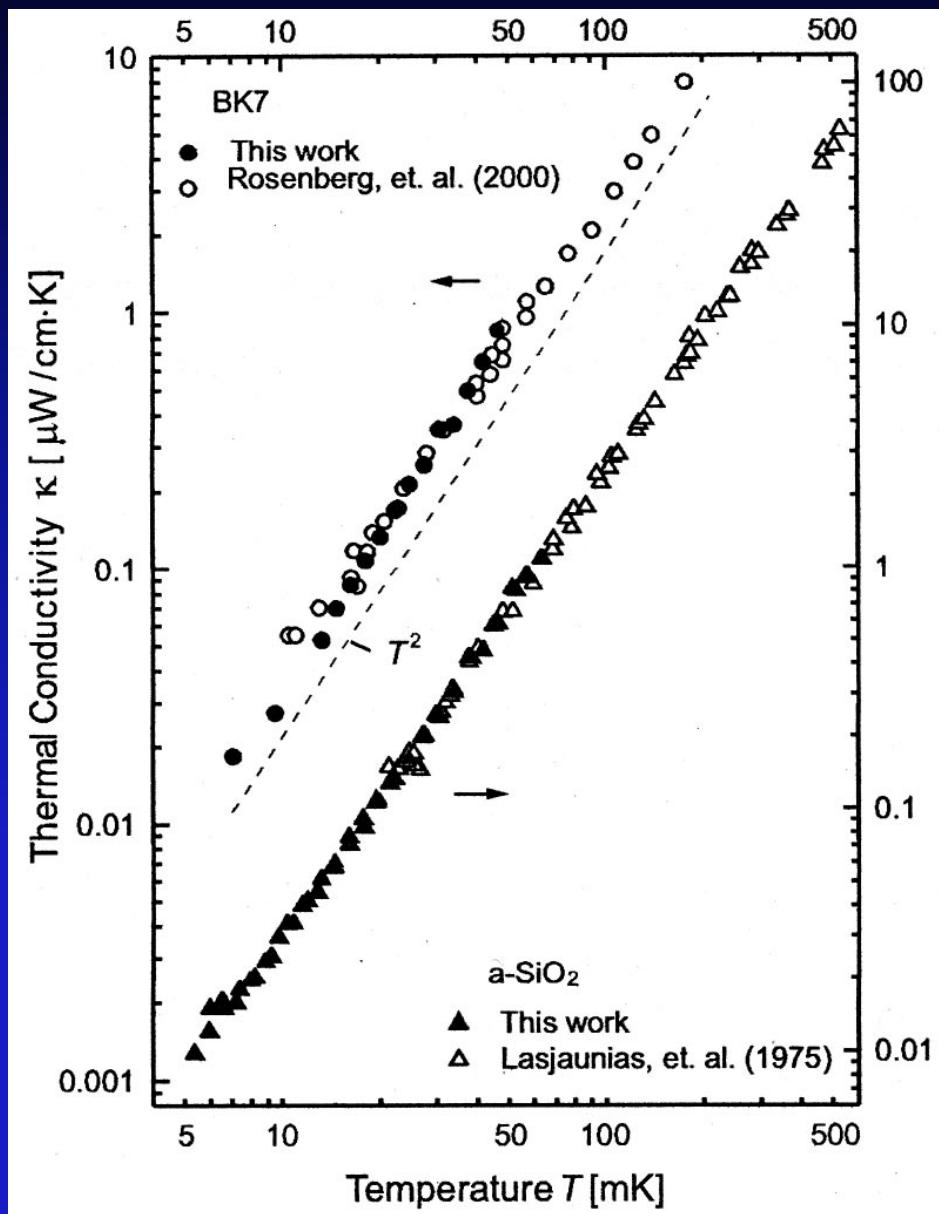
M. Schwark, et al., J. Low Temp. Phys. **58**, 171 (1985)

# Thermal Conductivity



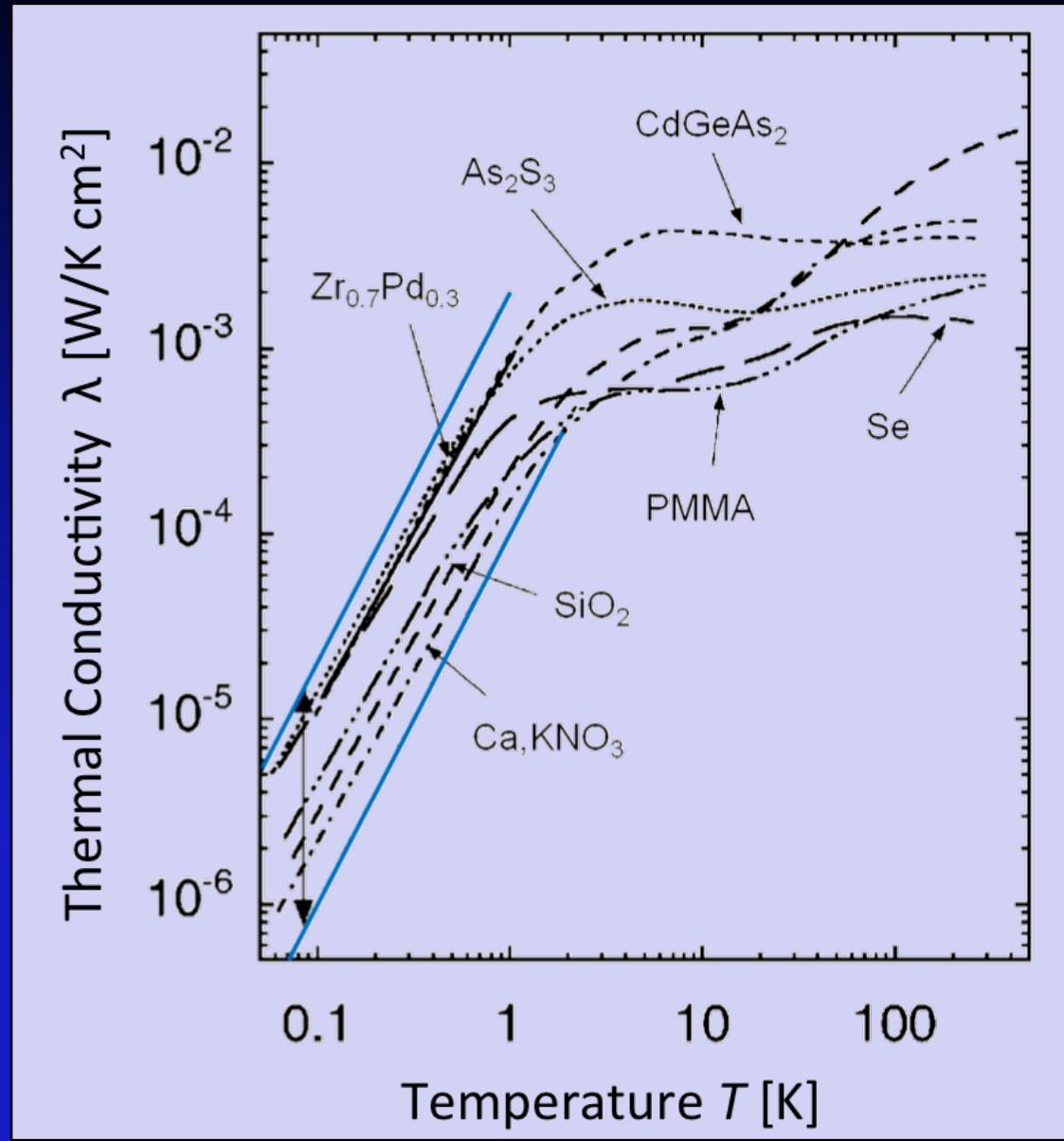
*strong coupling to phonons  
systems are localized*

# Thermal Conductivity



→ strong coupling to phonons  
systems are localized

# Universality



# Elastic and Dielectric Properties

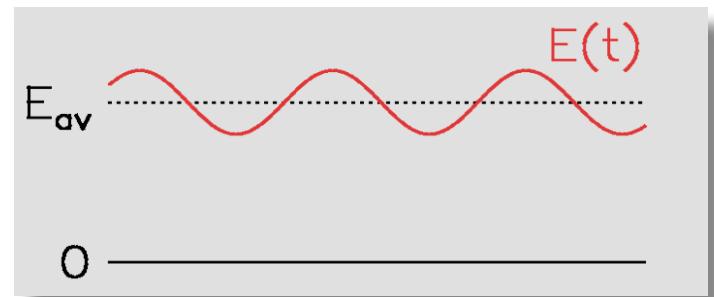
resonant processes



relaxational processes

→ modulation of  $\Delta$

$$\delta\Delta = 2\gamma e$$
$$\delta\Delta = 2\mathbf{p}\cdot\mathbf{F}$$



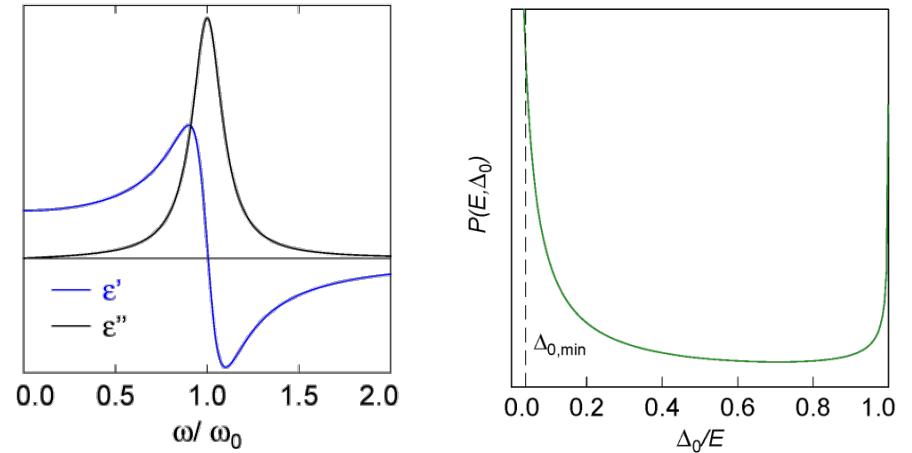
$T < 1 \text{ K}$  one-phonon relaxation → wide distribution even for fixed  $E$

$$\tau_1 = \mathcal{A} \left( \frac{E}{\Delta_0} \right)^2 \frac{1}{E^3} \tanh \left( \frac{E}{2k_B T} \right)$$

# Dielectric Susceptibility in the STM

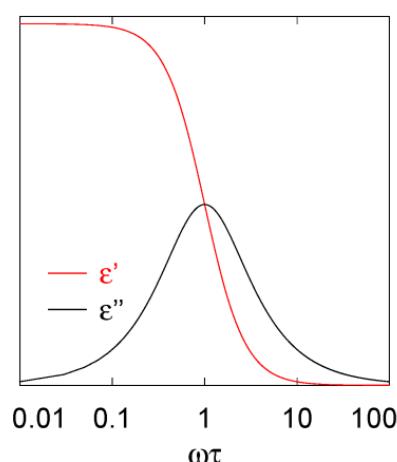
## Resonant Part

$$\frac{\delta\epsilon'_{res}}{\epsilon'} = \frac{2}{3\epsilon_0\epsilon'} \frac{p_0^2 P}{\hbar} \int_{\Delta_{0,min}}^{E_{max}} dE \int_{\Delta_{0,min}}^E d\Delta_0 \left( \frac{\Delta_0^2}{E^2} \right) \tanh \left( \frac{E}{2k_B T} \right) \left( \frac{(\omega + \omega_0)\tau_2^2}{1 + (\omega + \omega_0)^2\tau_2^2} - \frac{(\omega - \omega_0)\tau_2^2}{1 + (\omega - \omega_0)^2\tau_2^2} \right) \frac{E}{\Delta_0 \sqrt{E^2 - \Delta_0^2}}$$



## Relaxational Part

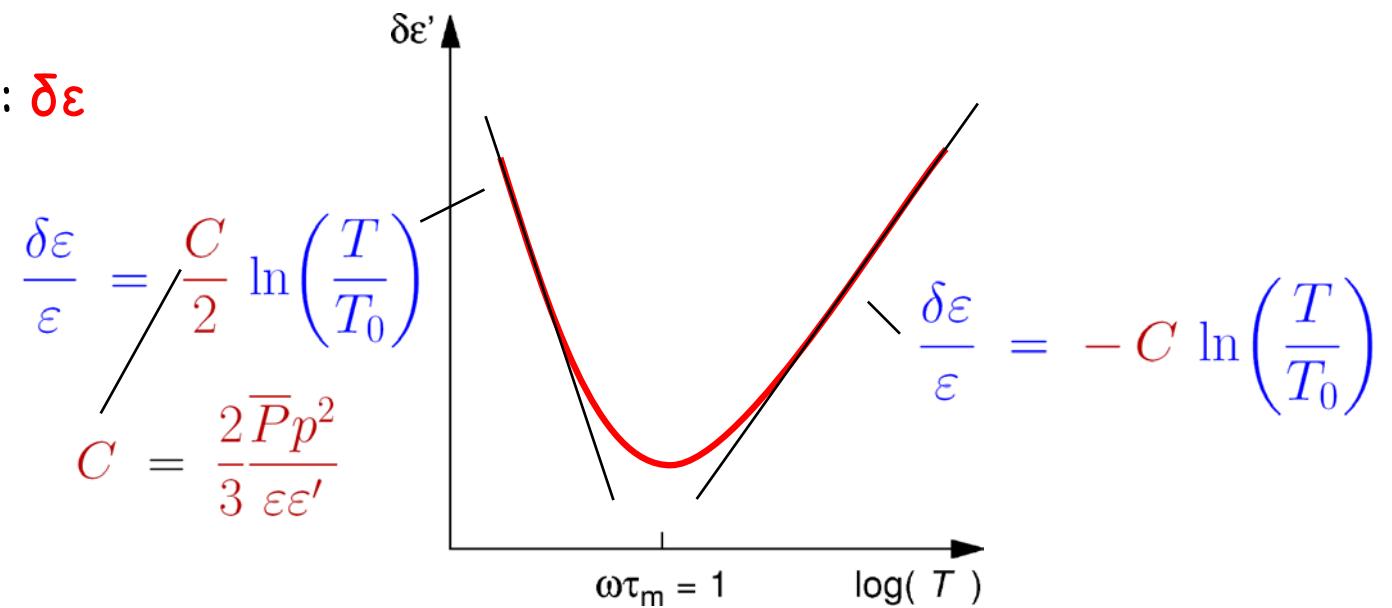
$$\frac{\delta\epsilon'_{rel}}{\epsilon'} = \frac{2}{3\epsilon_0\epsilon' k_B T} \frac{p_0^2 P}{\hbar} \int_{\Delta_{0,min}}^{E_{max}} dE \int_{\Delta_{0,min}}^E d\Delta_0 \left( 1 - \frac{\Delta_0^2}{E^2} \right) \operatorname{sech}^2 \left( \frac{E}{2k_B T} \right) \frac{1}{1 + \omega^2\tau_1^2} \frac{E}{\Delta_0 \sqrt{E^2 - \Delta_0^2}}$$



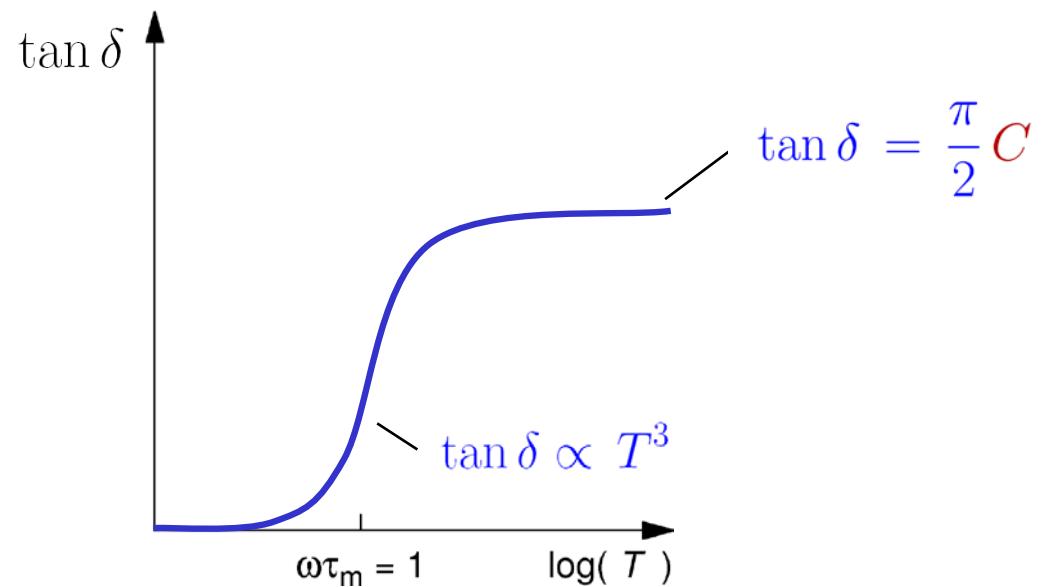
$$\tau_{\text{tot}}^{-1} = \tau_{1\text{ph}}^{-1} + \tau_{2\text{ph}}^{-1} + \tau_{?}^{-1} + \dots$$

# Dielectric Constant and Dielectric Loss

Dielectric constant:  $\delta\epsilon$



Dielectric loss:  $\tan\delta$

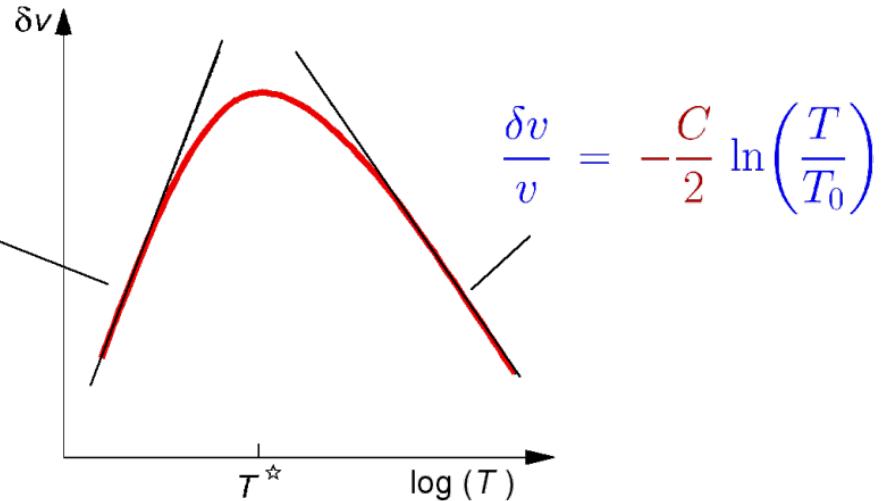


# Sound Velocity and Internal Friction

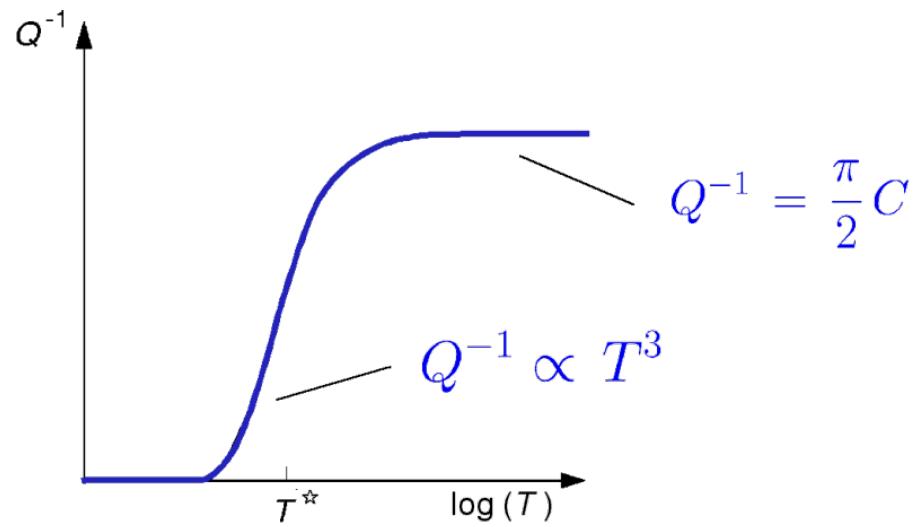
sound velocity  $\delta v/v$

$$\frac{\delta v}{v} = C \ln\left(\frac{T}{T_0}\right)$$

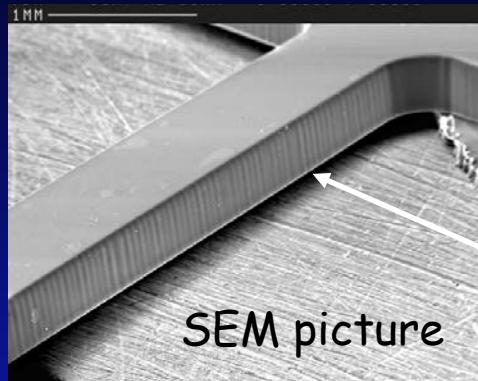
$$C = \frac{\bar{P}\gamma^2}{\rho v^2}$$



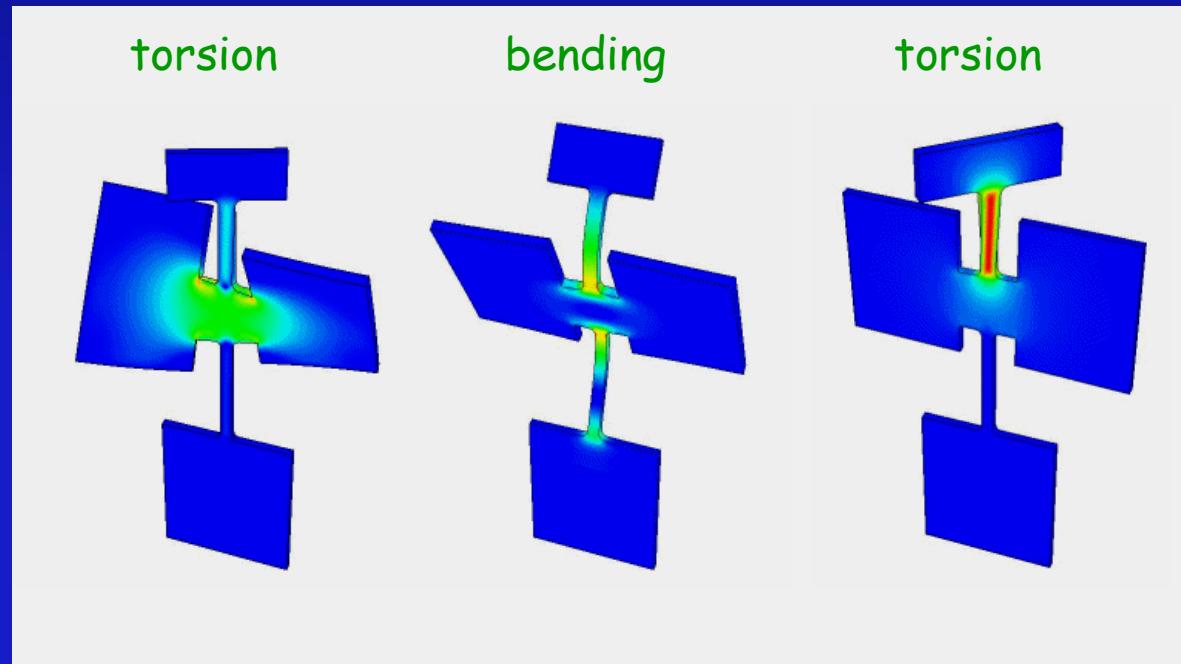
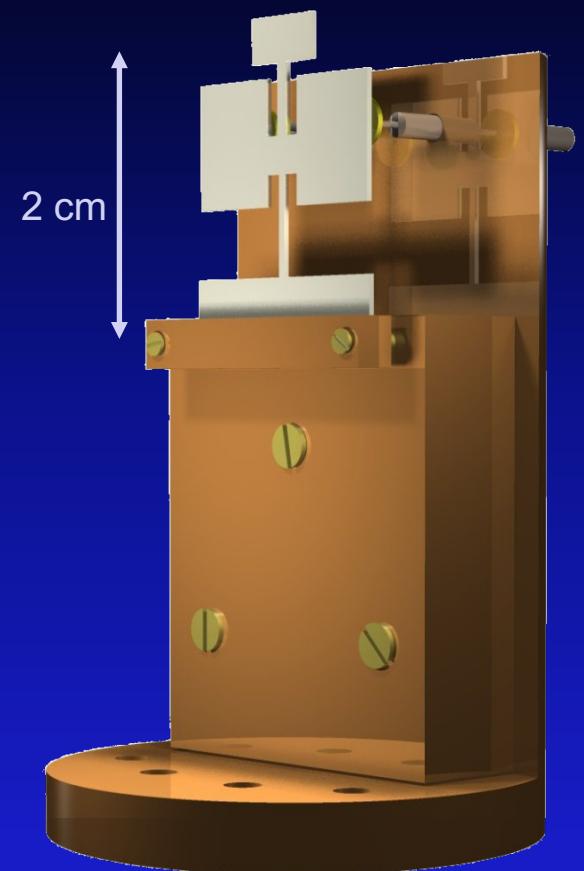
internal friction  $Q^{-1}$



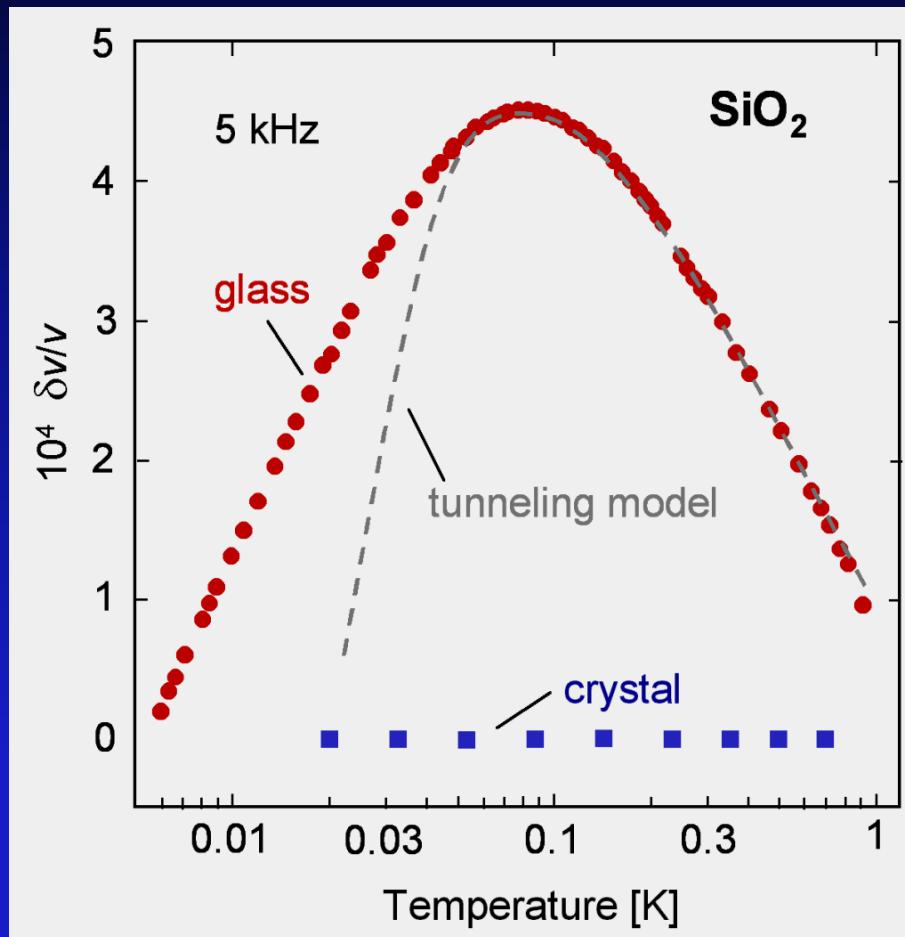
# Elastic Measurements with Mechanical Oscillators



1  $\mu\text{m}$  silver film  
→ good thermalization  
laser-cut glass  
neck



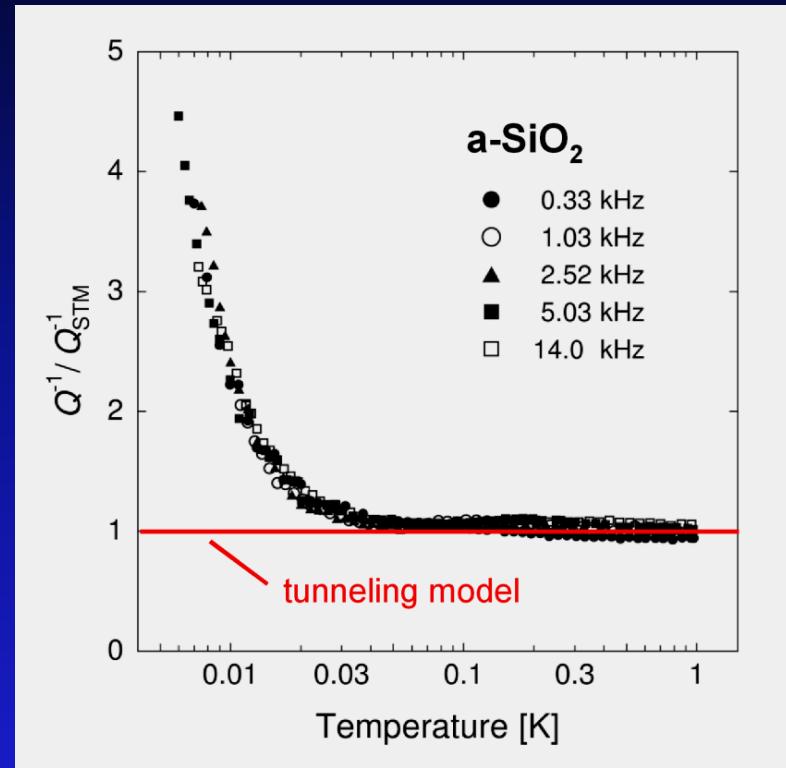
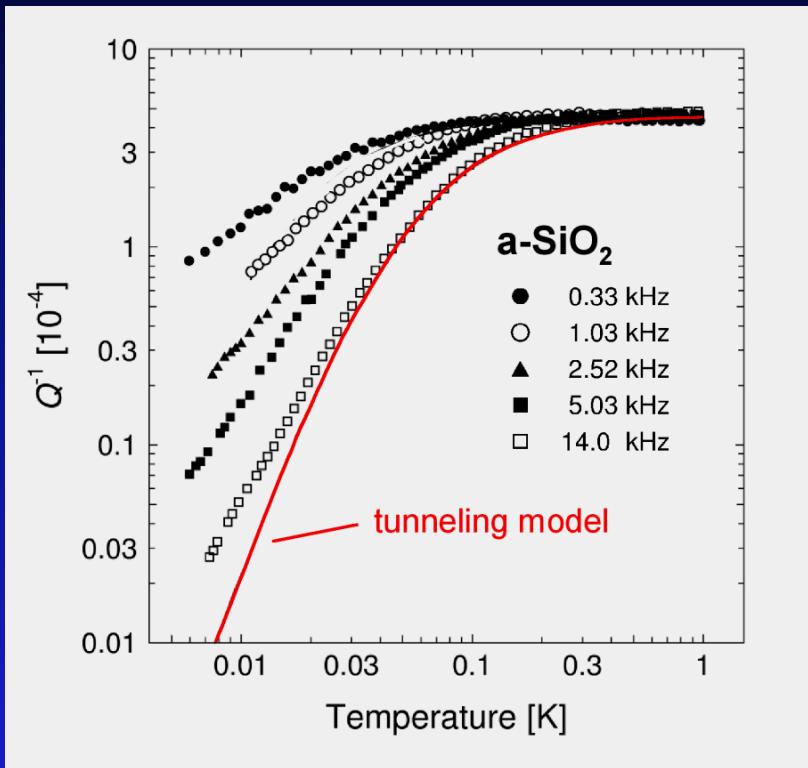
# Sound Velocity



discrepancy at low temperatures

J. Classen, T. Burkert, C. Enss, S. Hunklinger  
Phys. Rev. Lett. **84**, 2176 (2000)

# Internal Friction



$T < 30 \text{ mK}$

→ additional relaxation channel

J. Classen, T. Burkert, C. Enss, S. Hunklinger  
Phys. Rev. Lett. **84**, 2176 (2000)

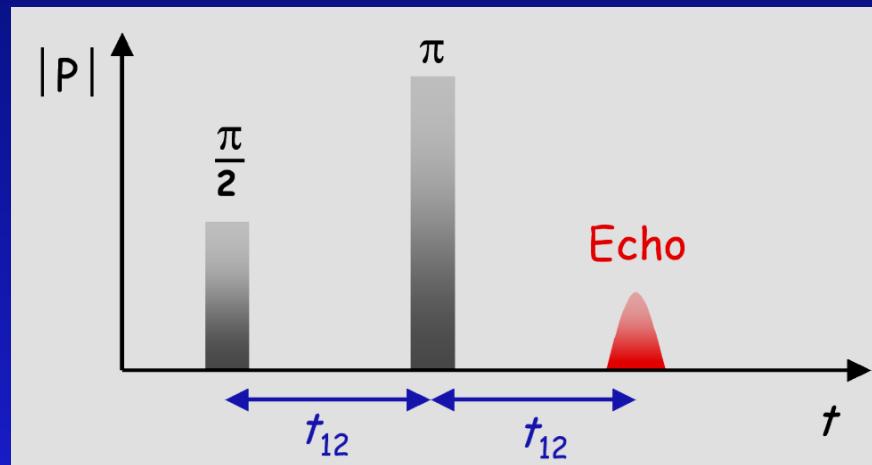
# Coherent Properties

$$t \ll \tau_1, \tau_2 \rightarrow \infty$$



coherent regime

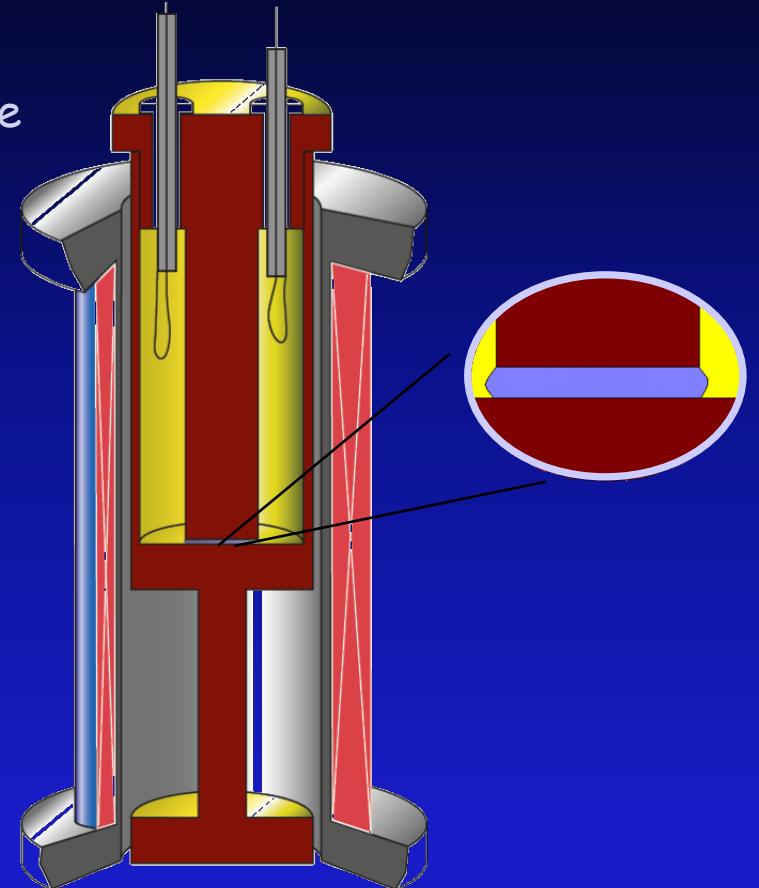
two-pulse polarization echoes:



$$\Theta_p = \Omega_R t_p$$

Rabi frequency

$$\Omega_R = \frac{1}{\hbar} \frac{\Delta_0}{E} \mathbf{p} \cdot \mathbf{F}$$



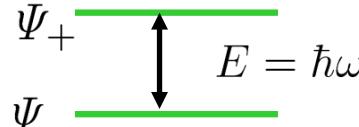
microwave cavity

$$1 \text{ GHz} \rightarrow 50 \text{ mK}$$

# Echo – Theoretical Background I

coherent regime:  $t \ll \tau_1, \tau_2 \rightarrow \infty$

two level approximation:


$$E = \hbar\omega$$

applied field:  $\mathbf{F} = \mathbf{F}_0 (\mathrm{e}^{\mathrm{i}\omega_r t} + \mathrm{e}^{-\mathrm{i}\omega_r t})$

Schrödinger equation:  $i\hbar \frac{\partial \Psi}{\partial t} = [H_0 + H_S] \Psi$  mit  $H_S = 2 \frac{\Delta_0}{E} \mathbf{p} \cdot \mathbf{F}$

ansatz:  $\Psi(t) = a_1(t) \Psi_- + a_2(t) \Psi_+$   $\left. \right\} \begin{aligned} a_1(t) &= \cos(\Omega_R t) \mathrm{e}^{-\mathrm{i}\omega_r t} \\ a_2(t) &= -\mathrm{i} \sin(\Omega_R t) \mathrm{e}^{-\mathrm{i}\omega_r t} \end{aligned}$

Rabi frequency:  $\Omega_R = \frac{1}{\hbar} \frac{\Delta_0}{E} \mathbf{p} \cdot \mathbf{F}_0$

# Echo – Theoretical Background II

polarisation vector:

$$\mathbf{P} = \begin{pmatrix} ab^* + ba^* \\ i(ab^* - ba^*) \\ aa^* - bb^* \end{pmatrix} = \begin{pmatrix} -\sin(\Omega_R t) \sin(\omega t) \\ \sin(\Omega_R t) \cos(\omega t) \\ \cos(\Omega_R t) \end{pmatrix} = \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}$$

Bloch equations:

$$\frac{d\langle S_x \rangle}{dt} = -\frac{2}{\hbar} \left( \frac{E}{2} + \frac{\Delta}{E} \mathbf{p} \cdot \mathbf{F} \right) \langle S_y \rangle - \frac{\langle S_x \rangle}{\tau_2}$$

$$\frac{d\langle S_y \rangle}{dt} = \frac{2}{\hbar} \left( \frac{E}{2} + \frac{\Delta}{E} \mathbf{p} \cdot \mathbf{F} \right) \langle S_x \rangle - \frac{2}{\hbar} \left( \frac{\Delta_0}{E} \mathbf{p} \cdot \mathbf{F} \right) \langle S_z \rangle - \frac{\langle S_y \rangle}{\tau_2}$$

$$\frac{d\langle S_z \rangle}{dt} = \frac{2}{\hbar} \left( \frac{\Delta_0}{E} \mathbf{p} \cdot \mathbf{F} \right) \langle S_y \rangle - \frac{[\langle S_z \rangle - S_z^0(\mathbf{F})]}{\tau_1}$$

$\tau_1$  energy relaxation

$T < 1 \text{ K}$   $\longrightarrow$  one phonon process

..... ?

$\tau_2$  phase coherence time

$\tau_1$  processes

spectral diffusion

spin diffusion

..... ?

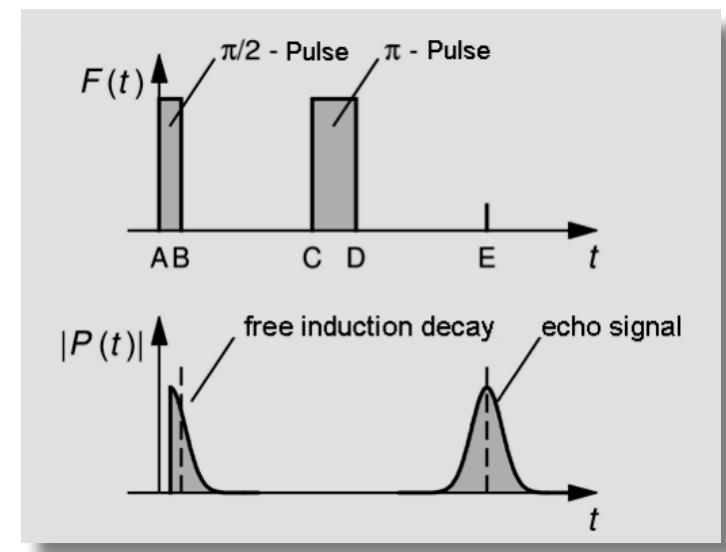
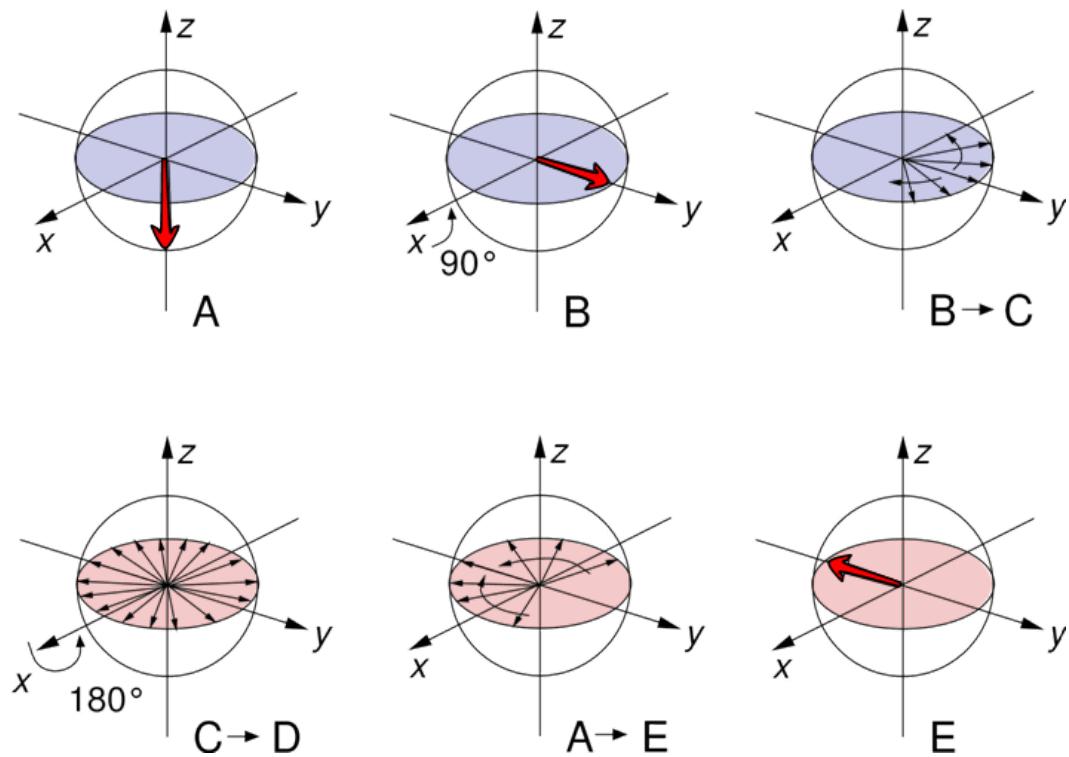


# Two Pulse Echo

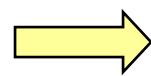
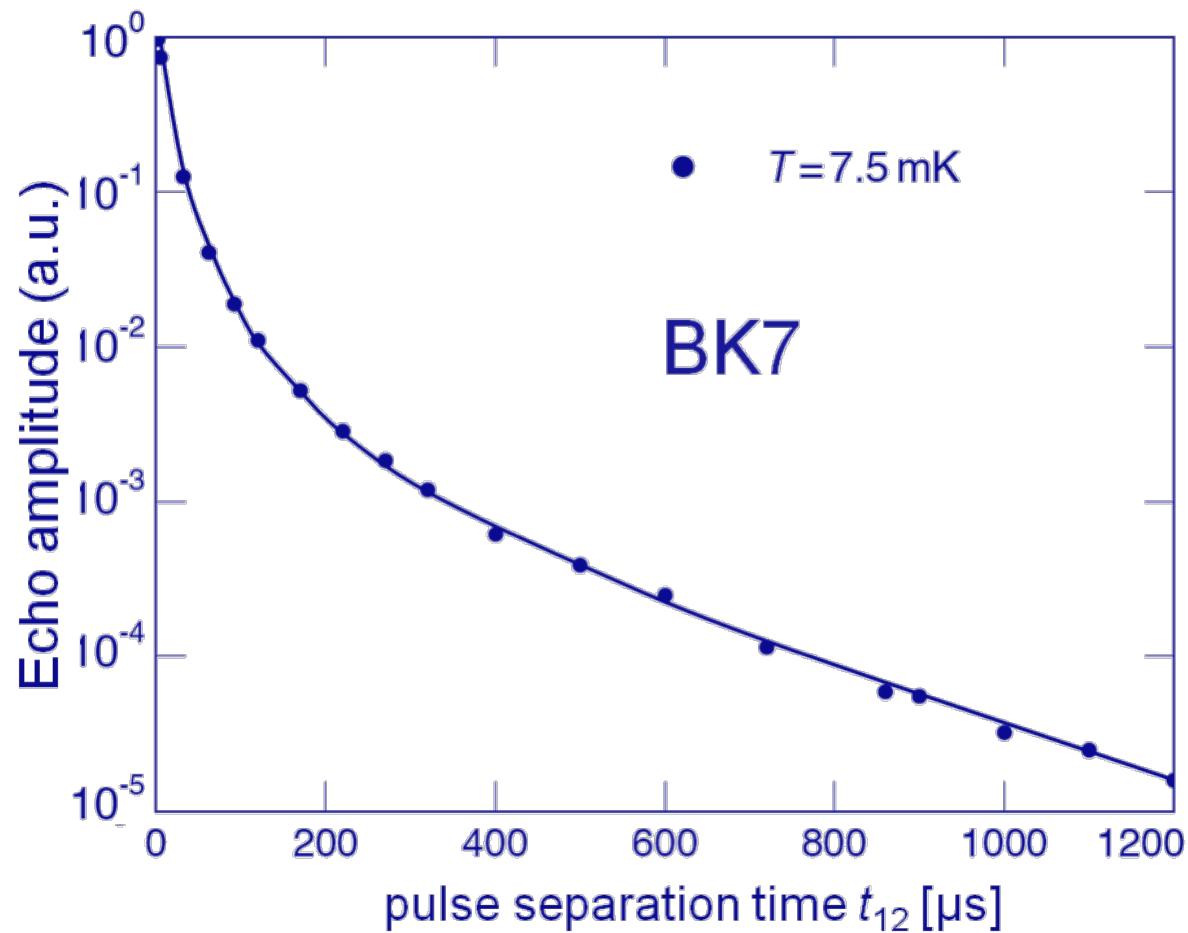
polarization vector

$$\mathbf{P} = (S_x, S_y, S_z)$$

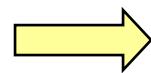
rotating frame



# Echo Decay

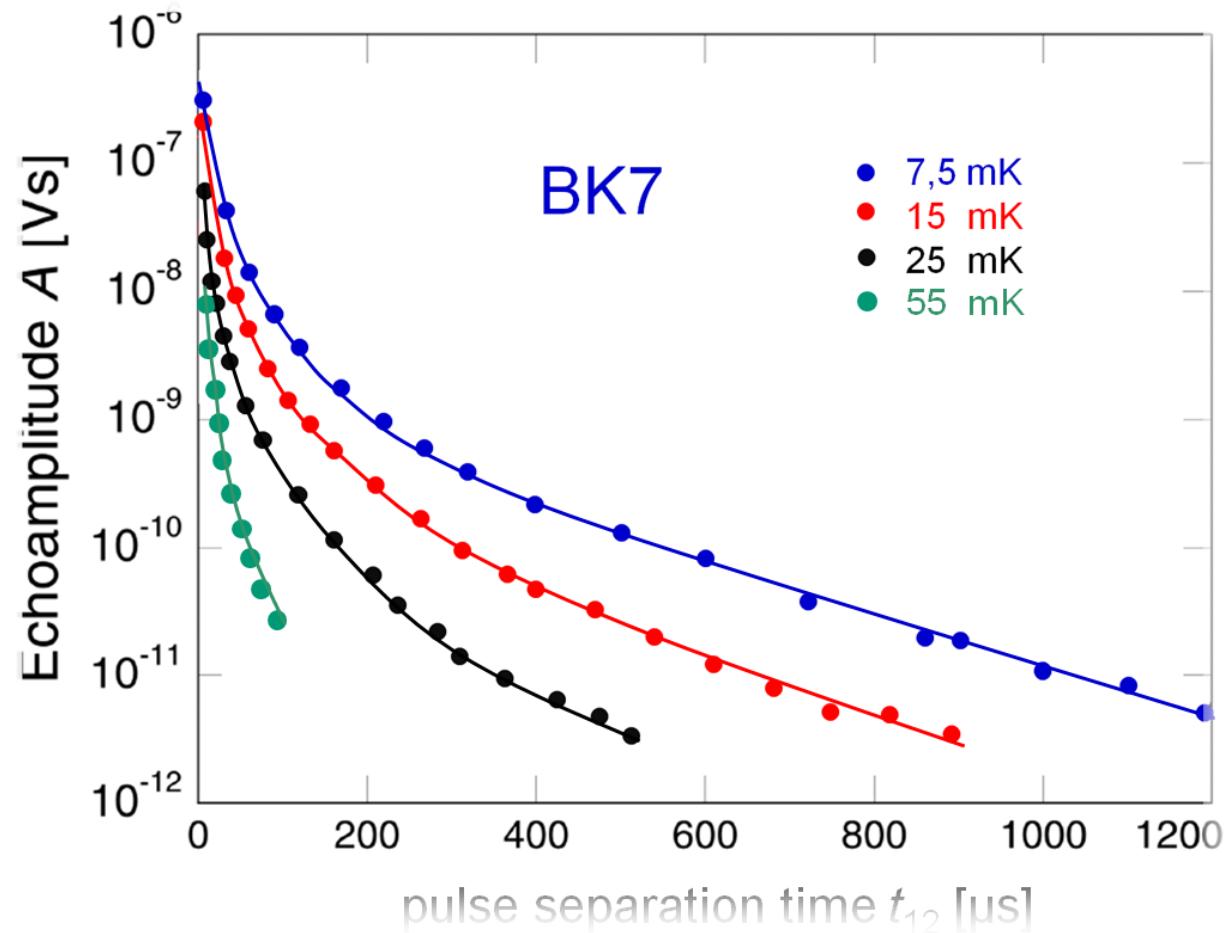


time window  $1200 \mu\text{s}$



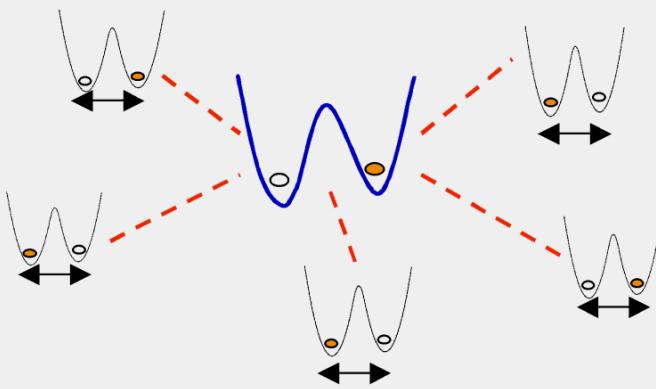
sensitivity: **five orders of magnitude**

# Temperature Dependence

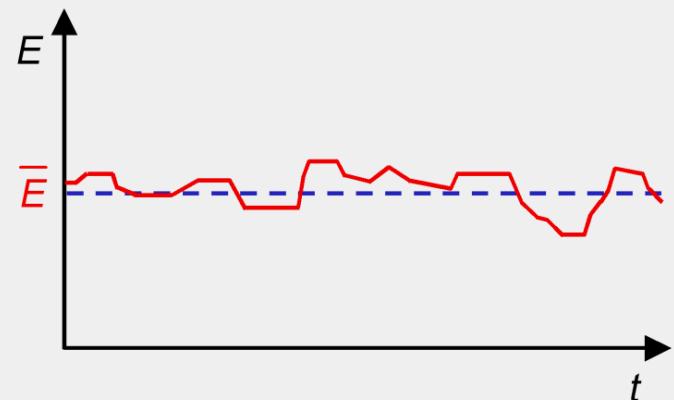


# Spectral Diffusion

interaction between resonant TS  
and thermally fluctuating TS



energy splitting of single TS  
fluctuating with time



- short time limit (no flip limit):  $t_{12} \ll \tau_{\min}$

$$\longrightarrow A(2t_{12}) = A(0) e^{-(2t_{12}/\tau_2)^2} \quad \text{Gaussian decay}$$

- long time limit (multiple flip limit):  $t_{12} \gg \tau_{\min}$

$$\longrightarrow A(2t_{12}) = A(0) e^{-2t_{12}/\tau_2} \quad \text{exponential decay}$$

# Temperature Dependence

short time limit (no flip limit):  $t_{12} \ll \tau_{\min}$

$$A(2t_{12}, T) \propto \tanh\left(\frac{E}{2k_B T}\right) e^{-m_0 T^4 (\Delta/E)t_{12}^2}, = A_0(T) e^{-m(T)(\Delta/E)t_{12}^2}$$

$$\tau_2 \propto 1/\sqrt{m(T)} \propto T^{-2}$$

long time limit (multiple flip limit):  $t_{12} \gg \tau_{\min}$

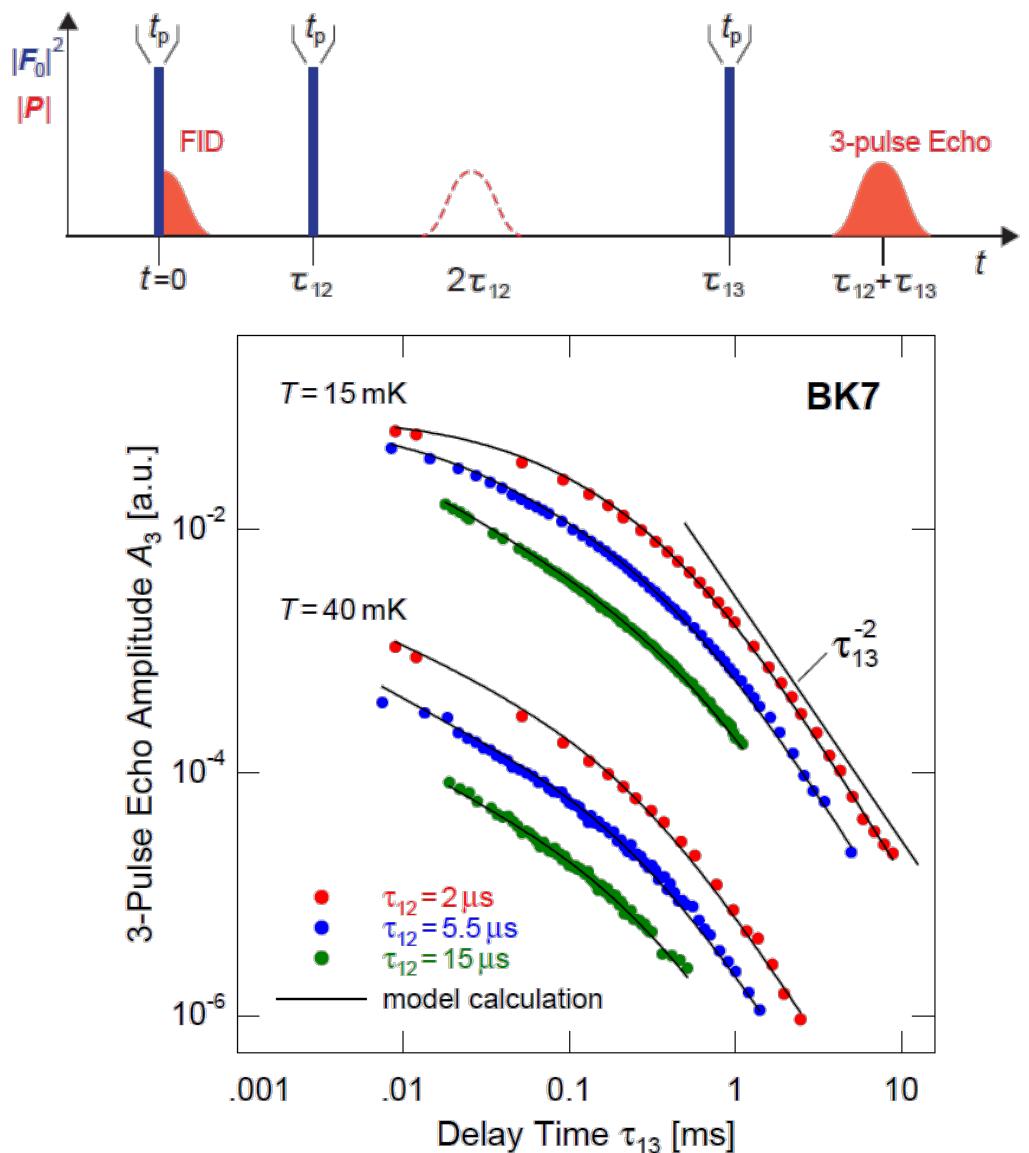
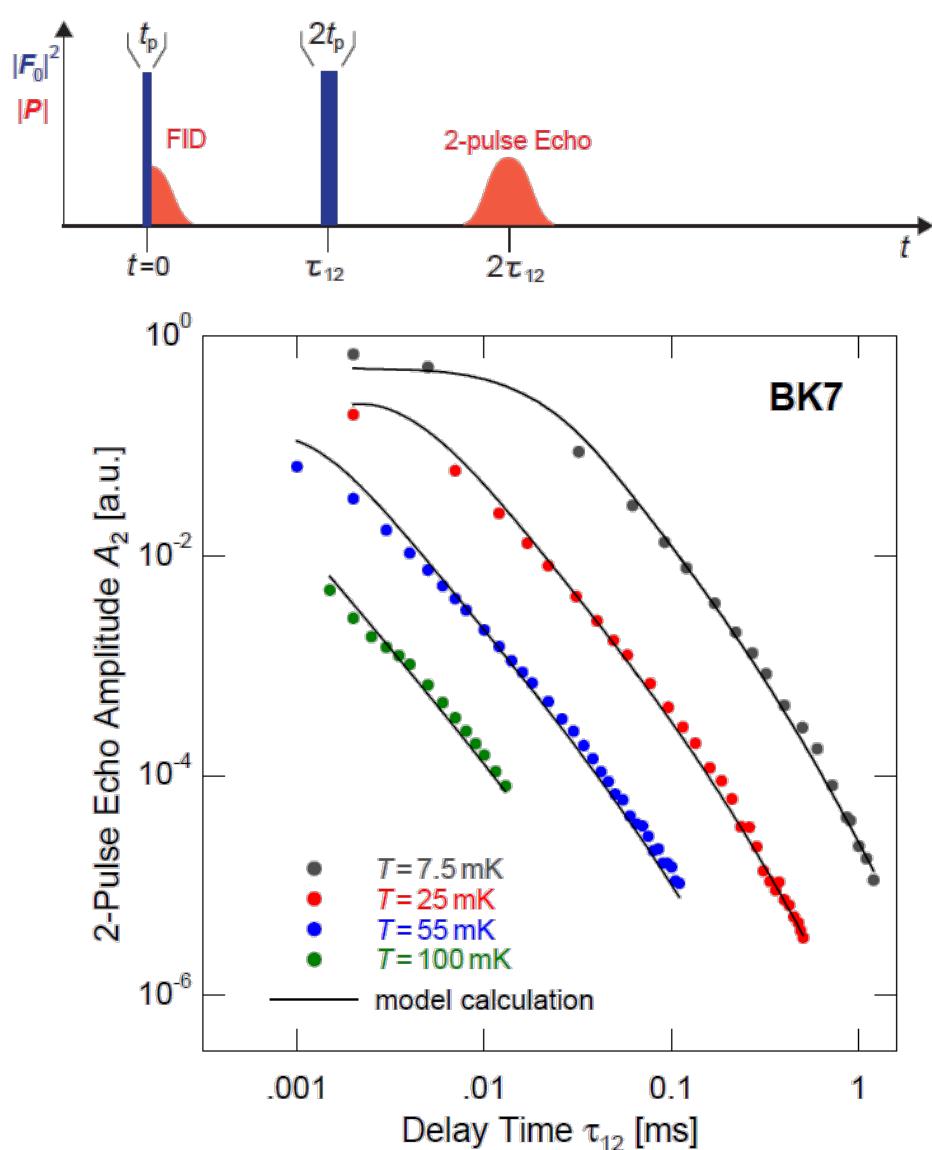
$$A(2t_{12}, T) \propto A_0(T) e^{-2t_{12}^2/\tau_2}$$

Theoretical papers:

$$\tau_2 \propto T^{-1}$$

- P. Hu, S.R. Hartmann, PRB **9**, 1 (1974)
- J.L. Black, B.I. Halperin, PRB **16**, 2879 (1976)
- P. Hu, L.R. Walker, PRB **18**, 1300 (1978)
- R. Maynard, R. Rammal, R. Suchail, J. Phys. Paris Lett. **41**, L-291 (1980)
- B.D. Laikhtman, PRB **31**, 400 (1985)
- Yu.M. Galperin, V.L. Gurevich, D.A. Parshin, PRB **37**, 10339 (1988)

# Temperature Dependence



A. L. Burin, J. M. Leveritt III, G. Ruyters, C. Schötz, M. Bazrafshan, P. Faßl, M. von Schickfus, A. Fleischmann, C. Enss, *Europhys. Lett.* **104**, 57006 (2013)

# Phase Jump Rotary Echoes

coherent regime:

$$t \ll \tau_1, \tau_2 \rightarrow \infty$$

applied field:

$$\mathbf{F} = 2\mathbf{F}_0 \cos(\omega t)$$

occupation number difference

$$\Delta n = \cos(\Omega_R t)$$



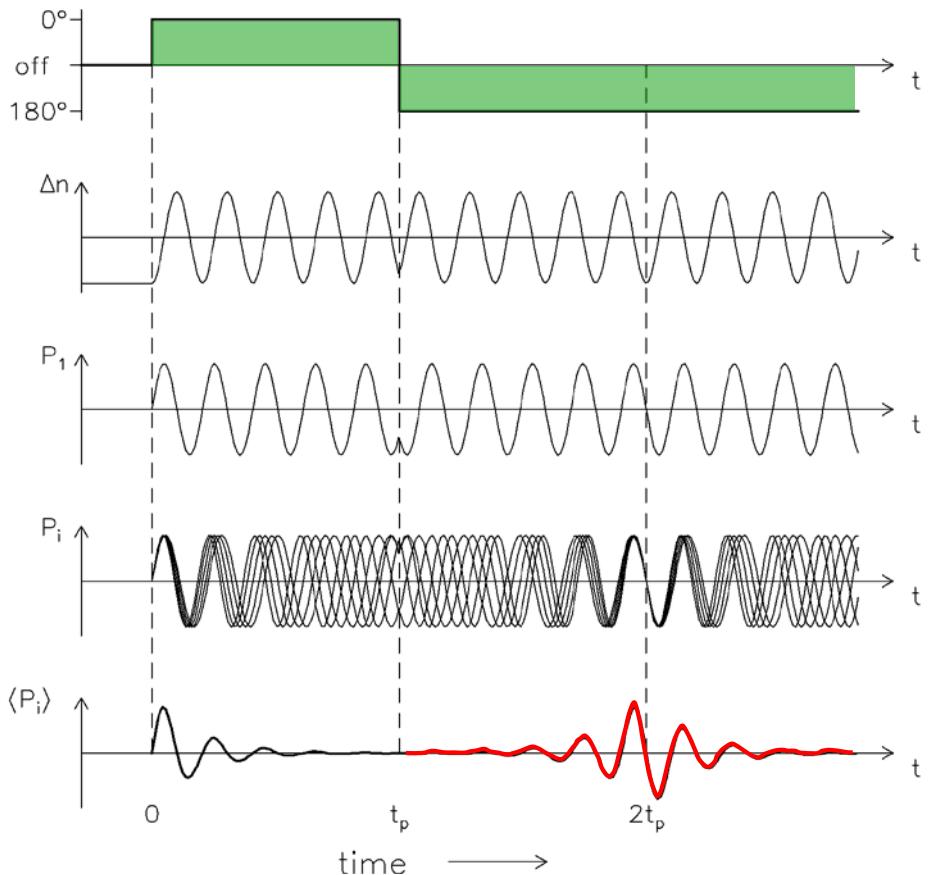
periodic change of polarisation

$$A_r(t) \propto \int_0^{+\infty} \int_0^E P(E, \Delta_0) \frac{\Delta_0}{E} \frac{\mathbf{p} \cdot \mathbf{F}_0}{|\mathbf{F}_0|} \left[ \frac{\Omega_R}{\Omega} \right]^3 e^{-\beta} \sin[\Omega(t - 2t_p)] d\Delta_0 dE$$

with  $\Omega = \sqrt{\Omega_R^2 - \omega_d^2}$

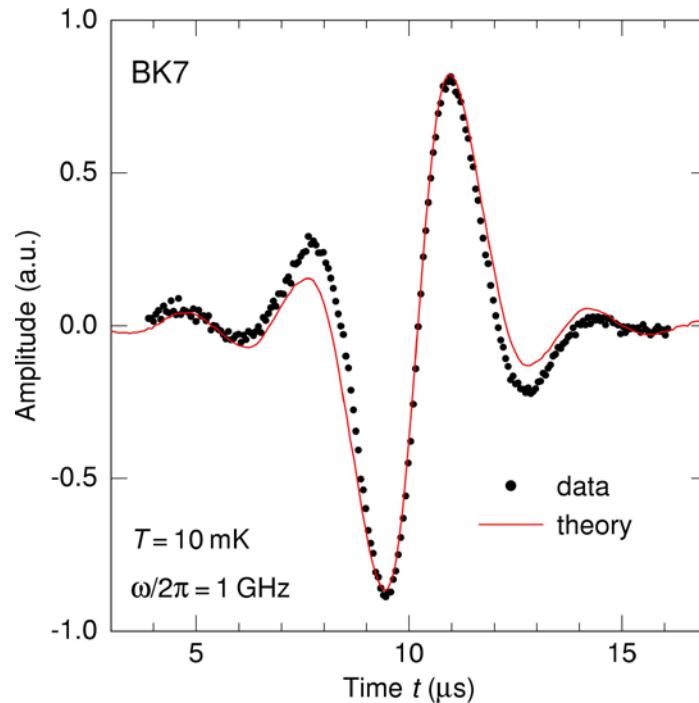
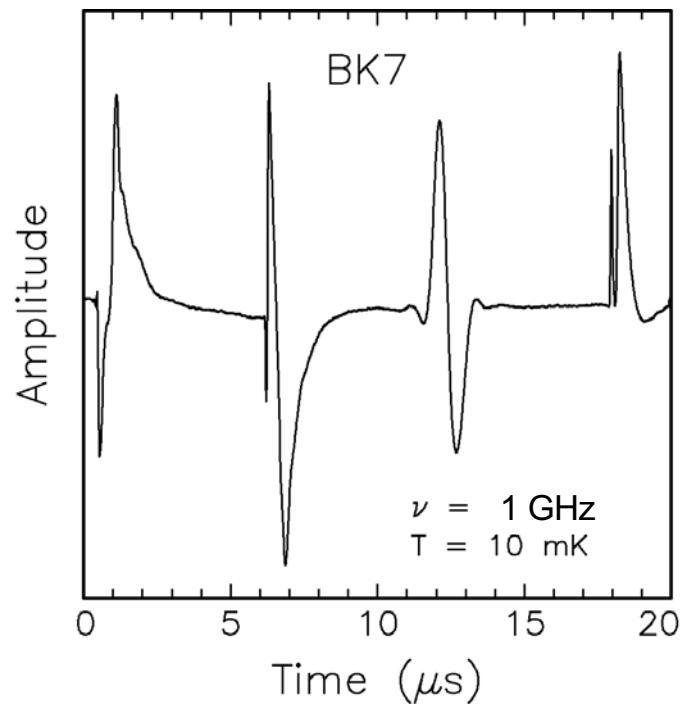
$$\omega_d = \omega_r - \omega$$

$$\beta = \frac{1}{\Omega^2} \left( \frac{\omega_d^2}{\tau_2} + \frac{\Omega_R^2}{2\tau_1} + \frac{\Omega_R^2}{2\tau_2} \right)$$



# Phase Jump Rotary Echoes

BK7: (SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, NaO, CaO, ... )



few oscillations  $\longrightarrow$  broad distribution of  $\Omega_R$

Fit: tunneling model distribution  
uniform distribution  
fixed dipole moment

C. Enss, R. Weis, S. Ludwig, S. Hunklinger,  
Czech. J. Phys. **46**, 3287 (1996)