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Muonium and Hydrogen Defect Centres in Solids

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MUONIUM AND HYDROGEN DEFECT CENTRES IN SOLIDS

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ABSTRACT

Hydrogen and its light isotope, muonium, may both be observed in insulating crystals as trapped interstitial atoms. Their difference in mass gives rise to a small dynamic isotope effect in hyperfine coupling constant and a large difference in diffusive behaviour – muonium showing in some lattices a striking minimum in mobility versus temperature.

Muonium may still be detected as isolated paramagnetic centres in the semiconductors whereas information on hydrogen in these materials is restricted to diamagnetic states in association with other impurities. Arguably one of the most significant findings of the μ SR technique is the coexistence of two distinct types of muonium centre in many of the tetrahedrally co-ordinated lattices.

In literature spanning more than a decade, the isotropic state was described as “normal” muonium and assigned to the tetrahedral interstitial site, while the nature of the “anomalous” anisotropic state remained a puzzle. Within the last few years the situation has entirely reversed: the anisotropic state has been recognised as the more stable of the two and its electronic structure and (bond-centre) location have been well established, whereas the precise location of the isotropic state and the nature of its metastability have become open questions.

1. VACUUM STATE MUONIUM

As far as atomic, solid state and chemical physics are concerned, the positive muon behaves like a light weight proton. Emphasizing this behaviour, it is able to bind an electron to form a hydrogen-like atom, μ^+e^- . This is known as muonium, and given the chemical symbol Mu. It contrasts with positronium in having an essentially central nucleus – the electron reduced mass is only 0.5% lower than in protium – so that its size and binding energy are very similar to those of ordinary atomic hydrogen and its more familiar heavy isotopes (Table 1).

| | | |
|---------|----------------------|---|
| μ^+ | Charge | $Q_\mu = 1 = Q_p$ |
| | Spin | $I_\mu = 1/2 = I_p$ |
| | Mass | $m_\mu = 0.11 (\approx 1/9)m_p$ |
| | Magnetic moment | $\mu_\mu = 3.18 \mu_p$ |
| Mu | Bohr radius | $a = 1.004a_0$ |
| | Ionisation potential | $I = 0.9961I_H$ |
| | Hyperfine constant | $A = 4.46\text{GHz} \approx (\mu_\mu/\mu_p)A_H$ |

TABLE 1. Properties of the positive muon, referred to those of the proton, and properties of (vacuum state) muonium, referred to those of protium.

Muonium shares with positronium the property of being an all leptonic system, however, and as such lends itself to extremely accurate QED calculations of its spectroscopic constants /1/. In hydrogen, these are limited by uncertainties in the proton size. Measurements of the muonium Rydberg constant and Lamb shift are as yet far from being precise enough to test the theory, although the relevant transitions (Figure 1) have been detected /2,3/. More ambitious measurements are in progress.

In these experiments the muon acquires an electron in passage through a thin target. Fine silica powder yields thermalised muonium which escapes or is ejected into the surrounding vacuum; thin metallic foil gives some admixture of excited states.

Figure 1. Energy level diagrams for atomic muonium, including hyperfine splittings (not to scale!). The $n=1$ to $n=2$ separation (the Rydberg constant) and the $n=2$ splitting (the Lamb shift) are shown and refer to the experiments mentioned in Section 1. The diagram is schematically equivalent to that for atomic hydrogen.

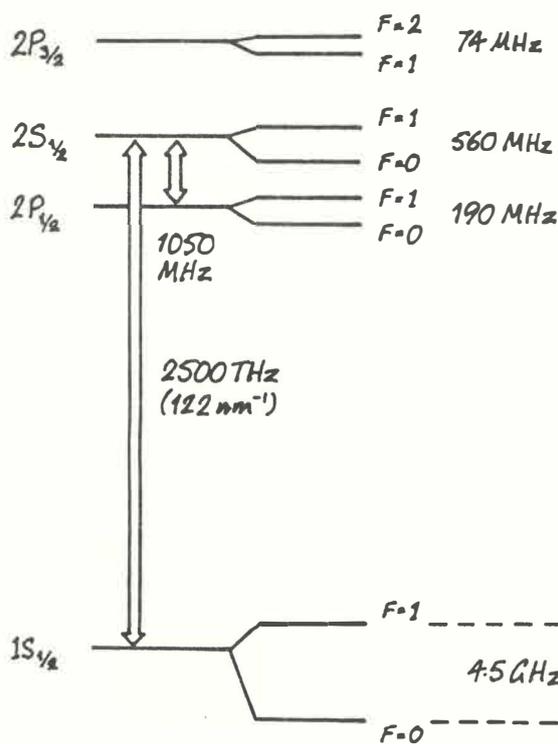
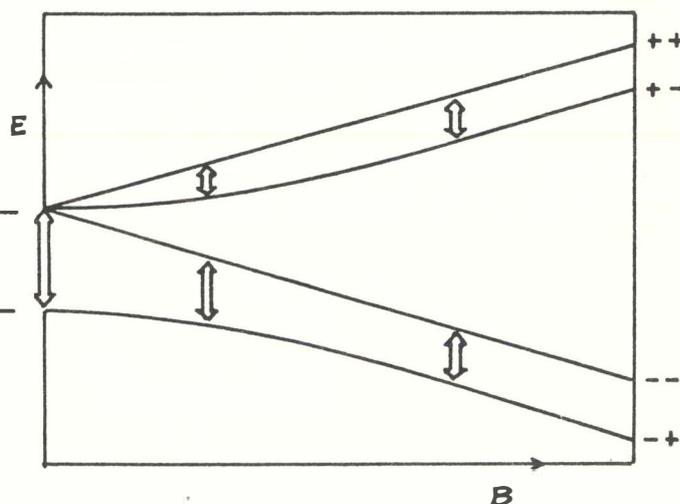


Figure 2. The hyperfine and Zeeman splittings of muonium in its ground state. A schematically equivalent diagram is valid for muonium in solids, in the case that the hyperfine interaction is isotropic and there is no interaction with other nuclear spins. μ SR spectroscopy of isotropic muonium centres in solids (Section 3 et seq) makes use of all the transitions indicated, although only the high field transitions may be detectable in the presence of super-hyperfine interactions.



2. HYPERFINE CONSTANT

The most precise spectroscopic measurement to date is of the muon-electron hyperfine coupling constant in the ground state. From the frequencies of the high-field transitions in

Figure 2, induced by microwave resonance on muonium formed by stopping muons in a low pressure gas, Caspersen et al./4/ obtained the value

$$A = 4.463\,302\,88\,(16)\text{ GHz (0.04ppm)}.$$

The remainder of this Lecture is concerned with muonium formed by stopping or thermalising muons in bulk solid media. For this purpose such precision is not required; the hyperfine constant of the free atom serves as a reference point and is essentially equal to that of free hydrogen, scaled by the ratio of magnetic moments of the muon and proton.

3. MUONIUM IN SOLIDS: SYSTEMATICS OF THE HYPERFINE CONSTANT

Values of hyperfine constant for muonium in a variety of solids are reported in Figure 3, scaled to the free atom value. This represents the data of various different groups, working world wide, though the precision measurements are principally from the Zurich group. Measurements are made from the μ SR precession frequencies detected in high field, intermediate field or (most directly) zero field; the transitions involved are indicated in Figure 2 and the techniques described elsewhere /5,6/.

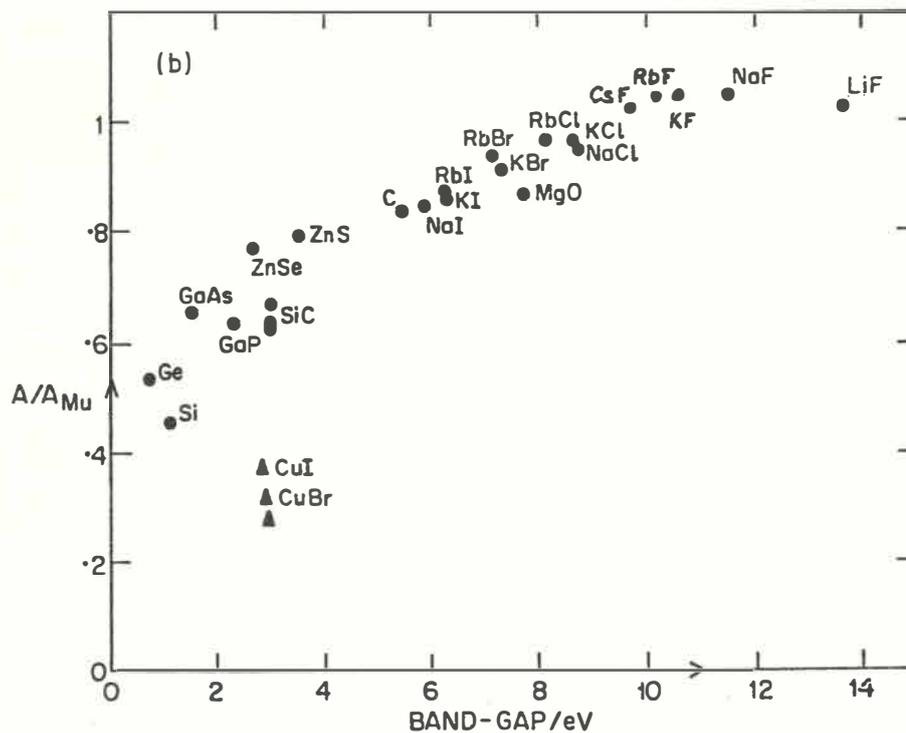


Figure 3. Hyperfine constants for isotropic muonium centres in various crystalline solids, scaled to the free atom value as a measure of "spin density" on the muon. The correlation with band-gap of the host material is taken from /6/, which contains references to the original measurements.

Values close to the free atom value (unity in Figure 3) indicate that the muonium, though trapped at interstitial sites in the crystal lattices, is only weakly perturbed by the host. Values slightly greater than unity must indicate that the hydrogen-like atom is slightly compressed or

squeezed in the interstitial cages: spin density is enhanced at the nucleus (the interstitial muon) as though the electronic wave function were forbidden to overlap with surrounding atoms in the most ionic hosts (the alkali fluorides). Slightly lower values suggest instead a dilation of the atom, i.e. overlap of the wavefunction onto the neighbours.

The substantial lowering of hyperfine constant in the semiconductors, to around 50% of the free atom value in silicon and germanium, must correspond to a very considerable overlap or delocalisation in these (covalent) lattices: a molecular orbital is now required to describe the electronic structure of these defect centres (see Section 7).

4. NOMENCLATURE

No entirely satisfactory (i.e. monotonic) correlation of hyperfine constant with an electronic property of the host material has been discovered. Ionicity, for instance, cannot be a relevant parameter since such similar couplings are found in diamond (perfectly covalent with tetrahedral co-ordination) and in MgO (highly ionic with octahedral co-ordination). A broad correlation with band gap, illustrated in Figure 3, is found for many of the centres /6/; it is reasonable to suppose that these have a fundamentally similar electronic structure and in the following they are designated Mu' centres (reserving plain Mu for the free atom). The scheme fails to embrace the data for the cuprous halides, which suggests that in these materials the electronic structure of the muonium defect centres is rather different; they are therefore distinguished by the symbol Mu''.

There are no such paramagnetic centres in metals, i.e. no states in which a magnetic moment is centred on the muon or proton. In metals, muonium and hydrogen adopt diamagnetic states. Conduction electrons are attracted to the positive charge of the interstitial muon or proton, screening the Coulomb potential so that a bound state with a particular electron is impossible /7/. In Figure 3, metals could be represented at the origin! The hyperfine or contact interaction which arises from a polarisation of the screening charge in magnetic metals, and the very high muon Knight shift in some semimetals which suggests incipient muonium formation, are dealt with elsewhere /6/.

The nature of the Mu' and Mu'' centres is examined in Sections 5-9. Not represented in Figure 3 are the highly anisotropic muonium centres which also exist in certain materials: these are commonly designated Mu* and are the subject of Sections 10-13.

5. COMPARISON WITH HYDROGEN

Hydrogen defect centres are well known in the oxides and halides: these are the traditional hosts for their study by ESR and optical spectroscopy /7/. The systematics of the hyperfine coupling from host to host are similar, but the absolute values of spin density are consistently lower (by about 5%) for muonium than for hydrogen /8/. This can be understood by the greater zero-point energy and vibrational amplitude or spread of the lighter particle. The muon explores more of the interstitial cavity in which it is confined than does the proton. It is on average slightly closer to the neighbouring atoms and forces greater overlap or delocalisation of its electronic wavefunction onto them.

Most interestingly, however, no such hydrogen defect centres are known in the semiconductors. Referring to Figure 3, this seems strange, since there is evidently no qualitative or step change in the nature of muonium centres on going from the octahedrally to the tetrahedrally co-ordinated lattices. Yet the hydrogen analogues have not been reported, either in the elemental (GroupIV) or compound (III-V) semiconductors; muonium appears to be a unique substitute for paramagnetic hydrogen in these cases.

Hydrogen is known to be present in diamagnetic states, however, especially in the compound semiconductors, and its existence in electronic grade material is now understood to be important. It is inevitably incorporated in material produced by the reaction of hydride gases and is in fact essential for the compensation or passivation of electrically active impurities - the non-observation of paramagnetic hydrogen is undoubtedly related to this point, which is examined in Section 14. The first exploratory μ SR studies on an amorphous semiconductor (α -Si:H, which contains a lot of hydrogen) are summarised in Section 15.

6. MUONIUM DIFFUSION

A recent and particularly elegant contribution to this field is a study of the diffusion, as opposed to the spectroscopy, of muonium in solids. In these experiments the relaxation time T_1 of the muon Zeeman energy is measured as a function of temperature. The relaxation is induced by fluctuations of the superhyperfine interaction with neighbouring nuclei as the muonium moves from site to site. A minimum of T_1 (well known in conventional magnetic resonance) is expected when the hop rate matches a transition frequency of the muon spin. Two such minima are observed, moving apart in temperature as the working field is increased. This implies that the muonium mobility itself goes through a minimum at a particular temperature and increases above and below this temperature (Figure 4). Results are available for various alkali halides and for a compound semiconductor /9/; these constitute a striking demonstration of the diffusive behaviour of a "small polaron" defect and the measurements will undoubtedly be extended to many other systems.

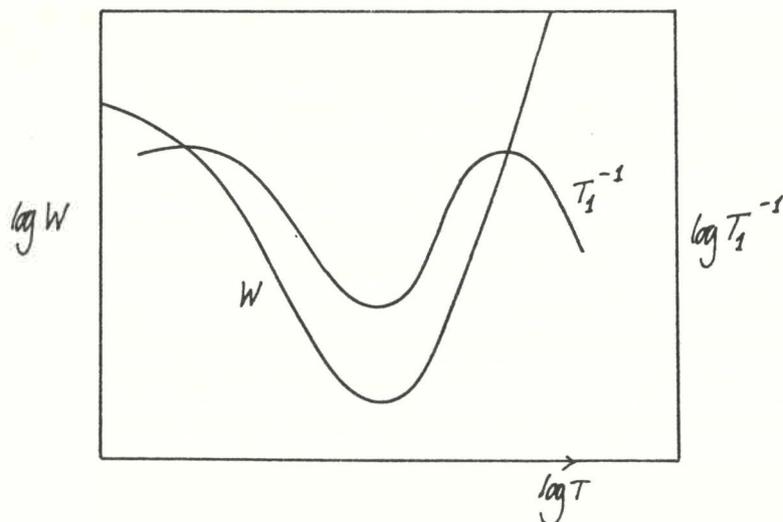


Figure 4. Behaviour of the muon spin-lattice relaxation rate T_1^{-1} for the case that the muonium hop rate W exhibits a minimum. (Sketched from /9/; the mobility minimum is at 50K in the "insulator" KCl and 90K in the "semiconductor" GaAs.

7. NATURE OF THE Mu' CENTRES IN SEMICONDUCTORS

The muonium defect centres represented in Figure 3 have muon-electron hyperfine couplings which are essentially isotropic. For a given material, their characteristic frequencies in the μ SR spectra are the same for all orientations of a single-crystal sample and may be detected equally well in polycrystalline or powder samples. These centres were assumed by all authors in the early μ SR literature to be located at the tetrahedral cage centre (Figure 5a), this being the only site with the necessary cubic symmetry. An objection was raised on chemical grounds by Cox and Symons (1986) /10/ who pointed out the tendency for muonium to react and bond with one of its nearest neighbours, weakening the in-line Si-Si bond and displacing the muon from the tetrahedral (T) site to an off-centre or antibonding (AB) site, as in Figure 5(b). The term "antibonding" emphasises how the unpaired electron delocalises via the vacant antibonding orbital on the Si-Si pair.

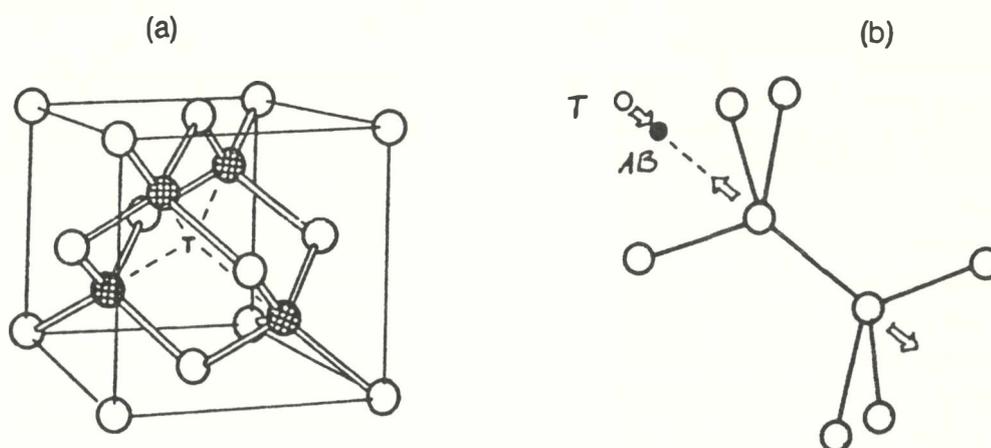


Figure 5. The diamond-type lattice showing a tetrahedral (body centre) interstitial site (a); the four nearest neighbours (nn) are shown shaded. Weakening of a Si-Si bond as the muonium (or hydrogen) is moved from the tetrahedral (T) to an antibonding (AB) site closer to one of these neighbours is detailed in (b).

There is at present no consensus on this point. In quantum chemical calculations performed on clusters of atoms, simulating the crystal lattice and defect centre, little relaxation of the tetrahedral cage is found when the muon or proton is placed and held at the cage centre - the T site /11/. Most authors have been content to leave it at that. Calculations of the potential surface on which the muon or proton move and seek their equilibrium position inevitably give a broad minimum at the T site, as in Figure 6(a), when relaxations of the neighbouring atoms are ignored or constrained to tetrahedral symmetry. Without this constraint, calculations become more expensive in terms of computer time, but tend to bear out the chemical expectation: some authors find local minima at the AB sites /12/; others, however, find only a saddle point /13/. The location and metastability (See Section 14) of the Mu' centres have therefore become open questions.

8. DYNAMICAL MODELS

An instantaneous location for the muon which is displaced from the T site would imply some sort of dynamical averaging to secure the effective isotropy of the hyperfine coupling. Various

possibilities are illustrated in Figure 6. Either there is a broad minimum of potential energy at the T-site, or local minima at the AB sites which are not deep enough to localise the muon. It is interesting to conjecture whether they are deep enough to localise protons, however, for which the zero point of energy is lower by a factor $(m_p/m_\mu)^{1/2} \approx 3$; this would also explain why isotropic hydrogen centres have not been observed in semiconductors!

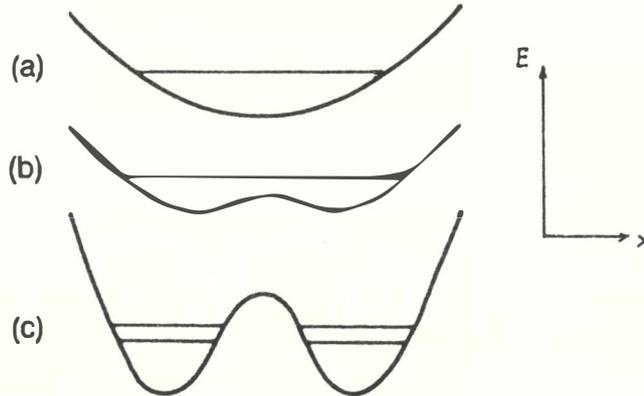


Figure 6. Potential energy surface and ground state energy for interstitial muonium. For simplicity, the surface is represented in one dimension with a broad minimum at the T site in (a), and with local minima of increasing depth off-set towards neighbouring atoms in (b) and (c). (There would be four such minima in the 3-D surface). In (a) and (b) the muon is delocalised over the cage by virtue of its zero point energy. In (c) the local minima are deep enough to contain the zero point energy but the degeneracy of levels in adjacent wells is lifted by tunneling.

Hyperfine coupling, as well as equilibrium geometry and energy, can in principle be obtained in calculations which do not use spin-restricted wave functions. Of especial interest would be values which are correctly averaged over the spread in position of the muon or proton. Calculations in which the muon (or proton) is held static at the T-site consistently overestimate the contact interaction, often giving values larger than for the free atoms themselves. This is itself an indication of the necessity for dynamical models, since spin density on the muon (or proton) is expected to fall off as the particle moves towards a neighbouring atom. The vibrational averages should more realistically model the measured couplings, as well as the isotope effect between muonium and hydrogen.

9. THE Mu^{\bullet} CENTRES

The muonium centres detected in the cuprous halides appear from Figure 3 to have a fundamentally different character to those in other materials, especially when they are considered as I-VII compounds and contrasted with the alkali halides! The cuprous halides are unusual materials in several respects, including the fact that they have vacant cation s-states lying energetically close to the top of the valence band. A CuMu^+ radical-cation model has been proposed for these centres /10/. It also implies that the muon will be instantaneously displaced towards a Cu^+ neighbour.

Cuprous chloride is interesting in that two distinct Mu^+ centres are observed, with slightly different hyperfine couplings – both isotropic /14/. Level crossing resonance experiments confirm that for *both* centres the muon has four equivalent copper neighbours /15/. This result is consistent with the situation represented in Figure 6(c), in which the two centres would correspond to the two distinct tunneling states.

These spectra are surely the most beautiful in the μSR literature; an example is reproduced in Figure 7.

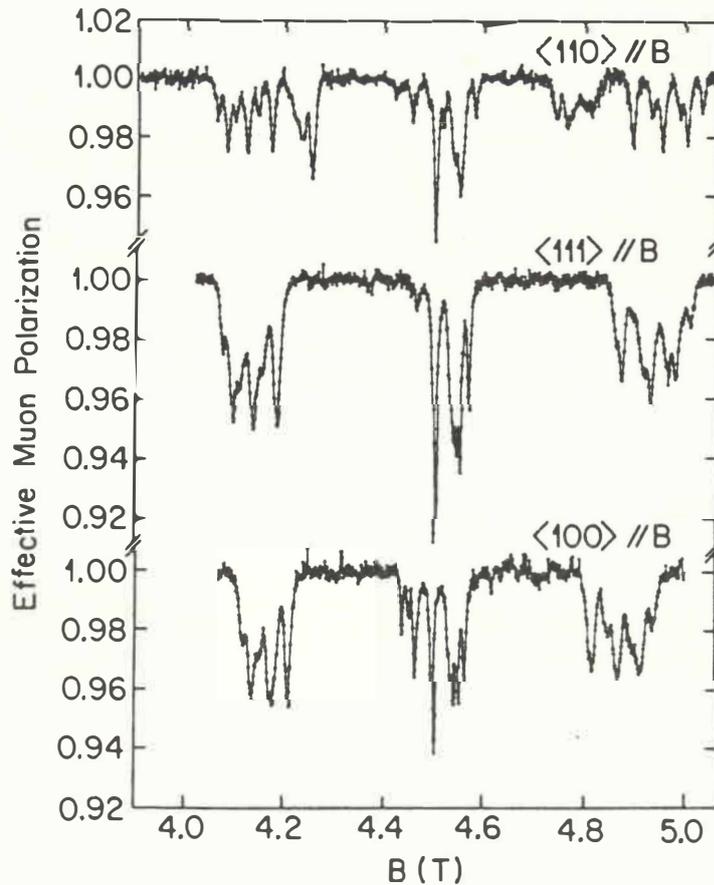


Figure 7. Level crossing resonance spectrum for one of the Mu^+ centres in CuCl reproduced from the thesis of Schneider (1990); see also Schneider et al. /15/. The spectrum represents resonant polarisation transfer from the muon to the neighbouring nuclei.

10. THE Mu^* CENTRES IN SEMICONDUCTORS

As if the observation of hydrogen-like defect centres was not already enough, μSR experiments have also demonstrated that a second type of muonium defect centre is formed in some of the semiconductors /16/. This was quite unexpected; it constituted a real scoop for the μSR technique. For the second type of centre, known as Mu^* , the hyperfine coupling is smaller again, and highly anisotropic. A characteristic spectrum is shown in Figure 8.

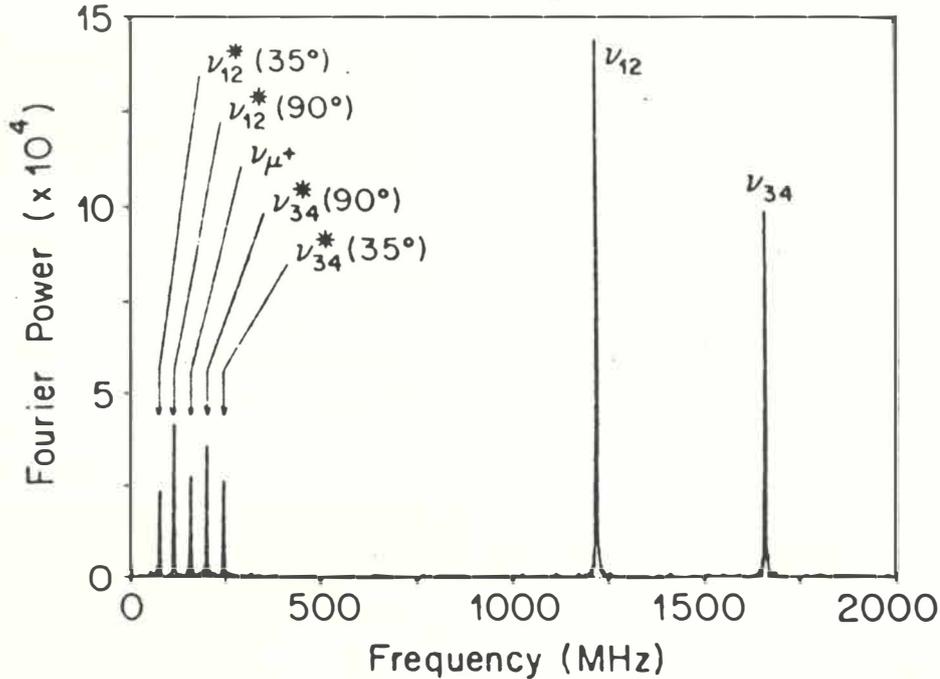


Figure 8. The μ SR spectrum of GaAs (taken from /17/), showing frequencies corresponding to the Mu' and Mu^* centres (a). The Mu' frequencies are independent of crystal orientation so that the hyperfine coupling is isotropic as implied in the Breit-Rabi diagram of Figure 2. The Mu^* frequencies vary strongly with orientation, indicating an anisotropic coupling /18/.

Such centres are formed in the Group IV elements with the diamond-type lattice, i.e. Si and Ge as well as diamond itself. They are also formed in most of the compound semiconductors having tetrahedral co-ordination (the "zincblende" structure), namely the III-V's GaAs and GaP and the II-VI's ZnSe and (zincblende itself) ZnS /18/. Although dubbed "anomalous muonium" in the early literature, the Mu^* centres are now thought to be to be more stable than the Mu' . That is, the isotropic centres are only metastable (both types are formed by muon implantation and they coexist at low temperature). Thermal conversion of Mu' to Mu^* has been observed directly, both in diamond and in silicon /19/.

11. THE BOND-CENTRE MODEL FOR Mu^*

Deduction of the spin Hamiltonian parameters for the various Mu^* centres from their orientation-dependent μ SR spectra is one of μ SR's most elegant and important achievements /18/. It is instructive to go further, and to decompose the principal values of the hyperfine tensor into isotropic and dipolar terms:

$$A_{\text{iso}} = 1/3(A_{\parallel} + 2A_{\perp}) \text{ and } B = 1/3(A_{\parallel} - A_{\perp}).$$

The isotropic term is then found to be negligible compared with its value for the Mu' centres. There is therefore virtually no contact interaction - the electronic density $|\psi_e|^2$ is extremely

small at the muon site. The dipolar term is surprisingly large, however, and indicates that the unpaired electron is nonetheless localised very close nearby - along a $\langle 111 \rangle$ direction from the muon.

These considerations led Cox and Symons /10/ to propose a bond-centre location for the muon, together with a molecular orbital model for the electronic structure which is illustrated in Figure 9(b). The singly occupied molecular orbital (SOMO) is non-bonding on the muon: it is antisymmetric about this location, which accounts for the negligible contact interaction. The unpaired electron is localised close by, as required, spending half its time on each nearest neighbour in this simplified 3-centre model. The SOMO may be thought of as deriving from the antibonding orbital of the original Si-Si pair (Figure 9a); the original bond must be stretched by about 40% to accommodate the muon so this orbital is lowered and detached from the conduction band. In other words, the neighbouring atoms relax from their normal positions and a localised electron state is created at the defect.

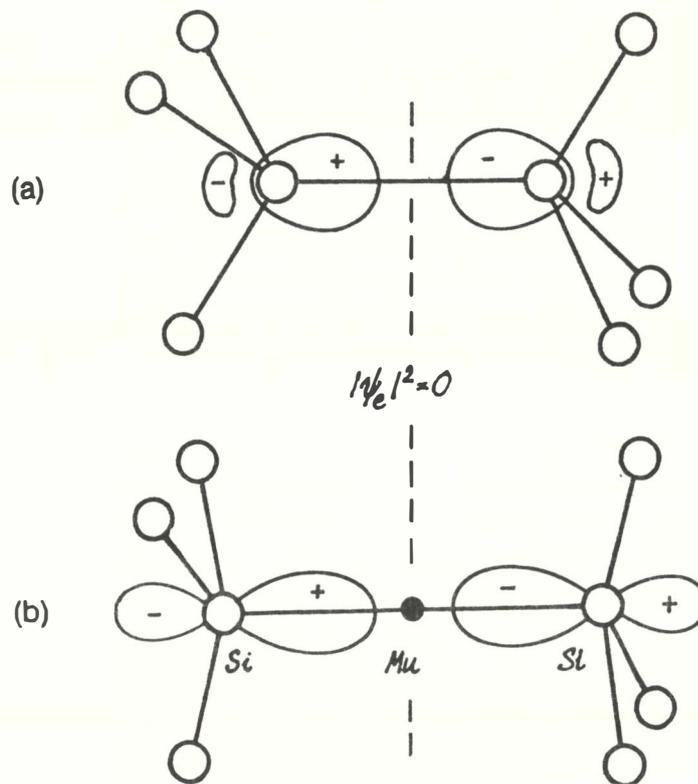


Figure 9. Bond-centre location for the muon in the Mu* centres depicting the undisturbed lattice before the arrival of the muon in (a), and the relaxation required to accommodate the muon in (b). The vacant antibonding orbital on the central Si-Si pair in (a) and the singly occupied molecular orbital for Mu* in (b) are sketched to show the nodal plane through this site.

Although greeted initially with considerable scepticism, the bond-centre model for Mu* is now thoroughly substantiated, both by experiment and theory! The experimental support is summarised by Estle and Kiefl /20/, in a short compendium which nicely updates the comprehensive review of early work given by Patterson /18/.

12. LEVEL CROSSING RESONANCE

The most compelling evidence comes from Level Crossing Resonance (LCR) experiments in GaAs and GaP, which are able to map out the electronic spin density on the atoms neighbouring the defect centre /21/. The findings may be summarised as follows (orbital populations are estimated using $a_s^2 = A_{iso}/A_0$ and $a_p^2 = 2B/2B_0$, where A_0 and B_0 are atomic values):

| Mu* in GaAs : | | | Mu* in Si : | |
|-----------------|-------|------|-----------------|-----|
| | nn Ga | nnAs | each nn Si | |
| a_s^2 | 8% | 2% | a_s^2 | 2% |
| a_p^2 | 30% | 43% | a_p^2 | 19% |
| $a_s^2 + a_p^2$ | 38% | 45% | $a_s^2 + a_p^2$ | 21% |
| a_p^2/a_s^2 | 4 | 23 | a_p^2/a_s^2 | 10 |

The essential feature is that over 80% (38% + 45%) of the spin density is located on the two nearest neighbours (so that the 3-centre model is a remarkably good approximation). The p/s ratios should be compared with the value for sp^3 hybrid co-ordination; they give an indication of the local distortion of the lattice. The greater s-character on Ga and p-character on As is also understandable in this slightly ionic material.

In silicon, delocalisation onto the surrounding lattice is evidently greater: LCR accounts for only 50% of the spin density on the nearest and next nearest neighbours. These experiments are harder in this material since only 5% of the nuclei (^{29}Si) possess a nuclear spin; the low isotopic abundance may be turned to advantage in interpreting the intensities of satellite lines in the μSR precession spectra, however – a procedure which also confirms the bond-centre site by demonstrating that the muon has two equivalent close neighbours.

13. QUANTUM MECHANICAL CALCULATIONS

The experimental findings and the qualitative molecular orbital model have stimulated quantitative quantum mechanical calculations by a number of groups /22/. These include cluster calculations using ab initio (e.g. Hartree Fock) or local density functional methods as well as supercell calculations using local density functional methods. All of these methods give results for the equilibrium configuration and energy; the more detailed produce a three dimensional potential energy surface on which the muon (or proton) finds its equilibrium position. Those which are not spin restricted also give results for the hyperfine parameters. All authors agree that the bond-centre location is the global minimum for the neutral interstitial defect, muonium or hydrogen, both for the elemental and for the compound semiconductors.

The earlier calculations identified an energy barrier between the T site and the BC site, qualitatively consistent with the metastability of Mu' and the thermal conversion of Mu' to Mu^* . In the light of the uncertainty now surrounding the precise location of Mu' (Section 7), details of the route to the BC site need to be re-evaluated. The basic picture is undoubtedly correct, however,

namely that Mu' is a mobile species moving between the open spaces of the interstitial cages and carrying only a small lattice distortion, and that an energy barrier has to be surmounted before the more stable bond-centred location, with its huge associated relaxation, can be reached. This barrier is the energy required to stretch the intrinsic bond so that the muon can be accommodated.

14. HYDROGEN, METASTABILITY, AND ASSOCIATION WITH OTHER IMPURITIES

μSR experiments have focused on the paramagnetic (neutral) states of muonium since comparatively little information is available on the diamagnetic state or states. Theoretical treatments for hydrogen, on the other hand, have addressed all possible charge states. The findings of various authors /23/ are summarised in Figure 10. The bond-centre site remains stable in p-type silicon, but the defect becomes positively charged (H^+). The cage interstitial site is only stable in n-type material, and then only as the negative charge state (H^-). This explains how hydrogen is so efficient in the compensation of electrically active impurities in semiconductors, and gives a clue as to why the isotropic paramagnetic state corresponding to Mu' has not been detected: the microsecond timescale of the μSR techniques is required to display this metastable state. Even the neutral bond-centre state is electronically or structurally unstable in the presence of other impurities, which is probably why illumination of the sample is needed to display the hydrogen analogue of Mu^* /24/.

Assuming these considerations carry over to pionium ($\pi^+ e^-$), ionisation provides an alternative explanation of the site change under illumination for pions in germanium, demonstrated by channeling experiments /25/. This result could simply represent the preferred locations of the various charge states.

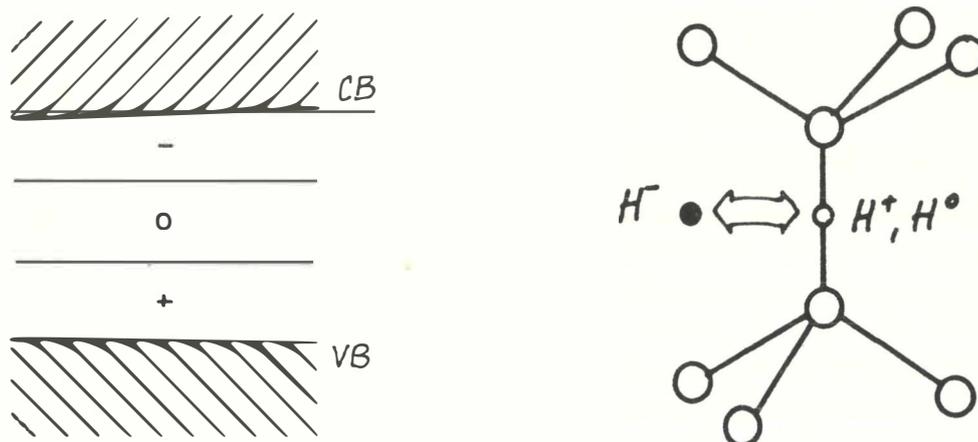


Figure 10. Variation of the location and charge state of interstitial hydrogen with Fermi energy /23/. The energy gap is divided into three zones. When the Fermi energy lies in the upper zone H^- is stable at a tetrahedral cage centre; when it lies in the lower zone, H^+ is stable at a bond-centre. H^0 is stable at a bond-centre in intrinsic material, i.e. when the Fermi energy is at mid-gap.

These compensation processes can in principle occur even if the hydrogen or muonium is spatially remote from the other impurities – it is the “recombination” mechanisms and rates which determine the metastable lifetimes of the muonium states. Structural equilibrium in the presence of other impurities (as for annealed material) is illustrated in Figure 11. Here the hydrogen is physically adjacent to the other impurities. In the case of shallow donors, the impurities are passivated. That is, electrically active levels are removed entirely from the energy gap. The stability of these complexes is predicted by various authors and there is now direct evidence for their existence from IR spectroscopy /23,26/.

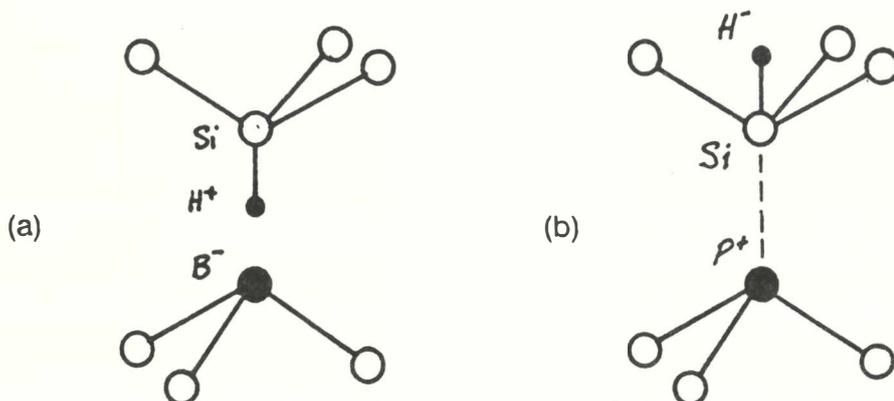


Figure 11. Hydrogen-impurity complexes. An acceptor (eg B in Si) may be compensated by electron transfer from hydrogen at an adjacent bond-centre (a); a donor (eg P in Si) may be passivated by transfer of an electron to hydrogen at a nearby antibonding site (b) /23,26/.

15. AMORPHOUS SILICON

What becomes of the Mu' , Mu^* and diamagnetic states on going from crystalline to amorphous material? The random network of amorphous silicon, for instance, might be expected to provide a variety of environments for Mu' (through the variety of cage sizes) and also for Mu^* (through the existence of strained Si-Si bonds). The possible locations are illustrated in Figure 12. Preliminary experiments on amorphous hydrogenated silicon (a-Si:H) suggest that

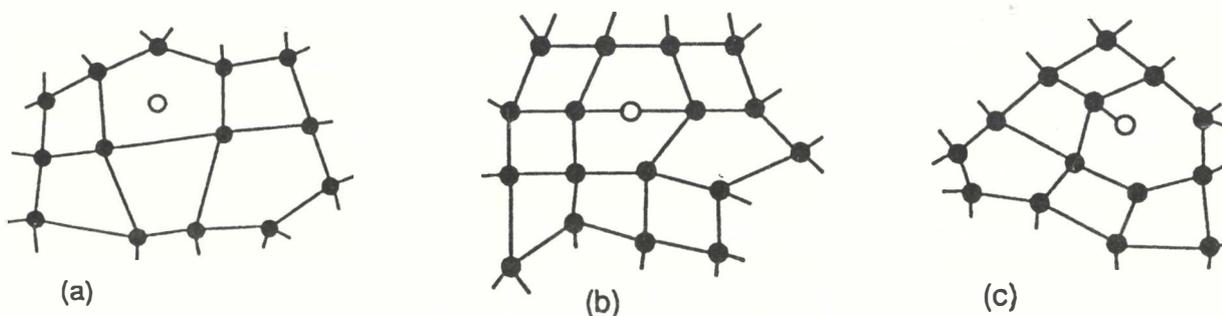


Figure 12. Schematic (2-dimensional) representation of amorphous silicon depicting proton or muon sites within cages (a), at bond-centres (b) or saturating dangling bonds (c)

both the Mu^* and diamagnetic fractions are enhanced at the expense of Mu' /27/. The increased Mu^* fraction can be attributed to easier formation of the bond-centred defect in the presence of weakened Si-Si bonds. The increased diamagnetic fraction is unlikely to represent trapping at dangling bonds since very few Si atoms remain undercoordinated in hydrogenated material (this role of hydrogen in passivating electrically active centres is in fact essential in electronic grade amorphous silicon); probably the diamagnetic fraction in both the amorphous and crystalline materials is ionised Mu^* . Evidence for a Mu' fraction in a-Si:H is to date inconclusive; it may be that the loss of periodicity greatly curtails the Mu' mobility - to the point where it becomes stuck at a particular site and is no longer isotropic - or indeed that rapid conversion to Mu^* is facilitated in the disordered structure.

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