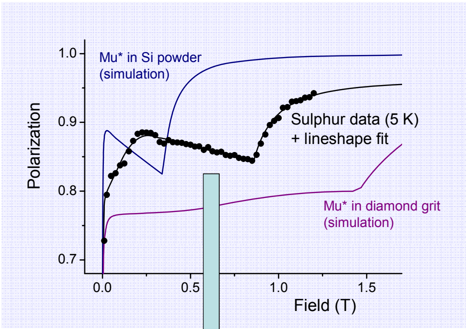
Science & Technology Facilities Council
ISIS

Muonium in sulphur — μSR's oldest puzzle*

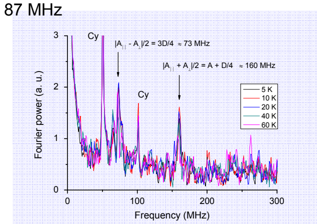
Steve Cox, James Lord, Iain McKenzie (ISIS Muon Facility), Jean-Joseph Adjizian (Sussex University), 'Jas' Jayasooriya (University of East Anglia) and Ivan Reid (Brunel University) UK

Repolarization and level-crossing resonance
(HiFi data, ISIS, 2009)



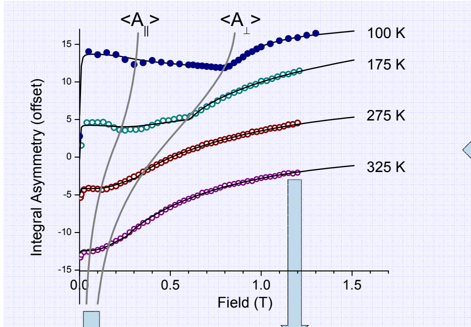
Sharp cusp, ∴ defect centre has an axial hyperfine tensor $(A_\perp, A_\perp, A_{//}) = (A-½D, A-½D, A+D)$
Steep to high-field side, ∴ A/D < 0
Cusp at 0.85 T, ∴ $A_\perp = -232$ MHz
Huge anisotropy!

$A_{//}$ can also be estimated from LF lineshape but is determined more precisely in conjunction with ZF data: $A_{//} = -87$ MHz

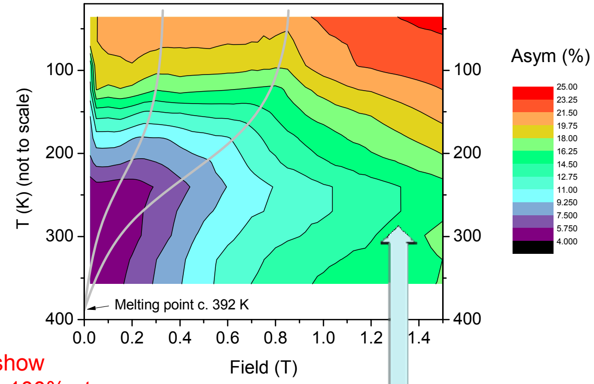


Zero-field spectrum (old GPD data, PSI, 1997!)

Extraordinary shift of resonance towards zero field, deepened by accelerating spin-lattice relaxation

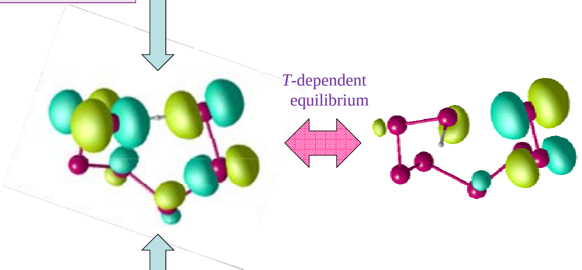


Integral asymmetry: contour plot of full data set
(12 temperatures, 5 - 350 K)



RESULT 1

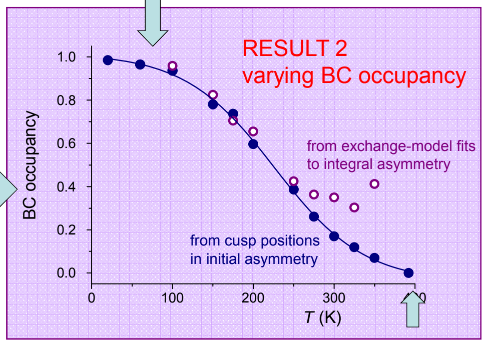
Bond-centred muonium in sulphur!



Time-average hyperfine parameters collapse to zero at MP (392 K) but fluctuating components grow, causing faster relaxation; the main $<A_\perp>_T$ cusp remains sharper in *initial* asymmetry scans, sliding towards zero field.

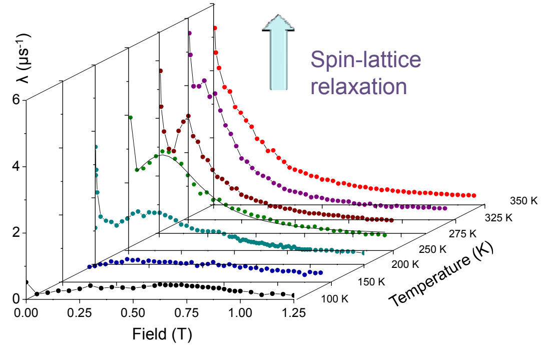
Chemical exchange or dynamical equilibrium between these structures must define the average hf parameters as well as cause such fierce spin-lattice relaxation

Fits with a 2-state exchange model show bond-centre occupancy varying from 100% at base temperature to zero at the melting point!



Melting point c. 392 K)

HiFi time-domain data shows peaks in spin-lattice relaxation rate, deepening the integral resonance and also sliding towards zero field. T_1-minima cuts suggest the exchange rate slows with T !



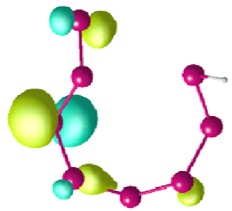
Spin-lattice relaxation

Full-lattice supercell dft calculations identify the stable site for H in orthorhombic α-octasulphur to be at the centre of a stretched S—S bond
(Aimpro calcs, Sussex Group, 2009)

But metastable structures exist with much smaller hf coupling, accessed by quite small excursions from the BC site

We envisage small-amplitude libration at low T, evolving to larger excursions with increasing temperature. Return to the BC site is necessary for intermittent hf coupling at all temperatures in the solid phase.

The chain-like species, corresponding to complete opening of the S8 ring, is the least stable structure but has negligible hf coupling. It is probably responsible for apparently 'diamagnetic' signals found in the melt.



*Low residual polarization noted by Swanson (1958); complete depolarization (in TF and ZF) claimed by Eisenstein *et al.* (1966). This solution is very different to those offered so far ... ... could it be *the* solution, at last?...