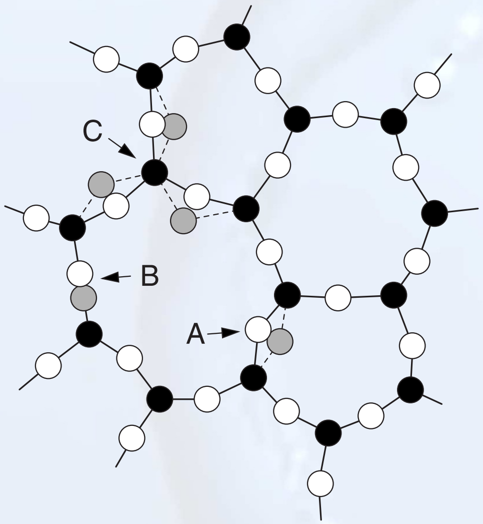
9. Atomic Tunneling Systems

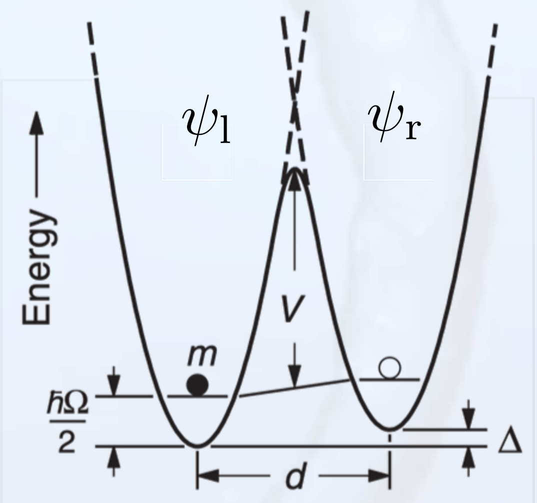
↗ crystal with point defects

↘ amorphous solids

possible structural configurations with atomic tunneling systems



double-well potential



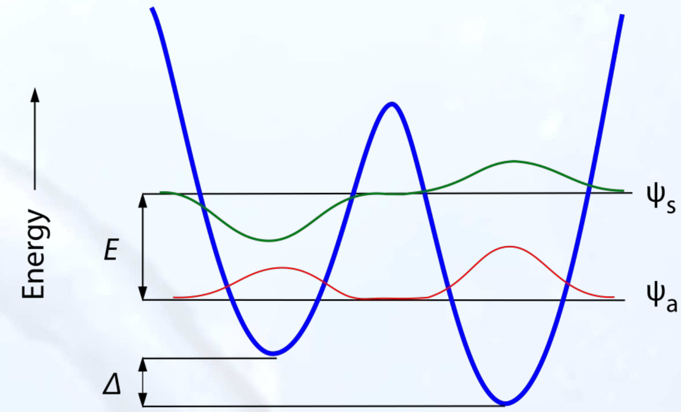
typical values: $\Delta / k_B < 10$ K

$d \sim 1$ Å

$\hbar\Omega / k_B \sim 300$ K

$V / k_B < 1000$ K

two-level-system approximation



total wave function

$$\psi = a\psi_\mathrm{l} + b\psi_\mathrm{r}$$

➡ eigenvalue problem: $H\psi = E\psi$

$$E = \frac{\int \psi^* H \psi \, \mathrm{d}^3x}{\int \psi^* \psi \, \mathrm{d}^3x} = \frac{a^2 H_\mathrm{ll} + b^2 H_\mathrm{rr} + 2ab H_\mathrm{lr}}{a^2 + b^2 + 2abS}$$

$$H_\mathrm{ll} = \int \psi_\mathrm{l}^* H \psi_\mathrm{l} \, \mathrm{d}^3x$$

$$H_\mathrm{rr} = \int \psi_\mathrm{r}^* H \psi_\mathrm{r} \, \mathrm{d}^3x$$

$$H_\mathrm{lr} = \int \psi_\mathrm{l}^* H \psi_\mathrm{r} \, \mathrm{d}^3x$$

$$S = \int \psi_\mathrm{l}^* \psi_\mathrm{r} \, \mathrm{d}^3x$$

minimizing E: $\partial E/\partial a = 0\,,\ \partial E/\partial b = 0$

$$a\,(H_\mathrm{ll} - E) + b(H_\mathrm{lr} - E\,S) = 0$$
$$a\,(H_\mathrm{lr} - E\,S) + b(H_\mathrm{rr} - E) = 0$$

➡ $(H_\mathrm{ll} - E)(H_\mathrm{rr} - E) - (H_\mathrm{lr} - E\,S)^2 = 0$

energy zero point $\quad H_\mathrm{ll,rr} = (\hbar\Omega \pm \Delta)/2$

in addition: $S \approx 0\,,$ overlap is small, V is large

$$E_\pm = \frac{1}{2}\left(\hbar\Omega \pm \sqrt{\Delta^2 + 4\,H_\mathrm{lr}^2}\right)$$

$$\boxed{E = E_+ - E_- = \sqrt{\Delta^2 + 4H_\mathrm{lr}^2} = \sqrt{\Delta^2 + \Delta_0^2}}$$

9. Atomic Tunneling Systems

WKB method

$$-2H_{\mathrm{lr}} = \Delta_0 \approx \hbar\Omega\, \underbrace{\mathrm{e}^{-\lambda}}_{\text{tunneling probability}} \qquad \underbrace{\lambda}_{\text{tunneling parameter}} \approx \frac{d}{2\hbar}\underbrace{\sqrt{2mV}}_{\text{isotope effect}}$$

- pure tunneling: $E = \Delta_0$
- classical asymmetry energy Δ

9.1 Tunneling systems in crystals

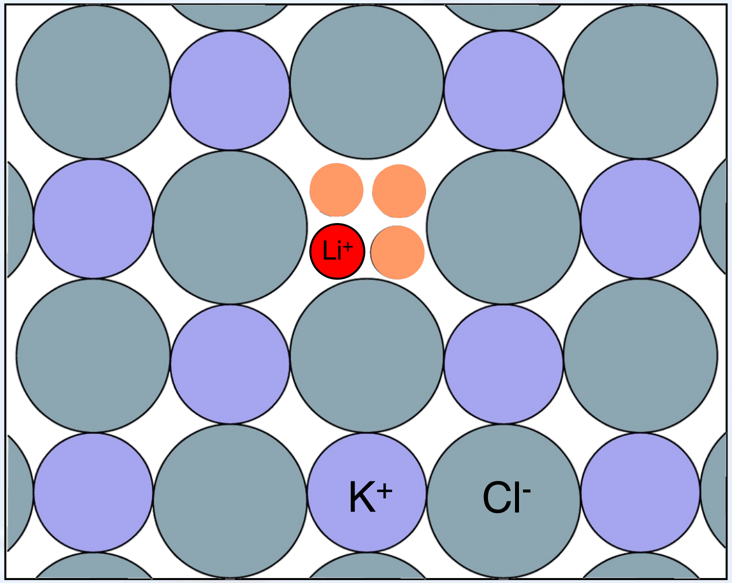
- often more than two minima
- $\Delta \approx 0$

example: KCl:Li

- ▶ Li^+ substitutes K^+
- ▶ ionic radius: $r_{\mathrm{Li^+}} < r_{\mathrm{K^+}}$

  → 8 off-center positions in $<111>$ direction

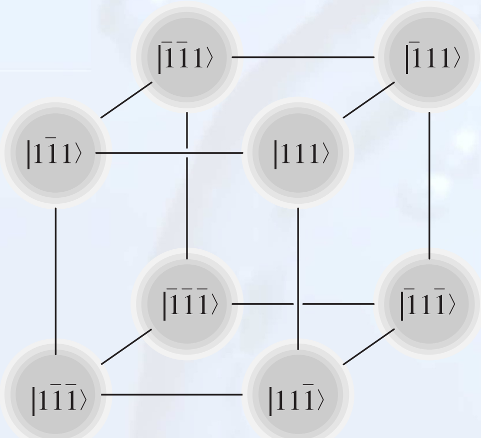
(100)-plane



9.1 Tunneling Systems in Crystals

potential minima at $\boldsymbol{r} = \dfrac{d}{2}(\alpha, \beta, \gamma)$ with $\alpha, \beta, \gamma = \pm 1$

quantum states



$$|\boldsymbol{m}\rangle = \frac{1}{\sqrt{8}} \sum_{\alpha\beta\gamma} \exp\left(\frac{\mathrm{i}\pi}{d}\, \boldsymbol{m} \cdot \boldsymbol{r}\right) |\alpha\beta\gamma\rangle \,,$$

localized states

$\eta' = \langle 1\,1\,1|\boldsymbol{H}|1\,1\,\bar{1}\rangle = \langle \bar{1}\,1\,1|\boldsymbol{H}|\bar{1}\,\bar{1}\,1\rangle = \ldots$ edge tunneling

$\mu' = \langle 1\,1\,1|\boldsymbol{H}|1\,\bar{1}\,\bar{1}\rangle = \langle 1\,\bar{1}\,1|\boldsymbol{H}|1\,1\,\bar{1}\rangle = \ldots$ face diagonal tunneling

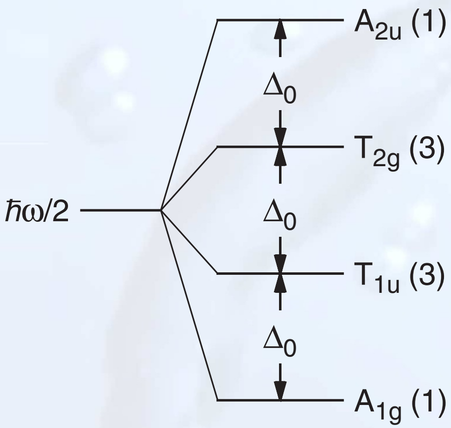
$\nu' = \langle 1\,1\,1|\boldsymbol{H}|\bar{1}\,\bar{1}\,\bar{1}\rangle = \langle 1\,\bar{1}\,1|\boldsymbol{H}|\bar{1}\,1\,\bar{1}\rangle = \ldots$ space diagonal tunneling

typically: $\eta' \gg \mu' \gg \nu'$

$$\begin{aligned}
\mathrm{A_{2u}} &: \quad (1,1,1)\,, \\
\mathrm{T_{2g}} &: \quad (1,1,0); (1,0,1); (0,1,1)\,, \\
\mathrm{T_{1u}} &: \quad (1,0,0); (0,1,0); (0,0,1)\,, \\
\mathrm{A_{1g}} &: \quad (0,0,0)\,.
\end{aligned}$$

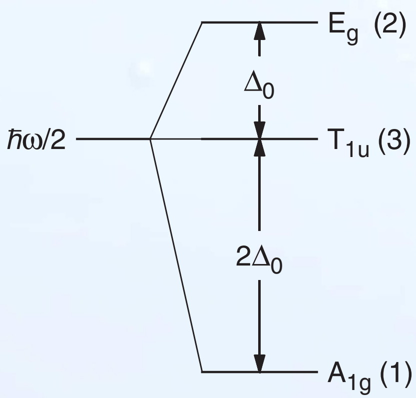
9.1 Tunneling Systems in Crystals

tunneling states with cubic symmetry



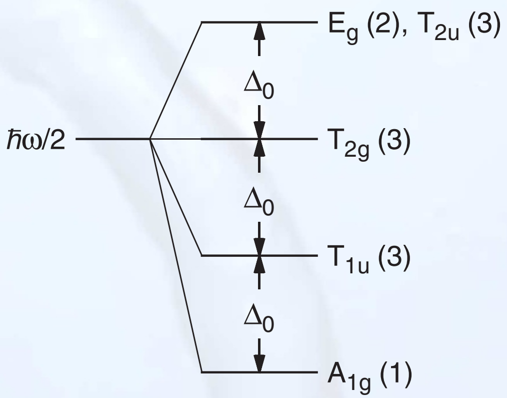
$\langle 111 \rangle$

KCl:Li, KBr:CN



$\langle 100 \rangle$

KCl:OH, LiF:OH

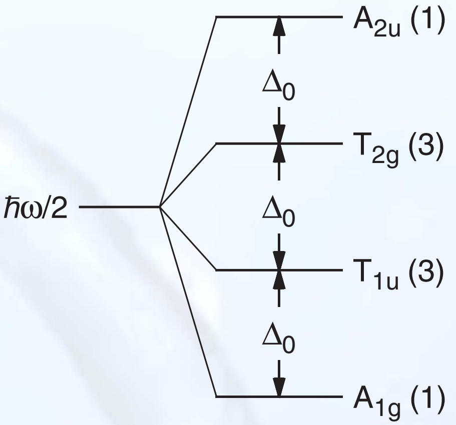


$\langle 110 \rangle$

NaBr:F

9.1 Tunneling Systems in Crystals

example: $\langle 111 \rangle$ tunneling states



a) partition function

$$Z = \sum_s e^{-E_s/k_B T} = 1 + 3e^{-\Delta_0/k_B T} + 3e^{-2\Delta_0/k_B T} + e^{-3\Delta_0/k_B T}$$

$$= \left(1 + e^{-\Delta_0/k_B T}\right)^3$$

b) internal energy

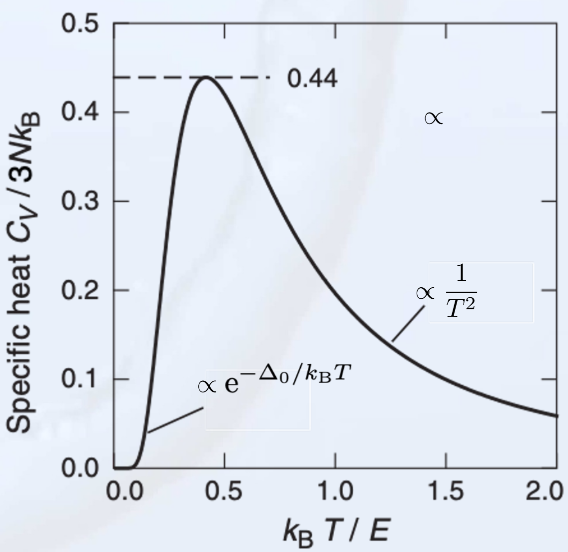
$$U = \frac{N}{Z} \sum_s E_s e^{-E_s/k_B T} = 3N\Delta_0 \frac{1}{1 + e^{\Delta_0/k_B T}}$$

$$\boxed{U = \frac{3}{2} N \Delta_0 \left[1 - \tanh\left(\frac{\Delta_0}{2k_B T}\right)\right]}$$

c) specific heat

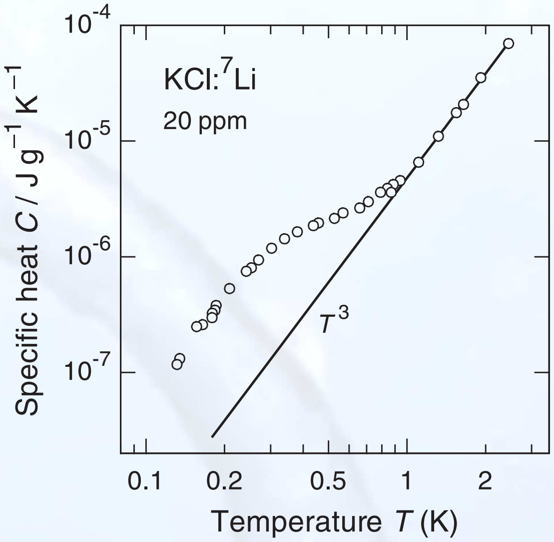
$$C_{TS} = \frac{3nk_B}{\varrho} \left(\frac{\Delta_0}{2k_B T}\right)^2 \operatorname{sech}^2\left(\frac{\Delta_0}{2k_B T}\right)$$

Schottky peak

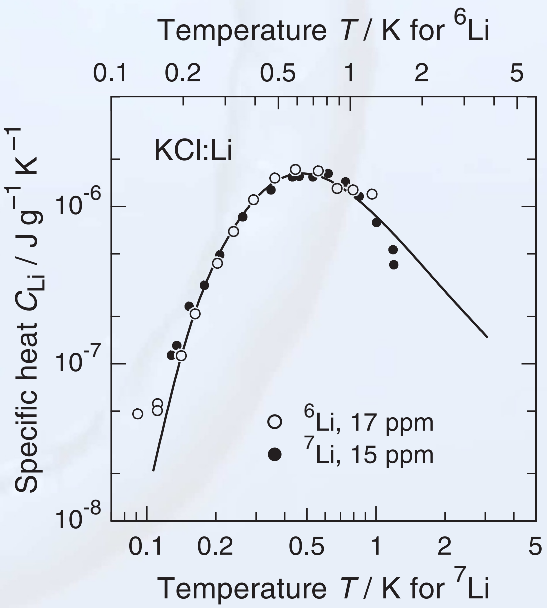


9.1 Tunneling Systems in Crystals

example: KCl: Li



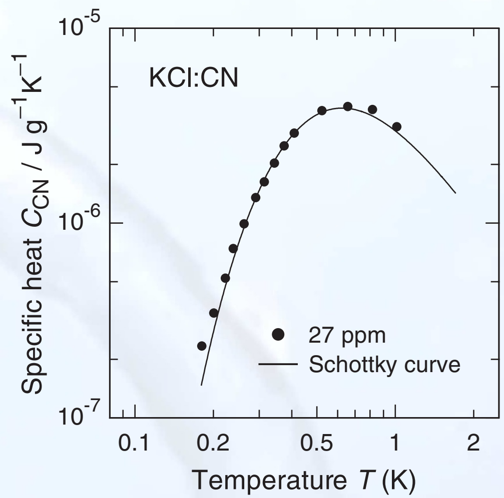
- above 1K T^3 dependence is observed
- below 1 K additional contribution: Schottky peak
- just 20 ppm Li dominates specific heat



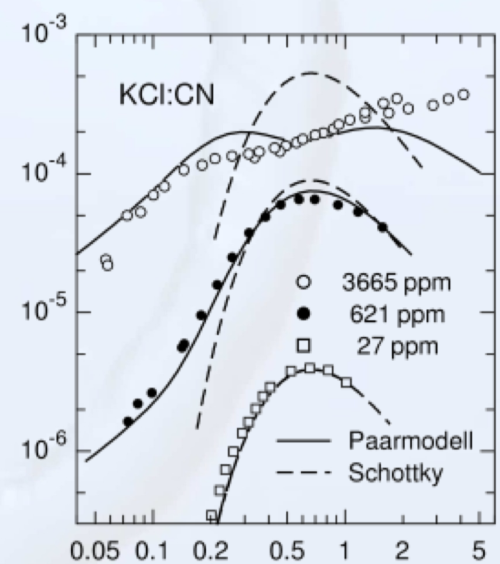
- tunneling system contribution to specific heat
- isotope effect observed: $\;{}^7\Delta_0/k_\mathrm{B} = 1.1\,\mathrm{K}$, $\;{}^6\Delta_0/k_\mathrm{B} = 1.65\,\mathrm{K}$
- proof of tunneling effect

9.1 Tunneling Systems in Crystals

example: KCl: CN (same symmetry than KCl:Li)



- T^3 dependence subtracted
- solid line: Schottky peak



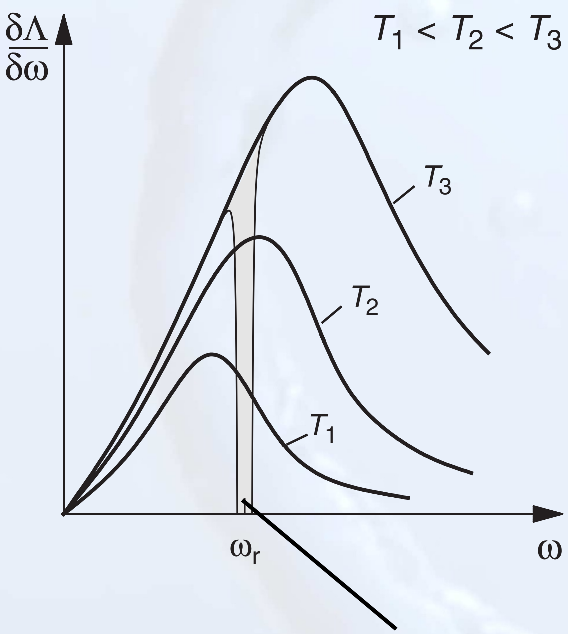
- broadening at higher concentrations
- contributions of pairs
- double maximum structure at highest concentration

9.1 Tunneling Systems in Crystals

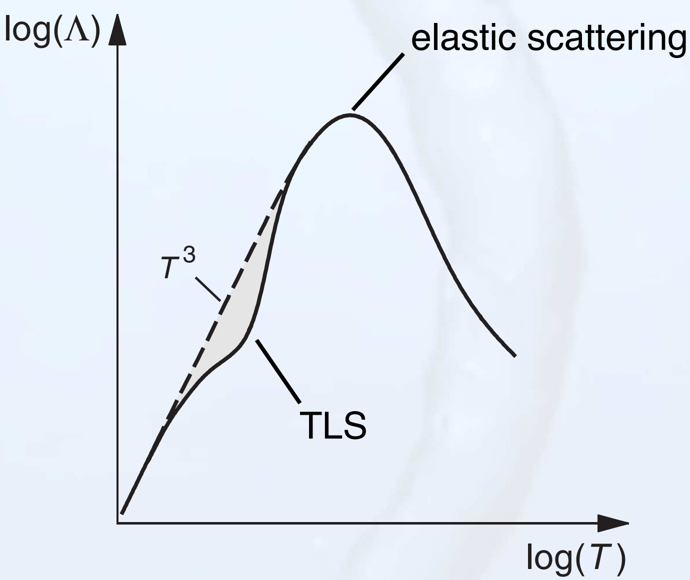
d) thermal conductivity:

phonon transport, but resonant absorption via TS

→ hole in differential thermal conductivity

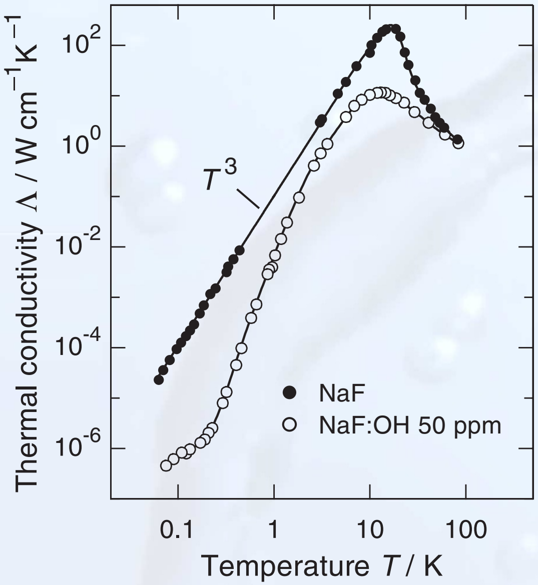


width is determined by coupling of TLS to phonons

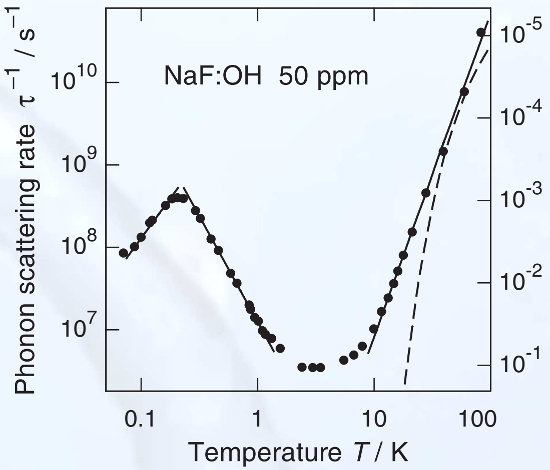


for $\hbar\omega_r \approx k_B T$ reduction of thermal conductivity

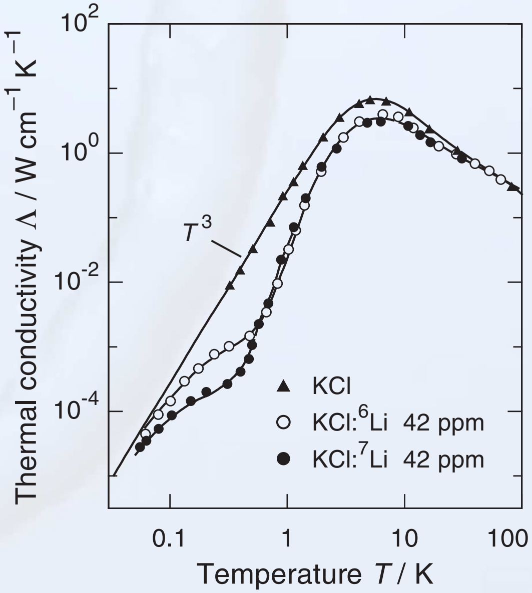
9.1 Tunneling Systems in Crystals



scattering rate / mean free path



- ► strong impact at maximum
- ► reduction of thermal conductivity
  ⟶ factor of 500 for 50 ppm OH^-

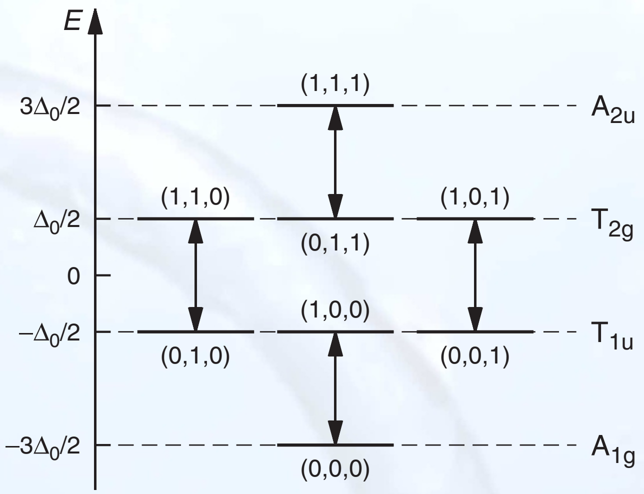


- ► isotope effect observed
- ► confirms that TS are responsible for heat resistance

9.1 Tunneling Systems in Crystals

e) Dielectric susceptibility:

- selection rules
- level scheme
- field dependence



static dielectric susceptibility

$$\varepsilon = 1 + \chi_\infty + \chi_{\mathrm{TLS}}$$

$$\mathcal{F} = -k_{\mathrm{B}}T \ln Z$$

$$P = -\frac{1}{V}\frac{\partial \mathcal{F}}{\partial F}$$

$$\chi = -\frac{1}{V}\left.\frac{\partial^2 \mathcal{F}}{\partial F^2}\right|_{F=0} = \frac{k_{\mathrm{B}}T}{V}\left.\frac{\partial^2 \ln Z}{\partial F^2}\right|_{F=0}$$

$$E_{(1,1,1)} = -E_{(0,0,0)} = \Delta_0 + \sqrt{\frac{1}{4}\Delta_0^2 + \frac{1}{3}p^2F^2}\,,$$

$$E_{(0,1,1)} = -E_{(1,0,0)} = \Delta_0 - \sqrt{\frac{1}{4}\Delta_0^2 + \frac{1}{3}p^2F^2}\,,$$

$$E_{(1,0,1)} = E_{(1,1,0)} = -E_{(0,1,0)} = -E_{(0,0,1)} = \sqrt{\frac{1}{4}{\Delta_0}^2 + \frac{1}{3}p^2F^2}$$

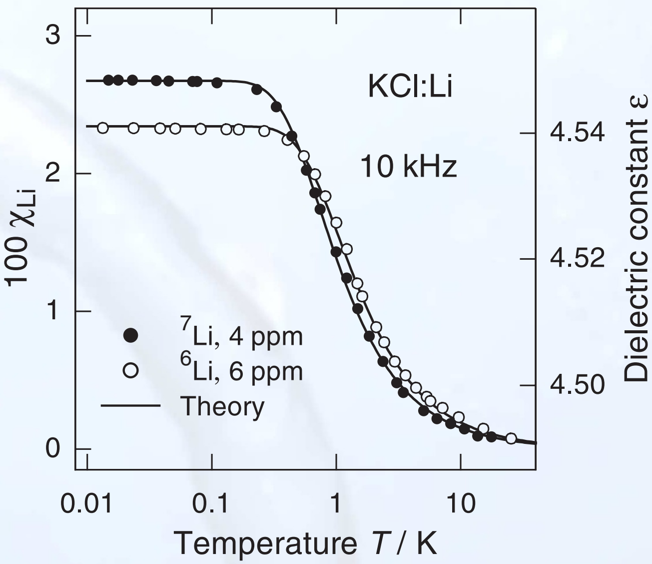
partition function in electric field

$$Z = 4\cosh\left(\frac{1}{k_{\mathrm{B}}T}\sqrt{\frac{1}{4}\Delta_0^2 + \frac{1}{3}p^2F^2}\right)\left(1 + \cosh\left(\frac{\Delta_0}{k_{\mathrm{B}}T}\right)\right)$$

$$\boxed{\chi_{\mathrm{iso}} = \frac{2}{3}\frac{np^2}{\varepsilon_0\Delta_0}\tanh\left(\frac{\Delta_0}{2k_{\mathrm{B}}T}\right)}$$

9.1 Tunneling Systems in Crystals

$$\chi_{\rm iso} = \frac{2}{3}\,\frac{np^2}{\varepsilon_0 \Delta_0}\tanh\left(\frac{\Delta_0}{2k_{\rm B}T}\right)$$

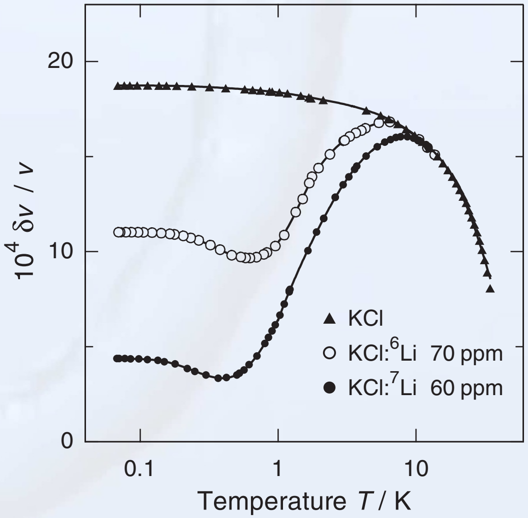


- high temperature: classical $1/T$ dependence
- low temperature: quantum mechanical plateau $\propto 1/\Delta_0$
- isotope effect clearly observed
- solid line → theoretical description assuming isolated TS

e) sound velocity

$$\frac{\delta v}{v} = \frac{-\varrho v^2}{2} s_{44} \qquad \text{torsional mode}$$

$$\frac{\delta v}{v} = -\frac{2n\gamma^2}{\varrho v^2 \Delta_0}\tanh\left(\frac{\Delta_0}{2k_{\rm B}T}\right) - \frac{n\gamma^2}{\varrho v^2 k_{\rm B}T}\,{\rm sech}^2\left(\frac{\Delta_0}{2k_{\rm B}T}\right)$$



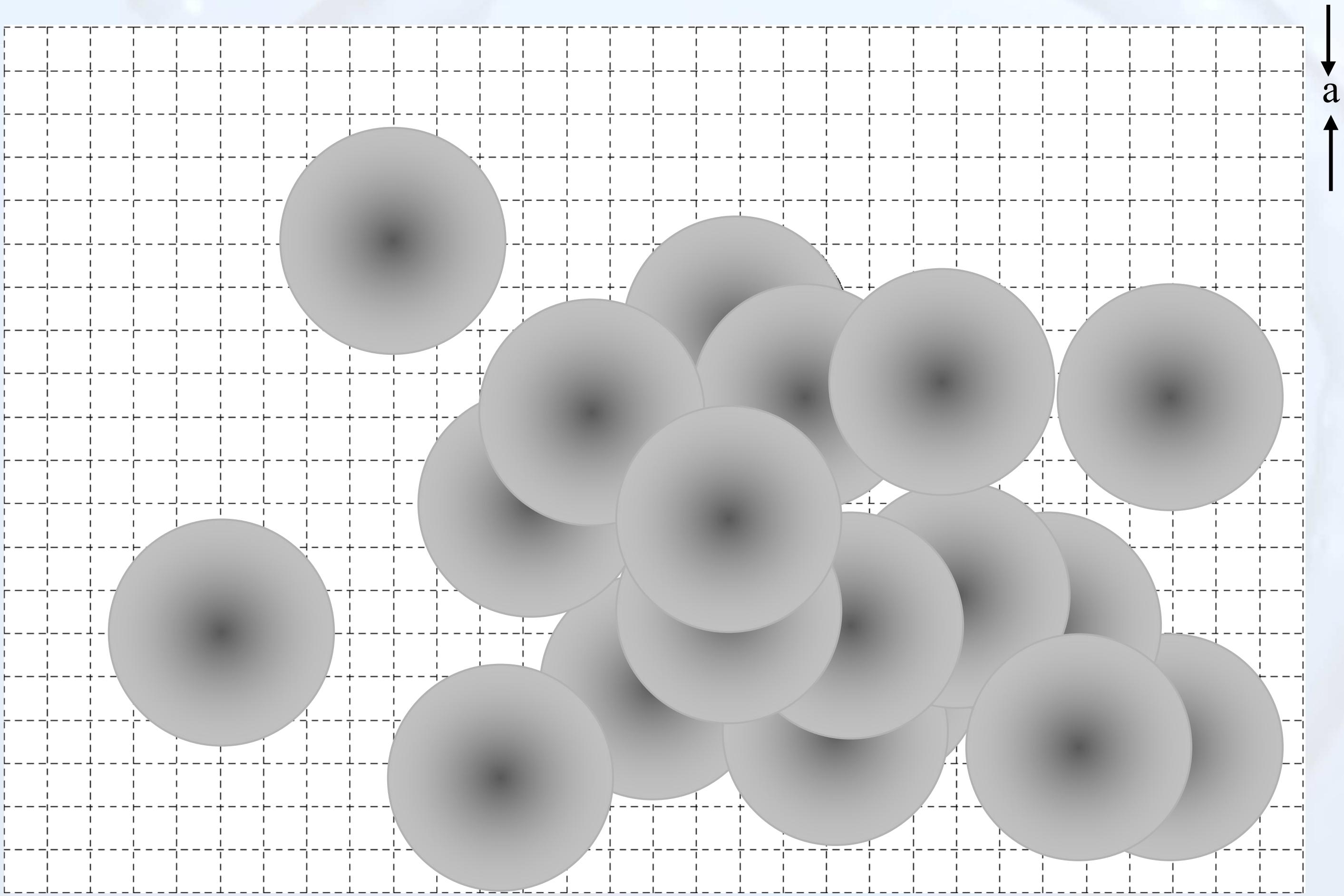
- high temperature: classical $1/T$ dependence
- low temperature: quantum mechanical plateau $\propto 1/\Delta_0$
- maximum in between: level contribute that couple linear to strain field

9.1 Tunneling Systems in Crystals

Concentration dependence: example dielectric susceptibility of KCl with TS

isolate TS ⟶ TS pairs ⟶ many particle interaction

transition to incoherent tunneling

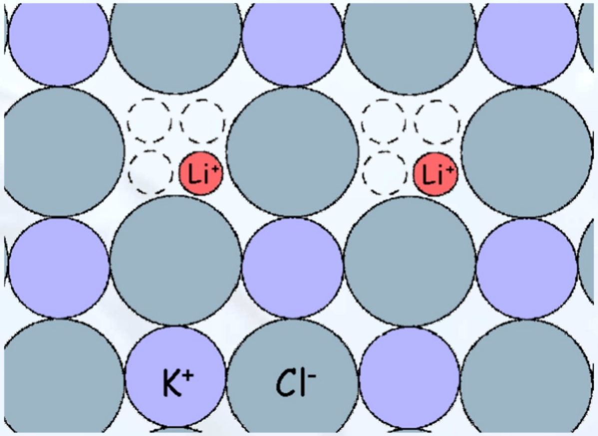


radius: $J(r) \approx \Delta_0$

9.1 Tunneling Systems in Crystals

pair interaction

$$J_{ij} = -\frac{1}{4\pi\varepsilon_0\varepsilon_{\mathrm{KCl}}}\left[\frac{\boldsymbol{p}_i\cdot\boldsymbol{p}_j}{r_{ij}^3} - \frac{3(\boldsymbol{r}_{ij}\cdot\boldsymbol{p}_i)(\boldsymbol{r}_{ij}\cdot\boldsymbol{p}_j)}{r_{ij}^5}\right]$$



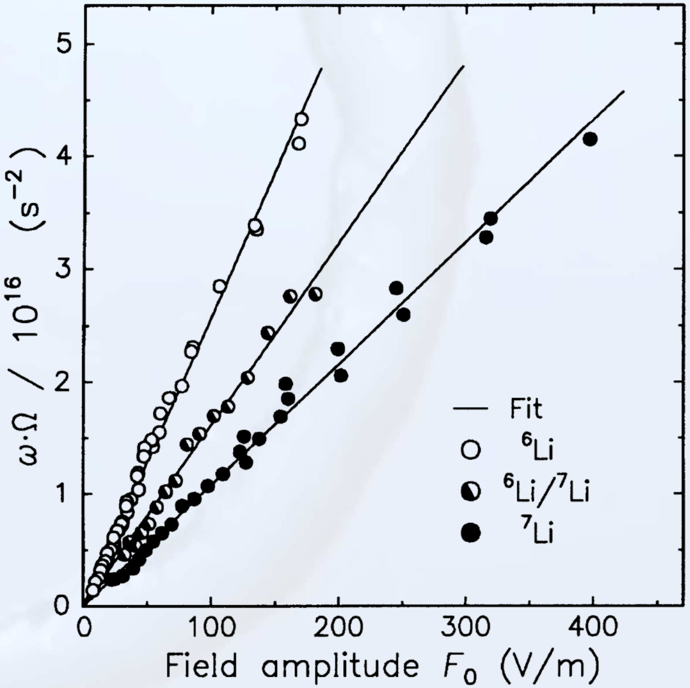
strongly interacting pairs ⟶ tunnel as one entity

Rabi frequency (ECHo experiments)

tunnel splitting of pairs

$$\Omega_{\mathrm{R}} = \frac{1}{\hbar}\frac{\Delta_0}{E}\,\boldsymbol{p}\cdot\boldsymbol{F}_0$$

dipole moment of pairs



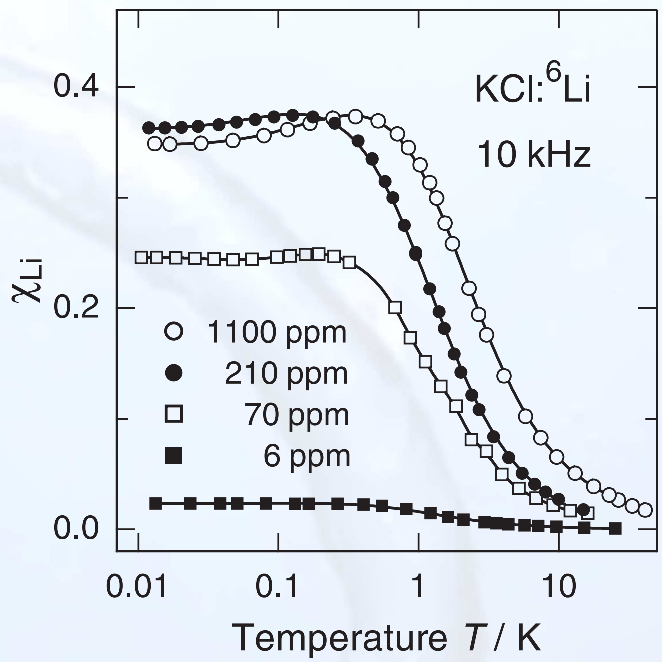
- KCl with ^{6}Li and ^{7}Li
- observation of mixed pairs
- experimental proof of pair tunneling

9.1 Tunneling Systems in Crystals

high concentrations

⬇

cross-over to incoherent tunneling

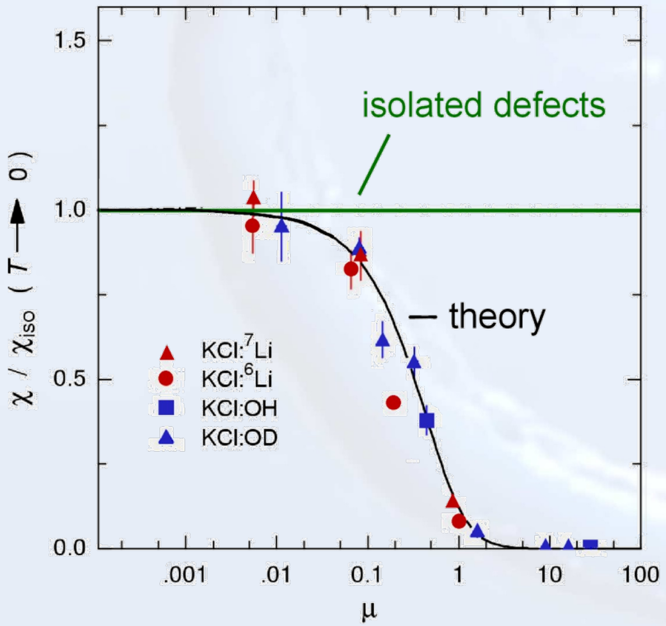


consequences:

- reduced resonant contribution (~ c tanh(x))

  ⟶ susceptibility does not scale with concentration

- new phonon-less relaxation channel



interaction parameter: $\mu = \dfrac{\bar{J}}{\Delta_0}$ mean interaction energy

expected zero-temperature susceptibility:

$$\frac{\chi'_{\mathrm{res}}}{\chi'_{\mathrm{iso}}}\,(T \to 0) = \frac{\left(\sqrt{1+\mu^2}-\mu\right)^2}{\sqrt{1+\mu^2}}$$