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Muons and Ionic Conduction

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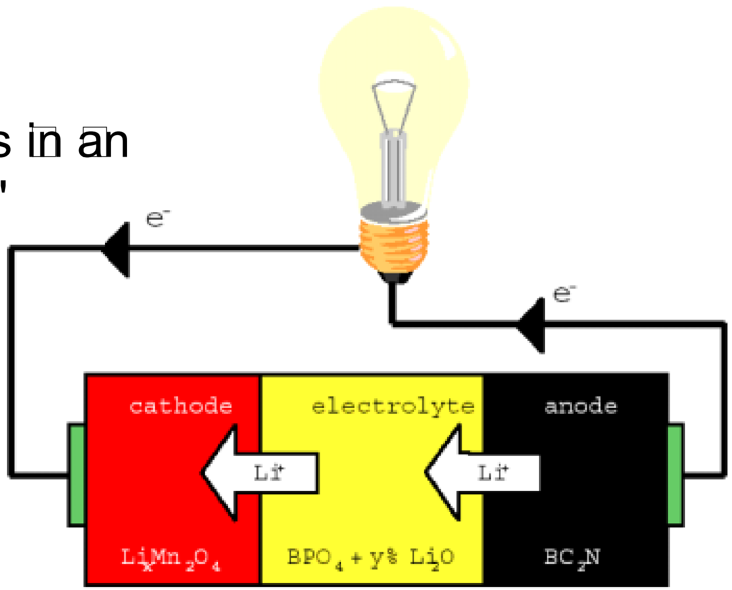
ISIS

Introduction

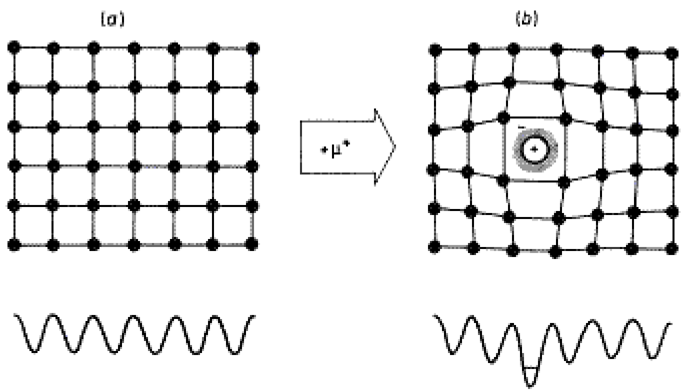
- Atoms and ions can often diffuse through solids
  - Some materials have disordered, mobile ions in an otherwise regular lattice - 'fast ion conductor'
- Many useful applications:
  - batteries
  - fuel cells
  - sensors
  - catalysts



- H^+ readily diffuses into, through and out of many materials
  - Presence of H affects properties
- Muons behave as light isotope of hydrogen and diffuse too
- Other ions diffuse, eg. Li^+ and Ag^+
- Static muons can observe the motion of other ions
- Muons may attach to molecular ions which are in motion
- Electron motion can also be studied

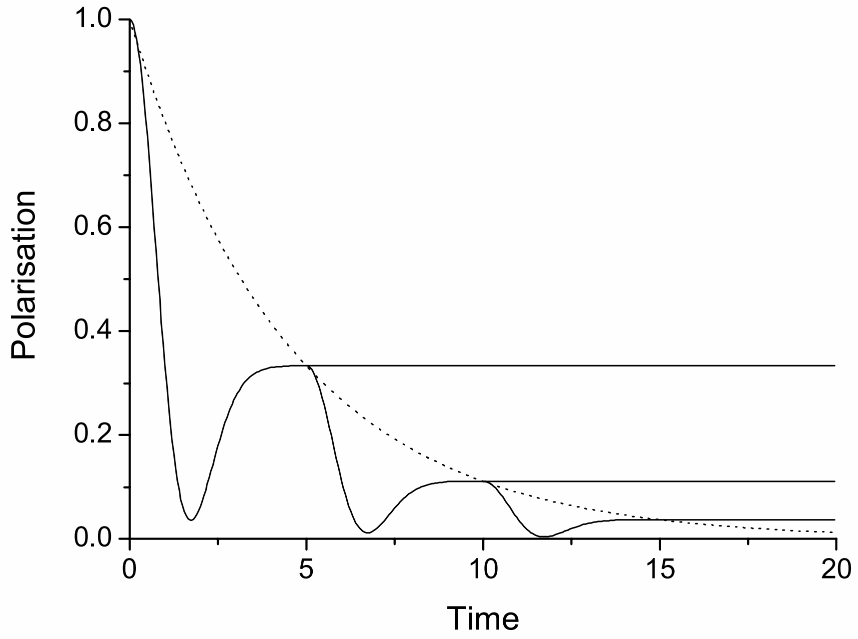
The Muon as a Proton

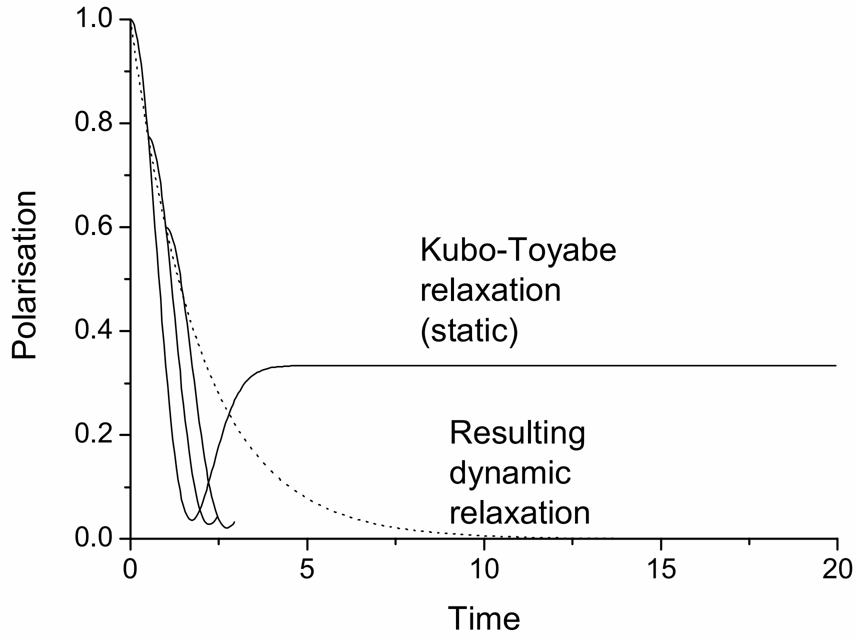
- Positive muon has same charge as proton - chemically the same
- Lower mass, so higher ground state energy when in a potential well and higher attempt rate at barrier
  - Usually results in faster diffusion
- Sometimes higher energy in intermediate state, giving lower tunnelling rate through barrier for μ compared to H or D
- Diffusion can start at <50K (Al, Cu and other metals) or the muon may remain static up to >500K (Boron)
- In metals the positive charge is screened by conduction electrons
- Some lattice distortion expected around an interstitial particle



Motional Narrowing

- The muon spin interacts with nearby nuclear (or electronic) moments
- Relaxation in zero field $P(t)=G_z(t)$ or transverse field $P(t)=G_x(t)\cos(\omega t)$
- May be enhanced by the presence of an electron (muonium)
- Static relaxation quadratic in form close to t=0, ie. $G(t) = 1 - \sigma^2 t^2 + \ldots$
- Motion takes the muon away from the near neighbours to a new equivalent site where relaxation re-starts as if from t=0



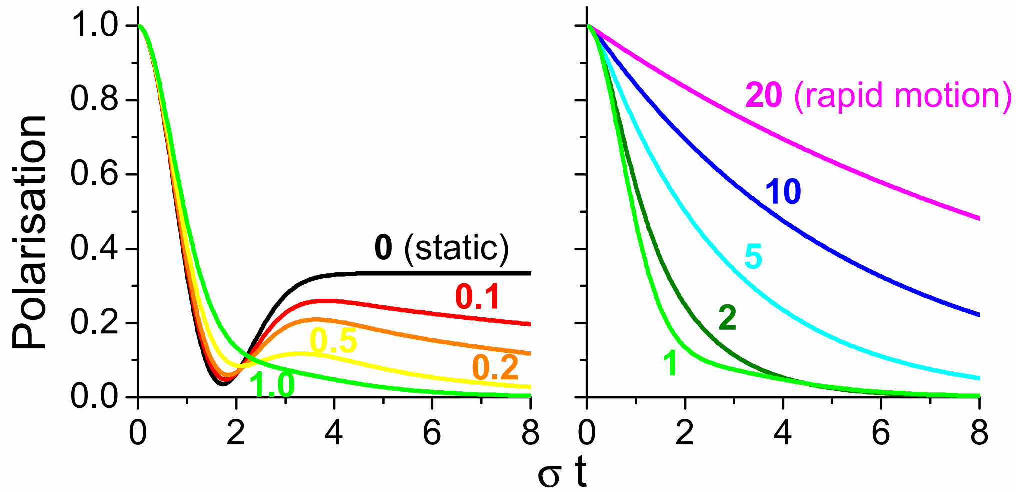


Motional Narrowing

- For fast motion the relaxation is Lorentzian in form with relaxation rate inversely proportional to hop rate

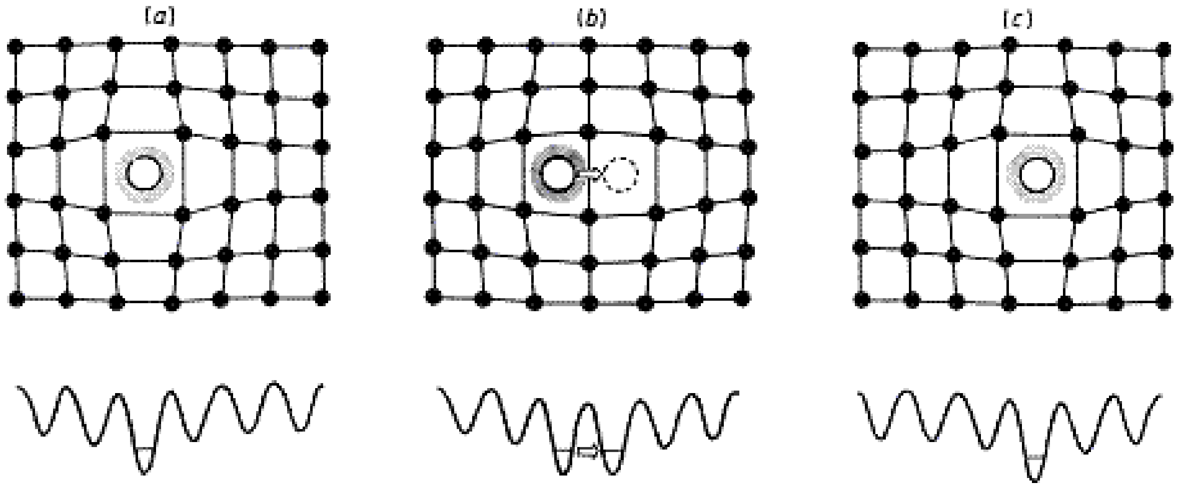
  for each hop interval τ, polarisation reduced by factor $(1-\sigma^2\tau^2)$

  polarisation after N hops = $(1-\sigma^2\tau^2)^N = (1-\sigma^2\tau^2)^{t/\tau} \approx \exp(-\sigma^2\tau t)$
- Hopping actually at random times with average rate $1/\tau$
- For slow motion the relaxation may be enhanced, eg. - the '1/3 tail' shows relaxation
- Full solution for zero field: Dynamic Kubo-Toyabe function

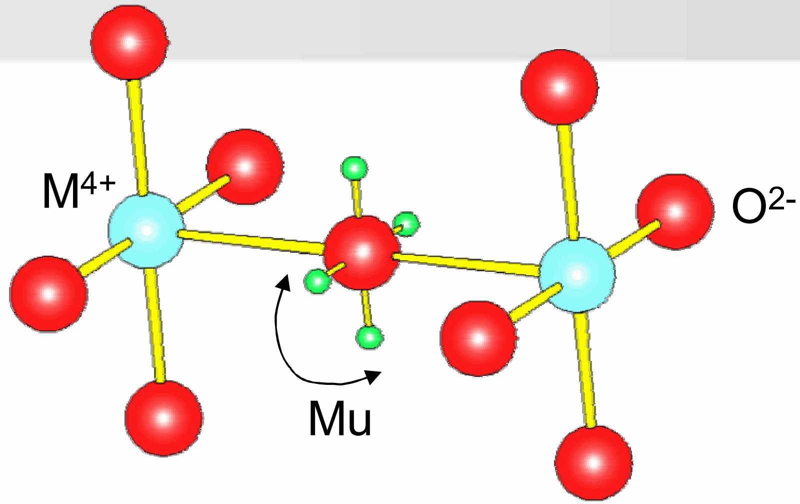


Thermally Activated Diffusion

- Distortion of the lattice around the muon generates a potential well
  - Self Trapped when in ground state
- If thermal vibrations of the lattice make a neighbouring site have the same energy
  - Muon can then tunnel between the two sites
- If the muon is excited into a higher energy level
  - Can cross the barrier
- Overall effect: diffusion hop rate follows Arrhenius law $\nu = \nu_0 \exp(-E_a/kT)$

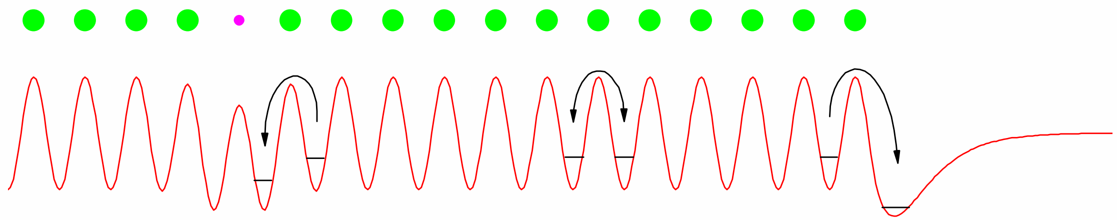


Restricted Motion



- The muon may be able to move between nearby sites but not escape the unit cell:
  - Several interstitial sites within one cage
  - Large amplitude vibration around the equilibrium site (shallow energy minimum)
  - Rotation of molecular ion eg. OMu^-, NH_3Mu^+ or $MuSO_4^-$
- For fast motion:
  - For fixed nuclear spins, average the local field over all possible muon sites
  - Sum over all possible nuclear spin configurations
  - New field distribution lower than for static muon, but not zero
- Long range diffusion usually follows at higher temperature

Trapping



- All real materials contain impurity atoms, crystal lattice defects, grain boundaries and surfaces
- Likely to have some lower energy sites for interstitial atoms such as μ^+
- At low temperatures the muons remain at their implantation sites and do not find the traps
- Higher temperature causes the muons to diffuse through the lattice and they may trap at these sites
- Static muon signal observed, with linewidth different to lattice site and dependent on local environment
  - change dopant ions and observe differences
- Further increase in temperature allows the muon to escape the trap

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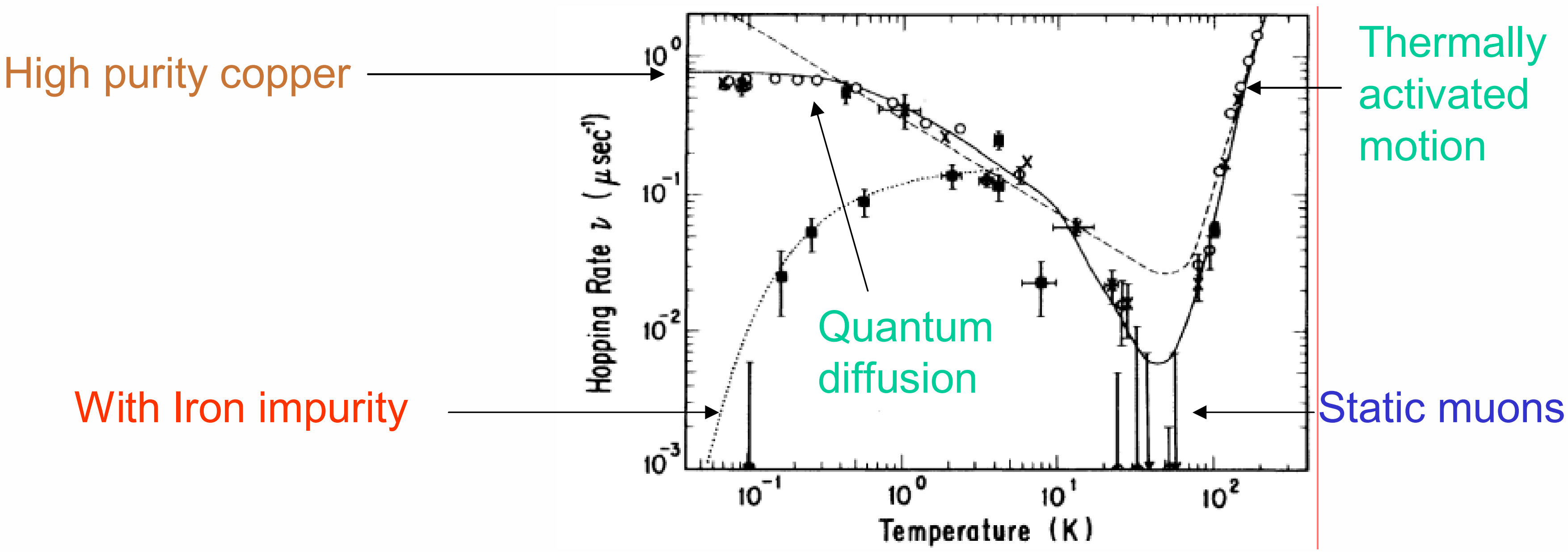
Quantum Diffusion

- In pure crystalline materials at very low temperature, the interstitial sites form a 'conduction band'
- Muons (or muonium) can travel freely through the lattice
- Thermally excited vibrations (phonons) disrupt the regular lattice and scatter the muons
- Muons now 'self trapped' at one site until thermally excited motion begins



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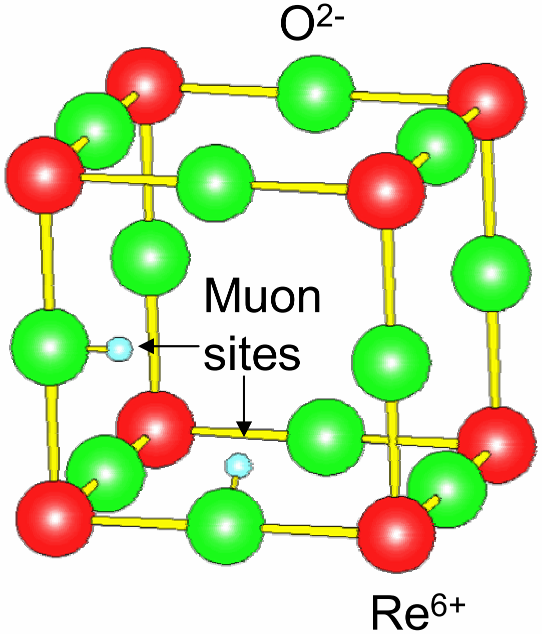
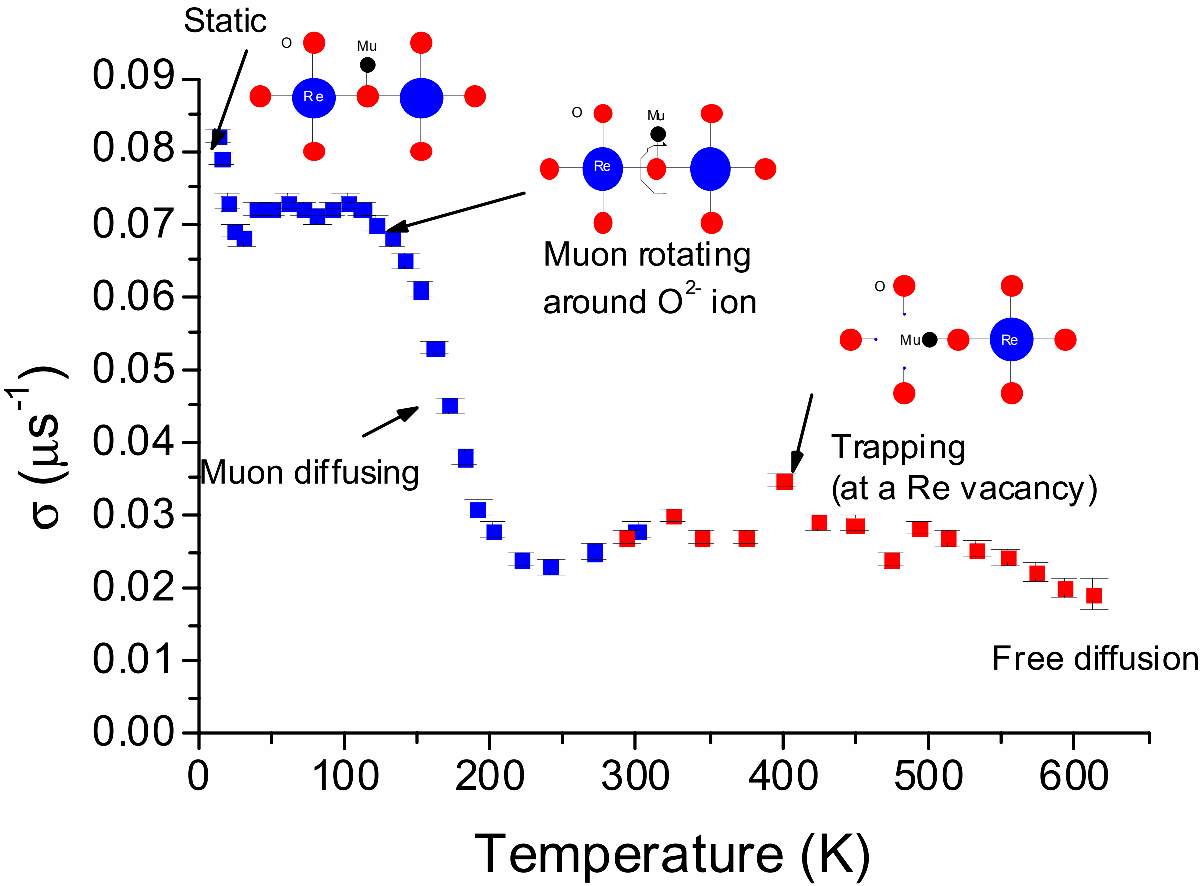
Modelling Proton Conduction

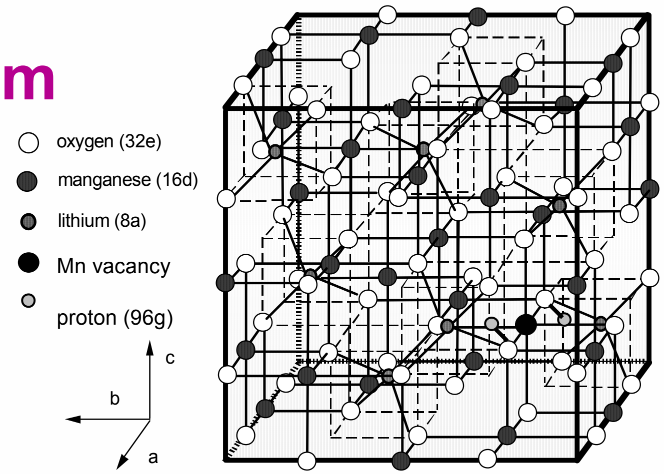
- Protons/muons in ReO_3 - one of a family of proton conductors HWO_3, $HMoO_3$
- Simple cubic structure, related to the perovskites
- Low relaxation rate fitted to Gaussian

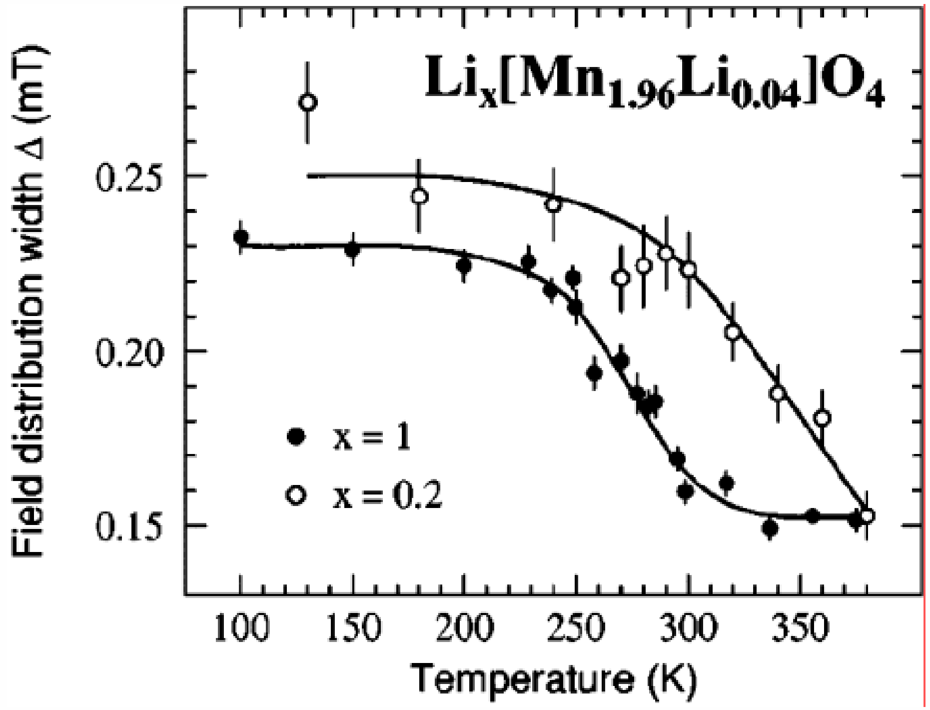




Monitoring ionic conduction - Lithium

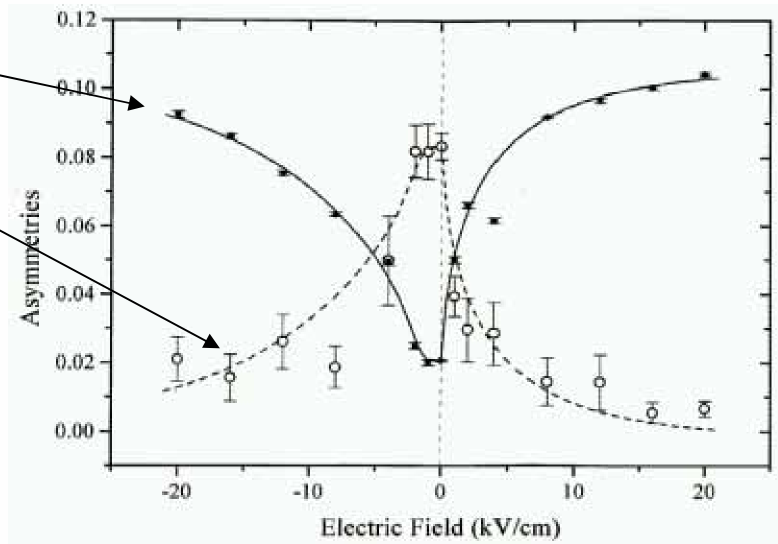
- $Li_xMn_yO_4$ battery materials ñ spinel structure
- Muon is static (bound to oxygen)
- Li^+ ions start to diffuse at 250 K
- Li contribution to linewidth is motionally narrowed while contribution of other lattice nuclei remains (eg. Mn)
- Linewidth reduces to that due to static nuclei only
- Further linewidth decrease would be expected as muons start to diffuse (above 350K)





Electronic conduction

- We can also use the muon to measure electron mobility in insulators and semiconductors
- The muon may initially come to rest as Mu+ (associated with some electron cloud but with net positive charge
  - May attach to a host atom or ion but retains net positive charge
- Electrons are formed by ionisation as the muon enters the material at 4MeV
  - These may be attracted to the muon to form muonium
- Apply electric fields to sweep the electrons away from the muon
  - Increased fraction remaining as Mu+
  - Reduced muonium fraction

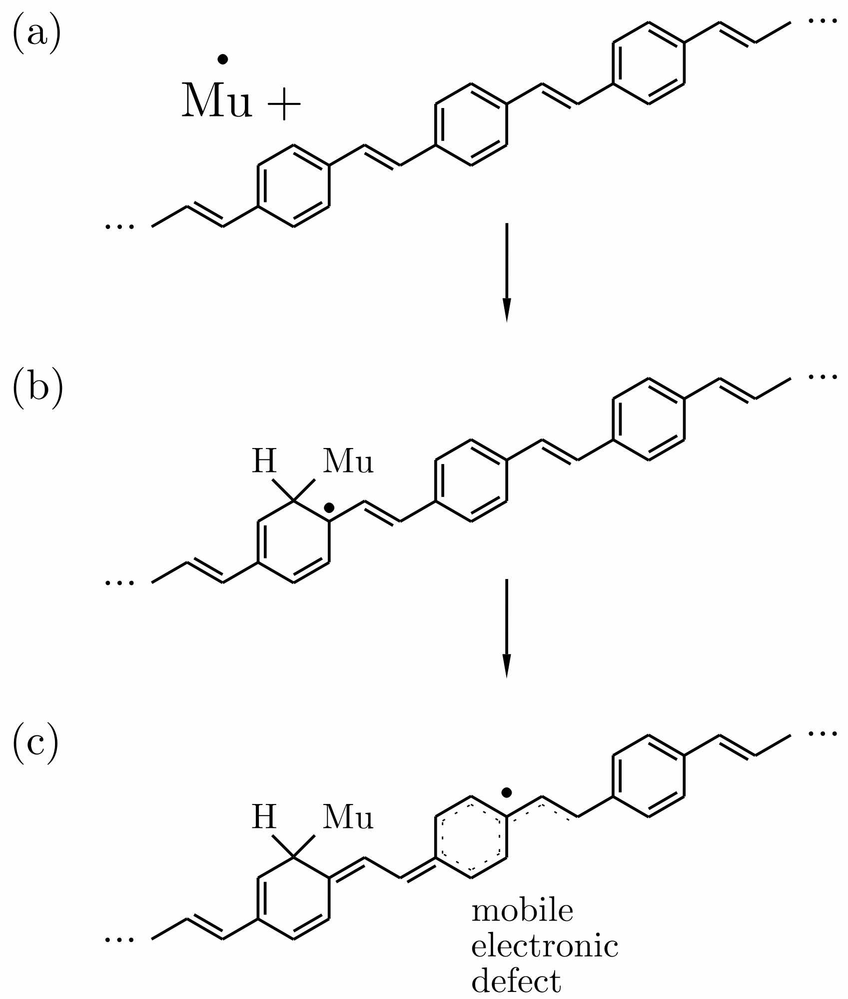


Asymmetry between E parallel and anti-parallel to muon path

(electrons may be swept towards muon)

Conducting Polymers

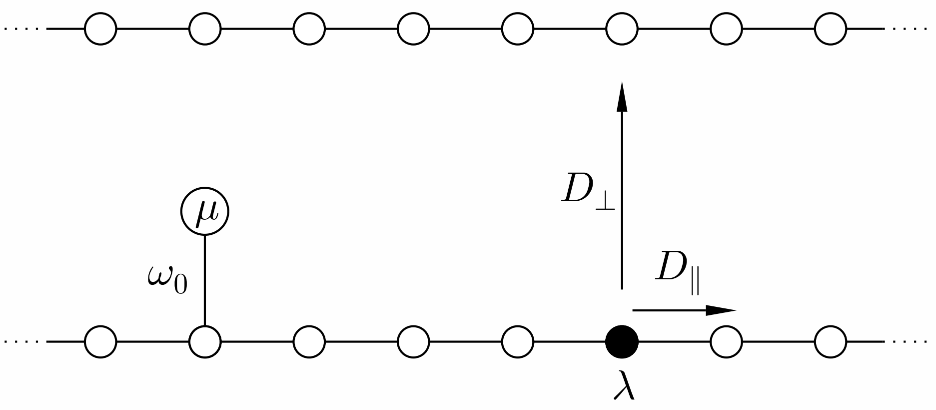
- Muon both generates a polaron and probes its motion, e.g. for PPV:

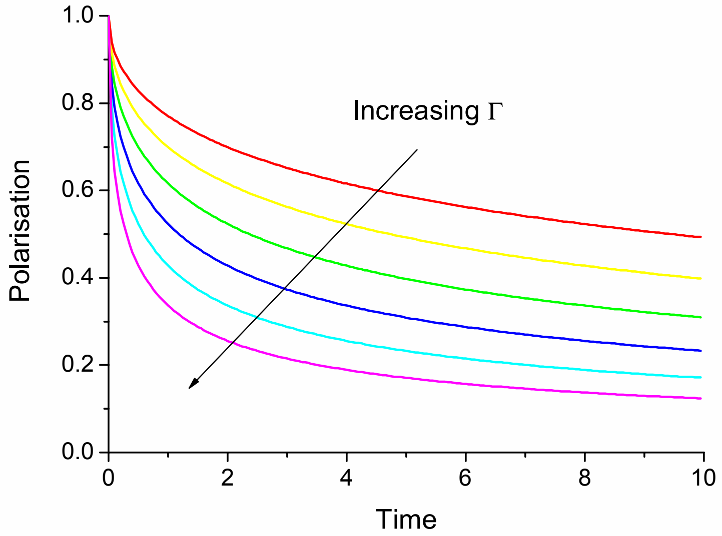


Diffusion and the Risch-Kehr Model

For 1-d diffusion a particle starting at x=0 will return from time to time, though with lower probability at later times. (Return much less likely in 3D)

Stochastic model describing muon relaxation due to intermittent hyperfine coupling with a diffusing polaron



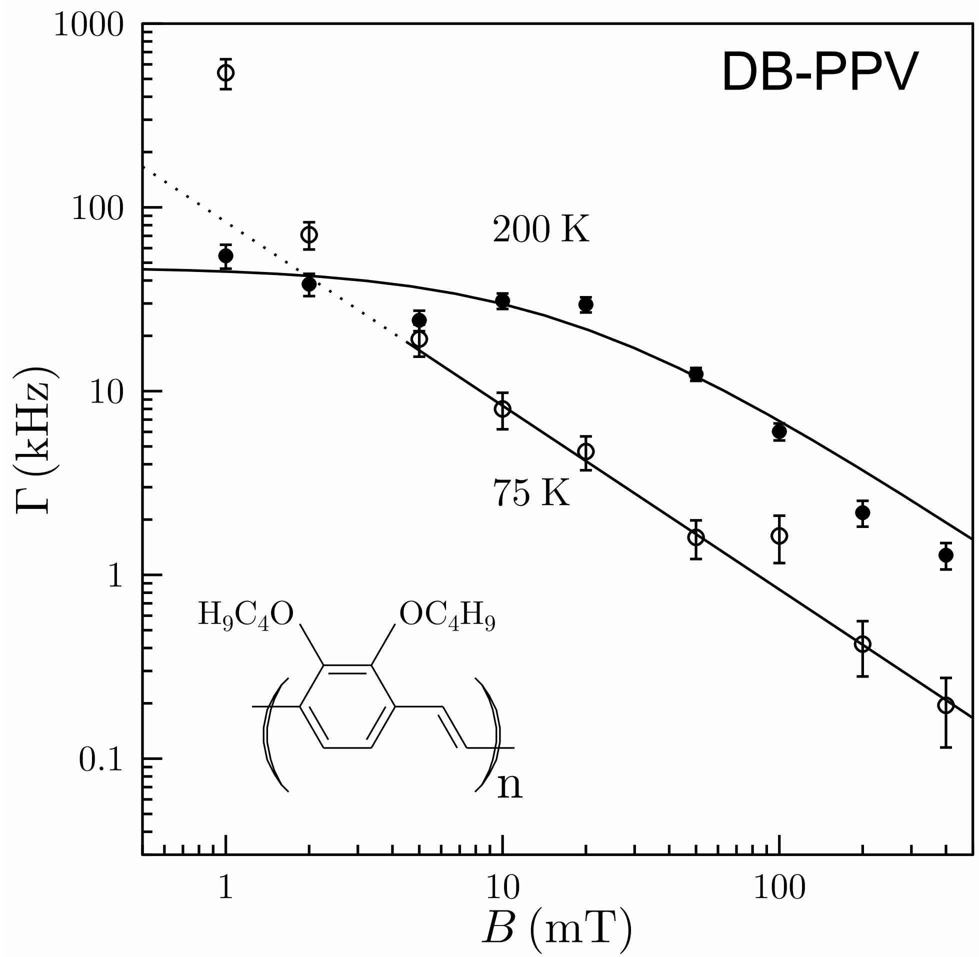


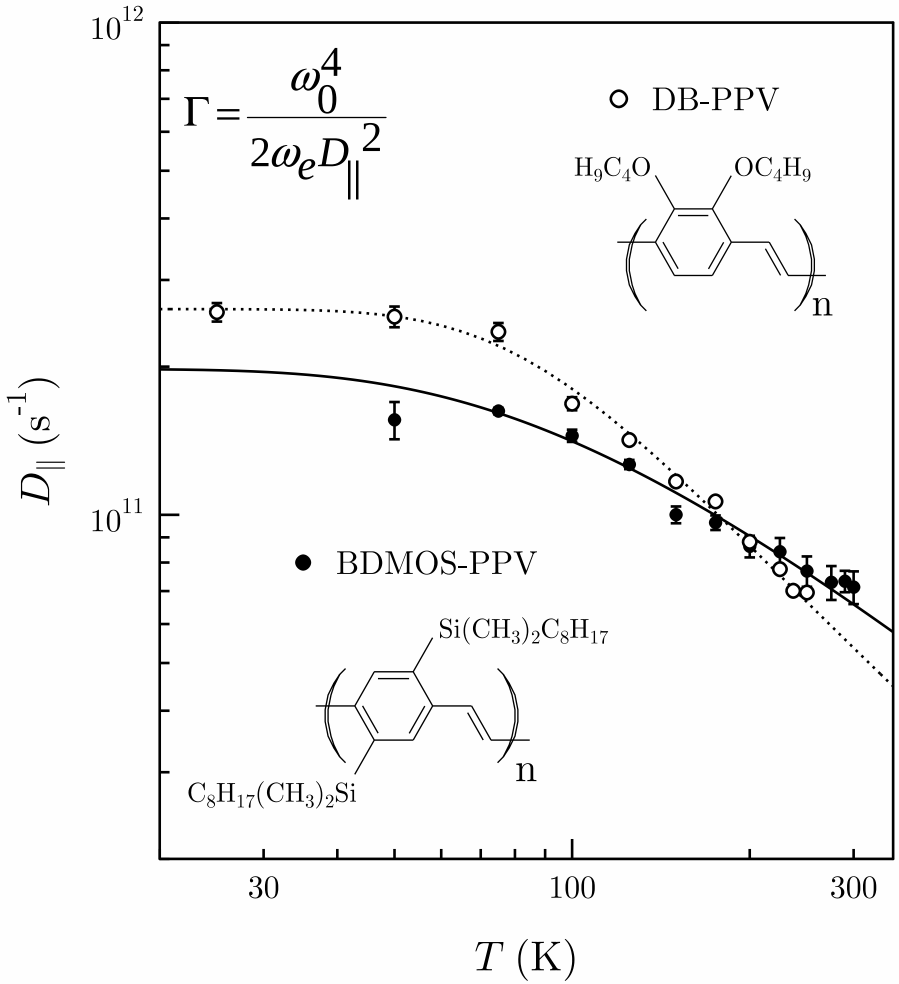
The relaxation function takes the form:

$$G_z(t) = \exp(\Gamma t)\,\mathrm{erfc}(\sqrt{\Gamma t})$$

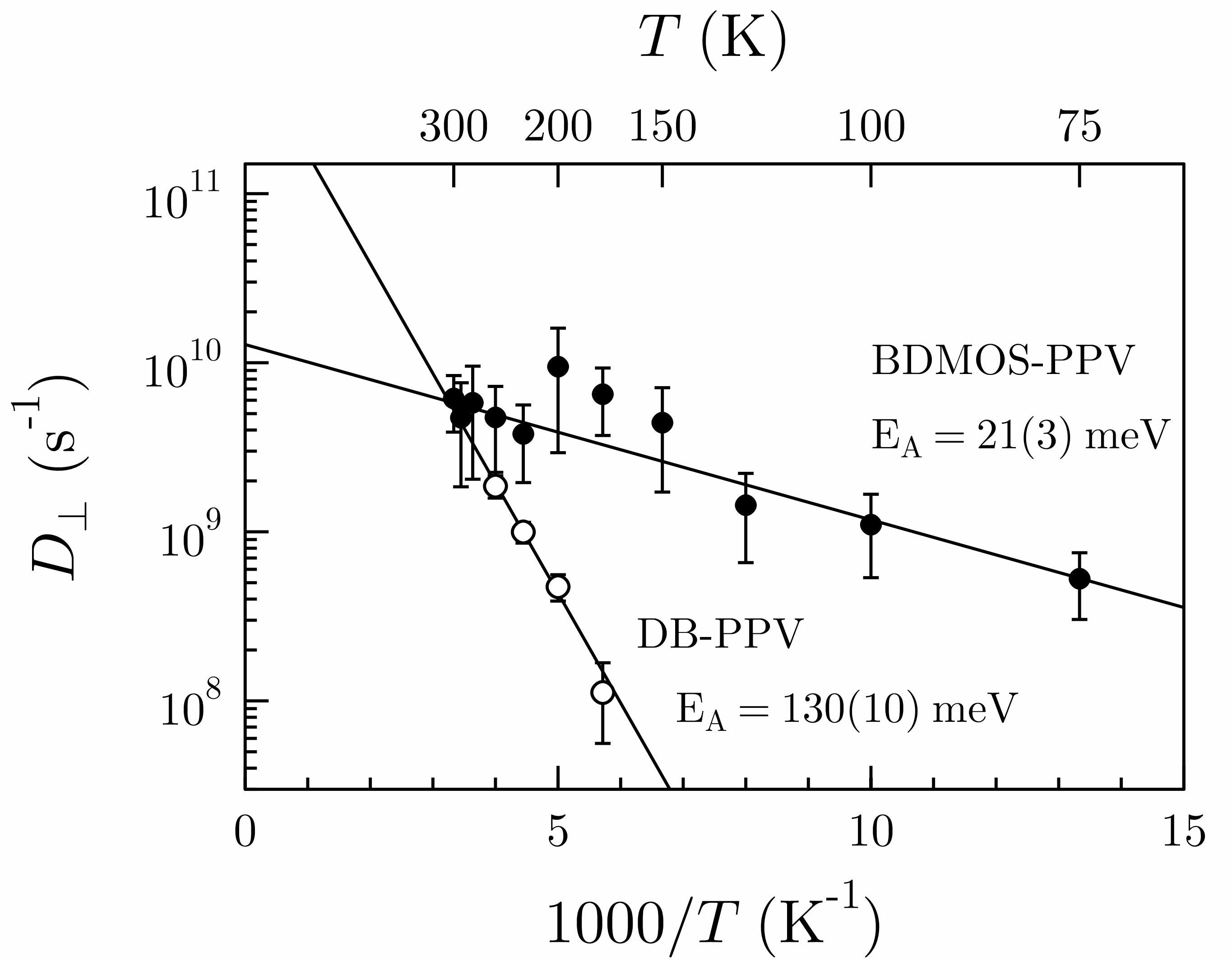
with the relaxation parameter Γ following a 1/B law at high field: $\Gamma = \frac{\omega_0^4}{2\omega_e D_\parallel^2}$

PPV - Field and Temperature Dependence





Interchain Diffusion Rate $D_\perp$



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Muons and other techniques

- Muons measure local conductivity, like NMR
- Many techniques measure bulk conductivity such as AC or DC resistivity
  - Often dominated by surface, grain boundary or trapping effects.
- Muons implanted into material
  - signal independent of temperature or magnetic field
  - independent of proton solubility
  - very low concentration limit
  - measure proton or ion conductivity even in presence of mobile electrons (metals)
- Limitations
  - Need nuclear moments in material
  - Paramagnetism causes muon relaxation - harder to analyse
  - muon may not be in equilibrium site or charge state