# Muonium in sulphur: $\mu$SR's oldest puzzle

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**Abstract**

New level–crossing resonance data shows the muonium defect centre in solid sulphur to have axial symmetry with huge dipolar anisotropy at low cryogenic temperatures. Above 100 K, the two principal values of the hyperfine tensor fall dramatically and *pro rata*, both apparently collapsing to zero at the melting point. The fall is accompanied by the onset of muon spin–lattice relaxation, visible on the microsecond timescale with low–field rates peaking around room temperature. In conjuction with old zero–field data, the low–$T$ hyperfine parameters are determined accurately. New supercell density–functional calculations suggest their assignment to muonium at a bond–centre (BC) site in a closed–ring $S_8Mu_{BC}$ complex. The striking decrease of time–average parameters and the appearance of fluctuations causing relaxation are attributed to a dynamic equilibrium or chemical exchange with neutral configurations having much lower hyperfine coupling, accessed by small cyclic displacements from the BC site. Time–average occupancy of this site falls with temperature and vanishes at the melting point.

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Somewhat to the embarrassment of the $\mu$SR community, the fierce depolarization of positive muons in sulphur has remained unexplained since reported as early as 1958 [1]! In this non-magnetic semiconducting element, muonium must surely be to blame, yet no entirely satisfactory model has been found for the paramagnetic defect centre or molecular radical that it might form in the solid lattice. Various studies have lately favoured interstitial SMu as the likely culprit, its hyperfine coupling matching the spectroscopy quite well and the strong spin–orbit coupling expected of this diatomic species accounting for many aspects the extraordinary spin dynamics [2], but they are far from conclusive. By the same token, the chemical fate of interstitial hydrogen or implanted protons is unknown, and has defied chemical intuition.

With the aim of finally identifying the elusive muonium centre or centres responsible, a new study of the hyperfine parameters and their variation with temperature has been undertaken on the HiFi instrument at ISIS [3], shortly after its commissioning in 2009. Figure 1(a) shows longitudinal–field (LF) data at base temperature. Level–crossing resonance is confirmed but—thanks to the stability of the HiFi instrument—is found to be much broader than previously appreciated. The sharpness of the resonance cusp at 0.855 T shows the hyperfine tensor to have almost perfect axial symmetry, and defines $|A_\perp|$ = 232.5 MHz. The steeper gradient on the high–field side indicates an oblate or 'pancake' tensor with the contact and dipolar terms of opposite signs: we anticipate that the contact term is negative, representing spin–polarization of bonding orbitals, rather than direct overlap of the singly occupied orbital onto the muon site.

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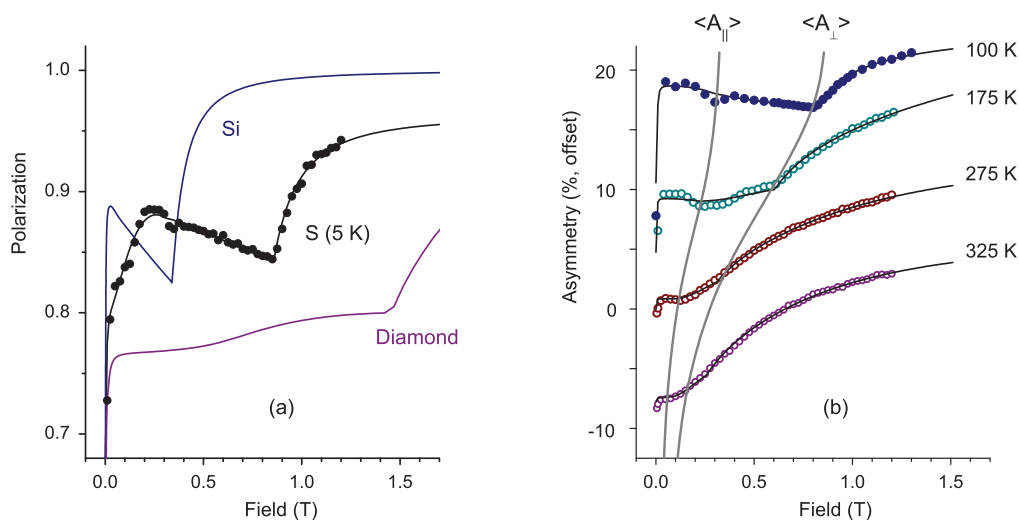[1] Now at TRIUMF, Vancouver

Figure 1: Repolarization and level–crossing resonance for the muonium defect in orthorhombic flowers of sulphur (HiFi data, December 2009). The field scan at 5 K is fitted in (a) for static hyperfine parameters. Spin–lattice relaxation is weak at this temperature but the fit includes an atomic muonium precursor (fitted lifetime 80 ps). Full repolarization is achieved assymptotically towards 3 T and there are no other significant features up to HiFi's maximum field of 5 T. Shown for comparison are simulations for Mu* or bond–centred muonium in polycrystalline silicon and diamond grit. The evolution of integral asymmetry above 100 K is illustrated in (b), fitted with the 2–state exchange model.

The low–field repolarization shows signs of an atomic muonium precursor at this temperature (5 K, also visible at 20 K), making estimation of $A_\parallel$ imprecise from this LF data alone. The HiFi discovery of such large axial anisotropy prompted us to re–examine old zero–field (ZF) spectra, however, recorded on the GPD instrument at PSI in 1997! The expected line near 233 MHz is absent in these spectra—this can now be understood as poor polarization transfer from the muonium precursor—but lines at 160 and 73 MHz are to be seen up to nearly 100 K. Belatedly assigning these to $|A_\parallel \pm A_\perp|/2$ gives, with the appropriate choice of signs, the low–temperature hyperfine parameters as

$$A_\perp \quad = \quad -232.5 \tag{1}$$

$$\text{and} \quad A_\parallel \quad = \quad -87 \quad \text{MHz.} \tag{2}$$

That is, an isotropic or contact term of $(A_\parallel + 2A_\perp)/3 = -184$ MHz and an overall dipolar anisotropy—second only to that of Mu* or bond–centred muonium in diamond—of $(A_\parallel - A_\perp) = 146$ MHz!

Above 100 K, the resonance begins to move to lower fields. Above 150 K, the shift becomes dramatic—the cusp in initial asymmetry has already fallen below 100 mT at 350 K (our highest temperature point). Such behaviour is quite unprecedented, the hyperfine parameters appearing to collapse and vanish at or near the melting point (c. 392 K)! Here we recall that only seemingly diamagnetic signals are seen, with no missing fraction, in the melt. The sliding resonance is accompanied by increasingly fast spin–lattice relaxation, however, visible in the HiFi time–domain data and peaking at some 5 $\mu s^{-1}$, in low longitudinal fields around room temperature. The effect on integral–counting data, illustrated with selected scans in figure 1(b), is to deepen the resonance as it slides towards zero field. (The full data set, including details of initial asymmetry and spin–lattice relaxation, is to be presented elsewhere [4].) We conclude that the hyperfine parameters begin to fluctuate towards 100 K, and that the fluctuations grow considerably in amplitude at higher temperatures, as the time–average values fall.

In response to these new data, and in order to build an atomistic picture of this unusual centre and its hitherto unknown hydrogen counterpart, new density–functional calculations have been undertaken at Sussex University using the AIMPRO code [5, 6]. Following earlier calculations of the cluster type [7], this is the first computational study of hydrogen in sulphur to include a supercell simulation of the solid–state chemistry. The cell contains 128 S atoms
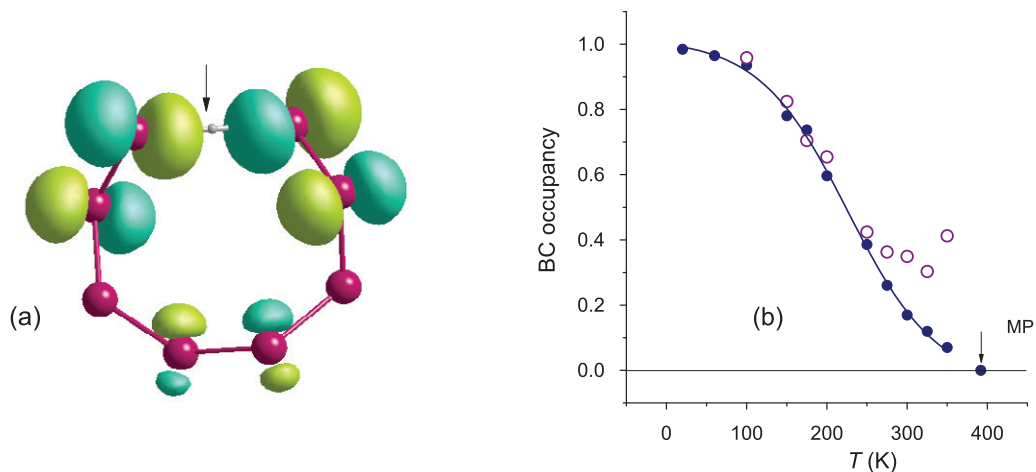
Figure 2: Bond–centred hydrogen and muonium in sulphur. The closed–ring molecular unit is shown together with its SOMO in (a); AIMPRO calculations at Sussex University (June 2010) find this to be the final chemical fate or ground state of interstitial hydrogen in orthorhombic octasulphur. Occupancy of the BC site by muonium is shown as a function of temperature in (b), deduced from the resonance cusp position in initial asymmetry (full circles, and line to guide the eye) and—somewhat less precisely—from exchange–model fits to integral data (open circles).

mimicking the orthorhombic lattice of $\alpha$–octasulphur, together with a single H atom. The neutral H atom is found to insert itself into the centre of an S–S bond of a molecular $S_8$ unit. The original bond is elongated by some 55%, but the ring structure is not broken. This bond–centred configuration proves also to be the most stable for the isolated $S_8H$ radical, though it is not so easily accessed in the vacuum–state addition reaction. In the full–lattice supercell, the bond centre (BC) site is reached easily from various starting positions. Interstitial sites and bridging structures are unstable.

We assign the low–temperature resonance of figure 1 to the muonium counterpart of this bond–centred structure, denoting the local unit $S_8Mu_{BC}$. This is our first main result. Local electronic structure is illustrated with an image of the singly occupied molecular orbital (the SOMO) in figure 2(a). Proton hyperfine parameters calculated in an all–electron local reconstruction [8], and scaled simply for the muon magnetic moment, give a dipolar term close to our experimental value but underestimate the contact or spin-polarization term. The values have so far only been computed for equilibrium geometry, however, i.e. without regard to quantum structure or hyperfine isotope effects due to the different zero–point energies of proton and muon. The SOMO image, together with calculated $^{33}S$ hyperfine parameters, suggest that some 60% of the unpaired electron spin density is located in p orbitals on the nearest–neighbour S atoms. Overall, the resemblance to bond–centred muonium or Mu* in Si, Ge, etc., is remarkable, considering the very different coordination of the surrounding lattice.

Various metastable configurations also emerge in the present calculations, corresponding to different degrees of strain or opening of the local ring structure. All of these have hyperfine parameters very much smaller than those of the ground state and several are reached with quite small displacements of the proton or muon from the bond–centre site. The extraordinary spin dynamics can then be explained if the bond–centred ground state dominates below 100 K but an increasing admixture of one or more of the metastable states develops at higher temperature. The position of the resonance cusp is then a simple measure of the BC occupancy. Displayed in figure 2(b), this is our second main result.

A gradual opening of the ring with increasing temperature does not explain the data; a fast chemical exchange or dynamic equilibrium between the different structures is needed, with intermittent hyperfine coupling causing spin

relaxation, as the BC site is revisited. Simplifying this situation to a 2–state model, with parameters set to the low–$T$ values (1,2) for State 1 and to zero for State 2, allows the integral data to be fitted and the time–domain relaxation to be modelled. For instance, the forward and backward transition rates are then equal, with fitted values near $50\,\mathrm{ns}^{-1}$, where the cusp has fallen to half field just above $200\,\mathrm{K}$. At higher temperatures the return transition rate and the overall cycle rate both appear to slow down—a result already suggested by the unusual shift of $T_1$ minima in the relaxation–rate data. This may indicate that more and more configurations of similar energy are accessed around room temperature. The chain–like species S–$S_6$–SMu corresponding to complete opening of the ring proves to be the least stable structure in the present calculations, though it may well be responsible for the seemingly diamagnetic $\mu$SR signal seen in the melt.

Our chemical exchange model is distinct from the charge exchange known to cause strong spin relaxation for muonium in Si, Ge, etc. The band–gap is $2.8\,\mathrm{eV}$ in S, so there are no conduction electrons at room temperature. Nor should $S_8Mu_{BC}$ ionize at accessible temperatures: our calculations suggest a defect level below mid–gap, some $0.9\,\mathrm{eV}$ above the valence band maximum. In our chemical exchange between neutral species, the spin–state of the unpaired electron is not randomized at each cycle, as it would be by capture and loss of successive electrons; it retains a memory of its evolution from one cycle to another. This provides a better—though not perfect—modelling of the field–dependence of relaxation rate. It is true that radiolytic electrons may not disperse so readily in sulphur as in other semiconductors, tending to self–trap as $S_8^-$ anions, so charge fluctuation of the form $S_8^- + Mu^+ \rightleftharpoons S_8Mu$ would show identical behaviour, but it seems less likely.

In conclusion, we offer a new solution to $\mu$SR's oldest puzzle, very different from those advanced previously. LF and ZF spectra are assigned to bond–centred muonium, identified for the first time in sulphur by the present calculations. Fast libration about this site, evolving to a slower opening and closing of the molecular ring, accounts for a broad peak in spin–lattice relaxation rate around room temparature and a remarkable collapse in time–average hyperfine coupling towards the melting point. This model appears at last to explain all the accumulated $\mu$SR data on sulphur, old and new [4]. Whilst the dynamics will be somewhat different, it seems likely that the bond–centre model describes the ground state of monatomic H in the other Group–VI semiconductors, Se and Te, too.

[1] R.A. Swanson *Phys. Rev.* **112** (1958) 580—the first '$\mu$SR' survey of simple materials,
    published the year after the classic papers on parity violation in muon decay and conjectures of muonium formation!
[2] S.F.J. Cox *Rep. Prog. Phys.* **72** (2009) 116501—see section 6 of this recent review, plus references therein.
[3] J.S. Lord, I. McKenzie, P.J. Baker, S.J. Blundell et al. *Rev. Sci. Instr.* (submitted April 2011)
[4] S.F.J. Cox, J.S. Lord, I. McKenzie, J–J Adjizian et al. *J. Phys. Condensed Matter* (a fuller account of the present work,
    and its relation to earlier data, submitted April 2011)
[5] P.R. Briddon and R. Jones *Phys. Stat. Solidi B* **217** (2000) 131
[6] J.P. Goss, M.J. Shaw and P.R. Briddon P R *Topics in Applied Physics* **104** (2007) 69
[7] R.M. Macrae *Physica B* **404** (2009) 862 (Proc. $\mu$SR'08 Tsukuba), plus references to earlier computational studies therein
[8] M.J. Rayson 2007 *Phys. Rev. E* **76** 026704

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*Author email address not to be published, please: bona fide correspondence is welcome at the postal address given.*
*The authors also make a special request to retain the English spelling of 'sulphur'! Thank you.*