Studies of Hydrogen in Semiconductors Using the Positive Muon as a Proton Analogue [and Discussion]

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Studies of hydrogen in semiconductors using the positive muon as a proton analogue

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Implanted in a material, the positive muon mimics the proton in its chemical and elastic interactions. In non-metals it can pick up an electron to form *muonium*, Mu $= [\mu^+ e^-]$, which behaves as a light isotope of hydrogen. This may be observed with remarkable sensitivity by the μSR techniques (muon rotation, relaxation and resonance), whereas hydrogen, when present only as a trace impurity, may be difficult or impossible to detect by conventional spectroscopies. Much of the structural information on isolated hydrogen defect centres in semiconductors has in fact come from μSR studies of their muonium counterparts: particularly important has been the discovery of metastability and identification of the bond-centred state. Current studies are of both fundamental and technological interest and concern the interplay of site and charge state, the trapping and detrapping of carriers at these deep level centres, and the nature of interstitial diffusion. Extension to the modelling of hydrogen *passivation* in doped material, the development of optical and IR spectroscopy and of thin-film or surface studies, all appear timely and promising.

1. Hydrogen in materials

The subject of 'hydrogen in materials' could cover systems where hydrogen is an intrinsic ingredient as well as those where it is a deliberate additive or an unavoidable impurity. In this summary overview, attention is focused on systems where hydrogen forms defect or impurity centres, in the sense that its presence perturbs the host system, since these are generally the systems where its properties and behaviour are least well understood. (The definition need not be exclusive, however, and many of the concepts and techniques introduced apply equally to materials where hydrogen is a stoichiometric ingredient.)

Even as a defect centre, the concentration of hydrogen can vary widely, and its effect on the desired properties of the material may be in some cases beneficial and in others deleterious. Thus in metals and alloys to be used as hydrogen storage media, high solubility and fast interstitial diffusion are desirable, whereas the requirements are exactly opposite for the material of storage vessels. Likewise protonic conduction must be optimized in oxides to be used as solid electrolytes or fuel cell media, whereas in other materials proton activity must be minimized or suppressed if it leads to corrosion or the degradation of mechanical properties. In semiconductors, the passivation of dangling bonds by hydrogen in amorphous silicon is essential for the production of electronic grade material, whereas the

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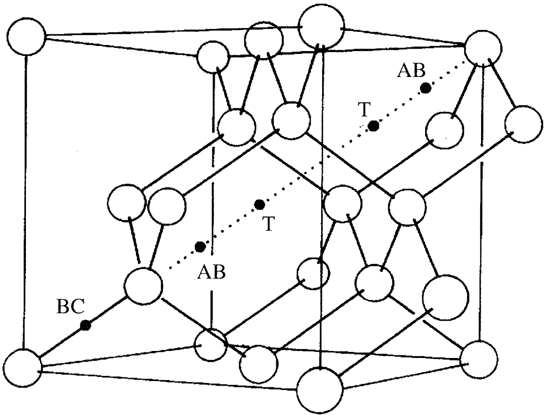

Figure 1. The diamond-type lattice of tetrahedrally coordinated semiconductors, depicting the sites considered in the text (along a single cube diagonal: T, tetrahedral cage centre; AB, anti-bonding or back-bonding site; BC, bond centre).

accidental passivation of electrically active dopants in crystalline semiconductors can have serious consequences for device performance.

Alas, we are given little encouragement nowadays to study phenomena merely because they are interesting! But from a fundamental point of view, hydrogen defect centres represent model systems which are sufficiently simple to encourage calculations of electronic structure and dynamical behaviour from first principles. The apparent simplicity is deceptive, however, and the semiconductors in particular provide a good illustration of the variety of states which hydrogen can adopt and the complexity of the interplay between site and charge state.

Referring to figure 1, a characterization of interstitial hydrogen requires determination of its preferred locations for each charge state, H^+, H^0 and H^-, the associated lattice distortions and local distributions of charge density (and, for H^0, spin density), the mobility and thermal stability of each state, etc., as well as the eventual interaction with other defects and impurities, especially substitutional dopants.

2. Muonium and μSR spectroscopy

Although invariably present in crystalline semiconductors, as a trace impurity hydrogen can be difficult to study directly by conventional spectroscopies. Several of its possible states were in fact identified and characterized in studies of their counterparts formed by the pseudo-isotope known as *muonium*. This article examines the validity of the analogy, and the extent to which muonium serves as a model for hydrogen in solids.

In muonium, Mu = $[\mu^+ e^-]$, the positive muon plays the role of atomic nucleus. This elementary particle has the same charge as the proton but about one ninth the mass. The muon also has the same spin 1/2 as the proton, with about three times the magnetic moment, and so responds to the local magnetic and hyperfine fields in a similar manner. This is the basis for the spectroscopy known as μSR, which stands for *muon spin rotation, relaxation and resonance* and covers the various ways in which muon polarization can evolve in different types of experiment (see Brewer *et al.* 1975; Schenck 1985; Cox 1987*a*). There are similarities here with conventional magnetic resonance, characteristic frequencies of the spin transitions giving information on structure and spin-lattice relaxation rates providing additional information, notably on dynamics and excitations. It is the experimental details which are unconventional. μSR experiments must be performed at those accelerator laboratories where suitable low energy muon beams are available; the muons are *implanted* in the materials of interest. They are produced with inherently high polarization from the decay of pions (themselves produced when a target of graphite or other light element is exposed to a sufficiently energetic primary proton beam): the polarization can be as high as 100% on implantation. Muons are themselves unstable particles, decaying radioactively to positrons with a lifetime of 2.2 μs. The β-emission is not isotropic but is strongest in the direction of the polarization vector, the degree of asymmetry providing a measure of the magnitude of the polarization (the *forward–backward* asymmetry is about 2:1 for 100% polarization).

The μSR methods therefore exploit both examples of parity violation in the decay chain $\pi^+ \rightarrow \mu^+ \rightarrow e^+$, the first to prepare the muon polarization and the second to analyse it. Monitored as a function of time following implantation, a diminishing asymmetry signal reflects how the muon spins exchange polarization with neighbouring spins or come to thermal equilibrium with the lattice. This is muon spin *relaxation*. Precession or oscillation of some component of the polarization in magnetic or hyperfine fields results in oscillatory signals referred to as muon spin *rotation*. These signals resemble the free induction decays of conventional magnetic resonance. Muon spin *resonance* covers the depolarization which can be induced by an RF or microwave field or by resonant cross relaxation to neighbouring spins. This latter technique is known as *level crossing resonance* (Abragam 1984) and allows a selective sampling of the charge or spin density distribution in the muon's vicinity. Combined with the techniques of single-particle detection the result is a remarkably high sensitivity *per spin*: spectra can be accumulated from 10^6–10^9 recorded muon decays (typically in minutes or hours at modern sources, depending on the nature of the experiment). An example of each type of spectrum is given in the figures below.

3. Paramagnetic states: metastability

An important early discovery was that two distinct paramagnetic states of muonium are formed in silicon and coexist at low temperature. Figure 2 shows their distinctive muon spin rotation spectra (Brewer *et al.* 1973). One of these states, originally called 'normal muonium', is characterized by a muon–electron hyperfine interaction which is isotropic; it is therefore generally described as a muonium atom located at the tetrahedral cage-centre or T-site – the spacious interstitial site of highest symmetry in the diamond-type lattice. This assignment is by no means firm: the state is highly mobile, so the motion could be between sites of lower symmetry, such as to average out any anisotropy. Indeed, there are grounds for supposing that the antibonding (AB) sites are involved (Cox & Symons 1986; Cox *et al.* 1990*a*), notably the fact that this muonium is anything but 'normal' – its hyperfine constant is only about half the vacuum-state value. Delocalization of the electron wavefunction is far greater than occurs, for instance, for the trapped atom state of hydrogen in oxides or halides. The contrast with

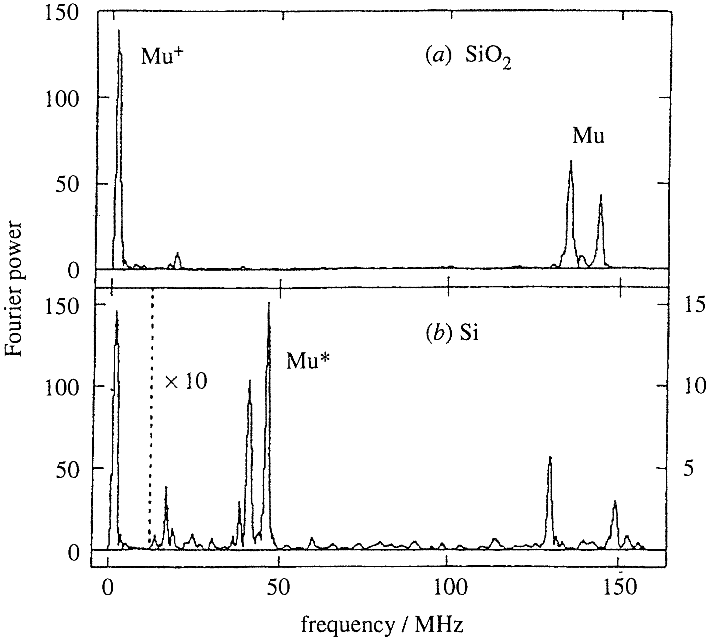

Figure 2. Comparison of the μSR spectra of (a) SiO_2 and (b) Si. These are Fourier transforms of the muon spin rotation signals. The pair of lines at high frequency, common to the two spectra, characterizes the isotropic state, with the different splittings indicating a much lower hyperfine constant for muonium in Si than for the trapped atom state in SiO_2. The additional lines at low frequency indicate coexistence of another (anisotropic) centre in Si, denoted Mu* (Brewer *et al.* 1973). (The diamagnetic signals – muons precessing at their Larmor frequency, denoted Mu^+ – are also visible.)

the trapped atom state of muonium in quartz is apparent between the spectra of figure 2*a*, *b*.

Figure 2*b* is the classic spectrum which revealed the presence of a second state. Quite unanticipated, this state was originally dubbed 'anomalous muonium' or Mu* (pronounced mu-star). It exhibits a hyperfine interaction which is smaller again and highly anisotropic, with axial symmetry about the $\langle 1\,1\,1\rangle$ or bond directions (Patterson 1988). Its structure remained a puzzle for many years until a model was proposed with the muon located at the *centre* of a stretched silicon–silicon bond (Cox & Symons 1986). The unpaired electron occupies an orbital whose wavefunction is antisymmetric about the muon site, as in figure 3*a*, and so is is non-bonding on the muon. Derived from the Si–Si antibonding orbital, such an orbital accounts for the relaxation of the bond, allowing the muon to be accommodated, and also for the low spin density at the muon site: the wavefunction has a node at the bond centre. Confirmation and acceptance of the model had to wait for measurements, by level crossing resonance, of how spin density is distributed on neighbouring nuclei, first in GaAs and GaP, where dipolar nuclei are naturally abundant (Kiefl *et al.* 1987), and more recently in Si, using the scarce ^{29}Si nuclei (Kiefl *et al.* 1988): the relevant spectrum is reproduced in figure 3*b*. Such spectra have now even been recorded for Mu* in diamond, suitably enriched with ^{13}C (Schneider *et al.* 1994).

In the following, the cage-centred state is denoted Mu^0_T and the bond-centred

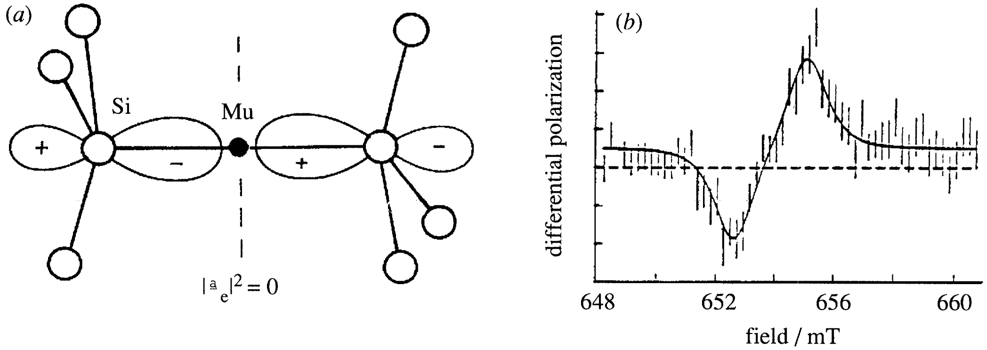

Figure 3. The bond-centre model for Mu* (Cox & Symons 1986), showing the singly occupied molecular orbital derived from the Si–Si antibonding orbital (*a*). The level crossing resonance which confirms the model by determining spin density on the nearest neighbour ^{29}Si nuclei (Kiefl *et al.* 1988) is reproduced in (*b*).

state $\mathrm{Mu}^0_{\mathrm{BC}}$, the superscript denoting the neutral charge state (the single unpaired electron offsets the muon's positive charge) and the subscript the site according to the notation of figure 1. A considerable zero-point uncertainty in the muon's position about these nominal sites must be noted, given the light mass of the muon (as well as a correspondingly smaller, but still significant, delocalization for the proton in the equivalent states of hydrogen, see figures 4 and 7 below). The coexistence of $\mathrm{Mu}^0_{\mathrm{T}}$ and $\mathrm{Mu}^0_{\mathrm{BC}}$ at low temperature (up to about 150 K) is a remarkable example of metastability in a defect centre. The analogous hydrogen states had not been observed at the time of the μSR discoveries. The bond-centred state has since been detected by ESR under suitable conditions (Gorelkinskii & Nevinnyi 1987, 1991) and identified with the donor level of hydrogen in silicon (Holme *et al.* 1991; Bech Nielsen *et al.* 1994). The existence of an acceptor level has lately been reported, inferred from somewhat controversial electrical measurements, and attributed to the cage-centred state (Johnson *et al.* 1994).

4. Ionic states: bistability

There is general agreement now, on the basis of theoretical studies, that the bond centre is the more stable of the two locations for hydrogen in silicon, but the difficulty in reaching this consensus reflects the fact that the calculated potential energy surface is actually rather flat for the neutral species. (The energy difference between $\mathrm{Mu}^0_{\mathrm{T}}$ and $\mathrm{Mu}^0_{\mathrm{BC}}$ is already less in Si than in diamond and may be inverted in Ge and GaAs (Estreicher 1994).) For the ionic counterparts of these states, the theoretical predictions are more clear cut, and there is little doubt that the positive ions should be located at the bond centre (denoted, therefore, $\mathrm{Mu}^+_{\mathrm{BC}}$ and $\mathrm{H}^+_{\mathrm{BC}}$) and the negative ions at the cage centre ($\mathrm{Mu}^-_{\mathrm{T}}$ and $\mathrm{H}^-_{\mathrm{T}}$) (Van de Walle *et al.* 1989; Briddon & Jones 1990). By implication, loss of an electron from $\mathrm{Mu}^0_{\mathrm{T}}$ or $\mathrm{H}^0_{\mathrm{T}}$ should incur a site change of the muon or proton, providing an interesting example of *bistability*. The major lattice relaxation is associated with the bond-centred location. Figure 4 shows energy level schemes of the types commonly used for deep-level centres, indicating the qualitative features required to describe hydrogen and muonium properties and the correspondence between

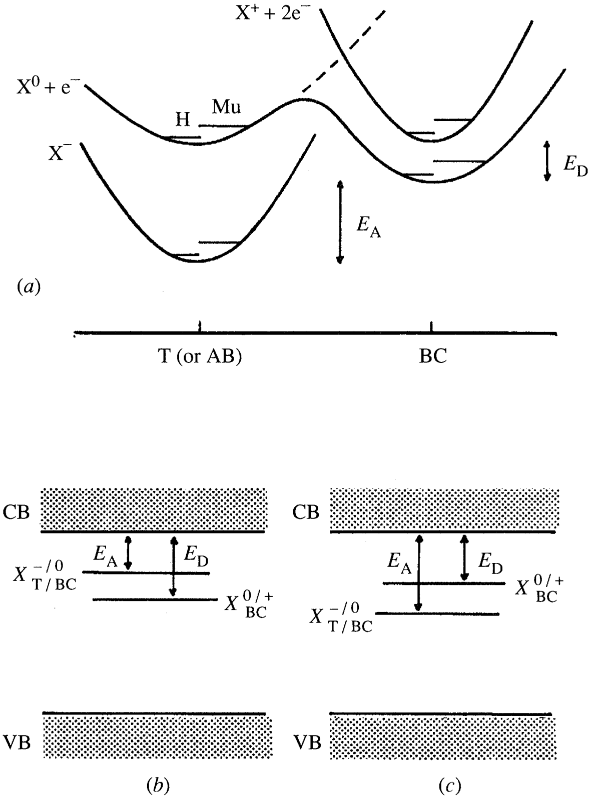

Figure 4. Energy levels for the hydrogen or muonium states (X = H, Mu). In (*a*), the variation of total energy is sketched with a configuration coordinate, subsuming lattice relaxation, which takes the proton or muon from the T (or, possibly, AB) to the BC site. The dashed line indicates that the BC site is unfavourable without lattice relaxation. A comparison of the energy of different charge states is permitted by including the energy of electrons ($+e^-$ and $+2e^-$) in the conduction band as appropriate; this suggests construction of the corresponding donor and acceptor levels in the energy gap as in (*b*) for 'positive-U', $E_D > E_A$ or in (*c*) for 'negative-U', $E_D < E_A$.

the two representations.† A question of current debate is how hydrogen may act as a deep donor or a deep acceptor, according to its position in the lattice, and whether the effective electron–electron correlation energy is positive or negative. If it is positive, the three states H^+_{BC}, H^0_{BC} and H^-_T should be stabilized in turn, as the Fermi level is moved upwards through the gap by doping. If it is negative, there is no position of the Fermi level for which singly occupied levels are stable. In either case, observation of Mu^0_{BC} and Mu^0_T together in μSR spectra implies that thermodynamic equilibrium is not achieved on the timescale of muon lifetime.

The ionic states are diamagnetic, i.e. have no unpaired electrons in the muon's vicinity. $Mu^-_T = [\mu ee]$ can be compared to a hydride ion with the two electrons spin-paired. Mu^+_{BC} has the molecular orbital of figure 3*a* empty of electrons but

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† To emphasize their importance, zero-point energies are shown explicitly on potential energy surfaces common to the two isotopes (see also figure 7). Another approach, perhaps better since the normal modes are not quite identical for H and Mu, would be to include zero-point energy in the *total* energy, giving slightly different curves for X = H and X = Mu.

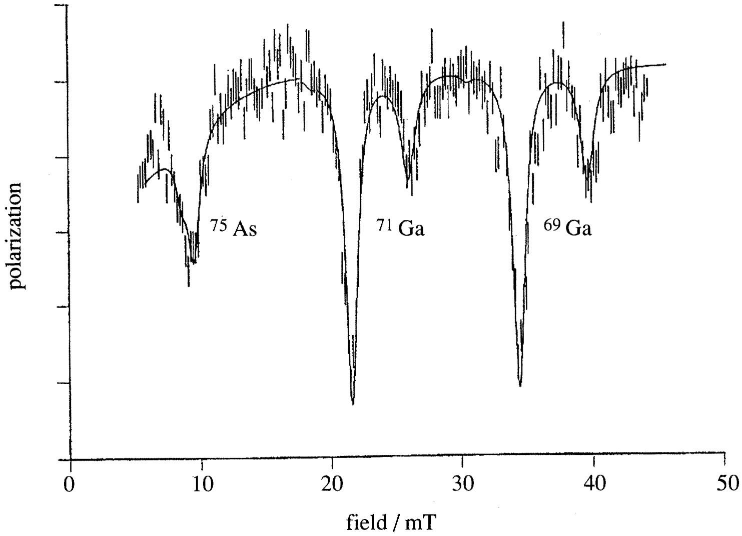

Figure 5. Level crossing resonance spectrum for the diamagnetic muonium state in heavily doped n-type GaAs, characterizing the quadrupole interactions on Ga and As nuclei neighbouring the muon site (Chow *et al.* 1995).

is in no sense a free muon, since it is located in a region of high electronic charge density formed by the Si–Si bonding electrons. The absence of a hyperfine interaction means that the diamagnetic states are not easily identified from the muon spin rotation spectra: the muon spins precess at a value close to their Larmor frequency.‡ However, quadrupole interactions can provide the necessary signature via level crossing resonance. In this technique, the muon Zeeman energy is tuned with the magnetic field to match the combined Zeeman and quadrupole energy on surrounding nuclei (Abragam 1984). Polarization transfer is then displayed as resonant dips in the muon decay asymmetry. (This is one of the simplest forms of μSR experiment, for which a time-average measurement of muon polarization is adequate.) Silicon contains no quadrupolar nuclei, but all the abundant nuclei in GaAs are suitable. The spectrum of figure 5 was obtained recently for highly doped n-type GaAs and can be assigned, almost certainly, to the Mu_T^- centre (Chow *et al.* 1995).

5. Excitations

(*a*) *Radiolysis and formation; low energy muon beams*

Details of the mechanism by which muonium is formed and thermalized shortly after muon implantation are uncertain. Probably the muon captures one of the electrons which are generated radiolytically by the implantation process itself, in competition with electron–hole recombination or exciton formation. The radiolysis products must disperse promptly, since there is no evidence that they

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‡ Chemical shifts of the precession frequency are expected to be small, with resolution limited by the muon lifetime. None the less it would be worth examining whether any are measurable in the μSR spectra, especially whether any difference can be discerned between highly doped n-type material (favouring formation of Mu^-) and highly doped p-type material (favouring formation of Mu^+).

influence the spectroscopy of the detected muonium states.† This conclusion is important if muonium spectroscopy is to be used to infer the electronic structure of hydrogen centres.

Further clues as to the role and importance of radiolysis may be forthcoming when muon beams of much lower energy become available. These should allow determination of the energy at which the partition between Mu_T^0 and $\mathrm{Mu}_\mathrm{BC}^0$ is decided irreversibly. The incident kinetic energy of the muons in beams in common use is close to 4 MeV so that the muons penetrate to the bulk of the sample (typically to a few tenths of a millimetre). Schemes for the production of slow muon beams are currently under evaluation, with penetration depths estimated as 1000 Å at 10 keV, 10 Å at 100 eV and perhaps lower values possible (Morenzoni *et al.* 1992, 1994). These developments should open up studies of muonium behaviour in thin epitaxial layers and even of surface muonium states.

(*b*) *Conversion and the role of phonons*

Whatever the details of formation, the coexistence of Mu_T^0 and $\mathrm{Mu}_\mathrm{BC}^0$ shows that some effective barrier exists to conversion from the metastable to the stable state. Illustrated in figure 4*a*, this barrier is associated with lattice response or relaxation, since a bond must be stretched to accommodate $\mathrm{Mu}_\mathrm{BC}^0$ or squeezed to expel it.† Thermal conversion of Mu_T^0 to $\mathrm{Mu}_\mathrm{BC}^0$ has been demonstrated explicitly in diamond (Odermatt *et al.* 1986) and indirectly in Si (Westhauser *et al.* 1986; Lichti, this volume), confirming that the bond-centred state is the more stable in these materials and demonstrating the role of phonons in assisting or preparing the lattice relaxation.

(*c*) *Ionization and recombination*

As the temperature is raised, the precession signals of the paramagnetic muonium states are lost as these states become ionized. Just above the ionization threshold, the resultant diamagnetic signal shows negligible spin–spin or spin–lattice coupling, but at higher temperatures a strong depolarization sets in, which appears in the raw data as in figure 6*a*. This can be understood as electrons hopping on and off the muon, reforming paramagnetic muonium for short but recurrent intervals: the hyperfine interaction with a succession of uncorrelated electron spins provides a powerful mechanism of muon spin relaxation.

(The onset temperatures are 400 K in Si and 220 K in Ge, that is, roughly in the ratio of the band gaps and corresponding to equivalent carrier concentrations. This indicates that thermal carriers are involved, and experiments with doped material suggest that the dominant process is the capture and loss of electrons at Mu^+, rather than of holes at Mu^- (Chow *et al.* 1993; Lichti, this volume).)

A surprising result is that the hyperfine coupling involved corresponds to Mu_T^0,

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† An attractive feature of an entity such as [μeh] is the additional dilation of the muonium wavefunction: could this account for the low temperature anomaly in the hyperfine constant reported for muonium in Si (Patterson 1988), the hole detrapping above about 50 K? As a rule, however, the simplicity of the muonium spectra and their similarity in semiconductors with direct bandgap such as GaAs and indirect bandgap such as Si must exclude the formation of exciton-related complexes.

† The bond centre site appears inaccessible in calculations which do not admit lattice relaxation (Mainwood & Stoneham 1984) yet the barrier is underestimated in those which assume complete instantaneous or classical relaxation (Van de Walle *et al.* 1989; Johnson *et al.* 1994), so it appears that the effective barrier relates to the timescale of the heavy atom response.

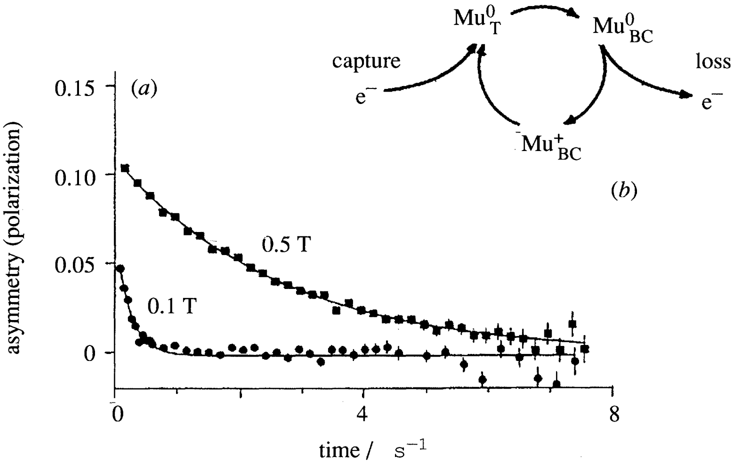

Figure 6. Muon spin relaxation in Si (*a*) due to repeated trapping and detrapping of carriers (at 600 K, for two values of applied magnetic field; Chow *et al.* 1993). Analysis of the variation of relaxation rate with temperature and applied magnetic field leads to a picture of a cycle (*b*) involving electron capture and ionization with associated site changes (Lichti, this volume).

so that the muon must spend significant time away from the bond centre, even though both the neutral and positive charge states are expected to prefer this site. (Spin or charge exchange relaxation involving Mu^0_{BC} is seen, at lower temperature, in n-type Si (Lichti, this volume).) The finding that the electron capture is an activated process suggests strongly that a change of charge state is accompanied by a change of crystallographic site: the simplest scheme consistent with the data is a cycle between three states, as depicted in figure 6*b*. A detailed analysis determines the relative energy levels of the states involved and the energy barriers between them, providing quantitative parameters for the configurational coordinate diagram (Lichti, this volume).

(*d*) *Illumination*

Of the various possibilities for external excitation of the muonium states, RF resonance is by far the furthest advanced. Typical spectra are given by Kreitzman (1990). The technique has the advantage over muon spin rotation experiments that the states displayed need not be formed promptly. It can analyse for states formed after some delay, e.g. after chemical reaction or thermal conversion. These experiments have made an invaluable contribution to understanding muonium state dynamics in crystalline silicon (Lichti, this volume) and have also revealed muonium spectra in amorphous material, a-Si and a-Si:H (Davis *et al.* 1991).

Optical illumination has received some attention, but so far only with coarse wavelength resolution and with only time-integrated signals reported (Major *et al.* 1992).† The apparent decrease in intensity of the integrated signal of all three muonium states (Mu^0_T, Mu^0_{BC} and diamagnetic) is undoubtedly due to enhanced relaxation by photo-generated carriers; this must now be compared systematically with the effects of thermally generated carriers. It is noteworthy that the

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† *Note added in proof.* See also Iwanowski *et al.* (1994), and, for the first reported time-domain signals under illumination, Kadono *et al.* (1994).

ESR spectrum of H^0_{BC} (the bond-centred state of hydrogen, known as the AA9 centre (Gorelkinskii & Nevinnyi 1987, 1991; Bech Nielsen *et al.* 1994)) is only seen under suitable illumination, so that optically induced changes of site, configuration or charge state may reasonably be anticipated. Of particular interest would be to combine the information on optical transitions ('vertical' transitions in figure 4*a*, at constant lattice configuration) with the threshold energies deduced from electrical and thermal excitation to map out a fuller version of the configuration coordinate diagram. Particularly important would be a μSR determination of the donor level (figure 4*b*, *c*). In due course it should be possible to relate all these parameters to the results of electrical and other measurements for the heavier hydrogen isotopes. (Although keeping in mind the differences in zero point energies between muon, proton and deuteron, the propensity of the muon to tunnel through energy barriers (see § 7, below) and the timescales of the various experimental techniques, this will be a formidable task!)

(*e*) *A proposal for infrared spectroscopy*

Vibrational spectroscopy is widely used to characterize defect centres, yet its feasibility has scarcely been considered for muonium. This may be because the muonium centres are not formed in sufficient concentration, even with pulsed beams, to allow conventional absorption or emission techniques. However, for those states where (non-centrosymmetric) geometry permits IR excitation, a form of trigger detection could be envisaged in which the μSR signal is monitored while a laser frequency is swept to excite a vibrational transition (Cox 1987*b*). Since the hyperfine frequencies are highly sensitive to vibrational state, it would be possible to detect the excitation of a local vibrational mode in this manner. The small mass of the muon means that its normal modes will normally be well separated from the rest of the IR spectrum, and a check of the vibrational frequencies that can be calculated (Briddon & Jones 1990) would provide another valuable test of electronic structure.

6. Isotope effects

(*a*) *Zero-point energy*

To recap, although the muon is an order of magnitude lighter than the proton ($m_{\mathrm{Mu}}/m_{\mathrm{H}} \approx 1/9$) it is heavy enough to provide a central nucleus so that the reduced mass of the electron, the size (Bohr radius) and the binding energy (ionization potential) are the same for free muonium and hydrogen to within a fraction of a percent (Walker 1983). For all intents and purposes, muonium may be considered as a light isotope or pseudo-isotope of hydrogen. The elastic and chemical interactions of muonium with a host lattice may therefore be expected to be very similar to those of hydrogen, and this is confirmed for all systems where a direct comparison has been possible. A proviso is that small differences may result from the greater *zero-point energy* of muonium when confined in a cavity or chemically bound to the host. Within the Born–Oppenheimer approximation the electronic structure must be identical for muonium, hydrogen and deuterium in a given configuration, but the uncertainty in nuclear coordinates associated with zero-point energy (crudely stated, the different amplitudes of zero-point motion) results in slightly different averages of observables such as hyperfine and quadrupole constants (Claxton *et al.* 1990; Claxton & Cox 1994). (This averaging

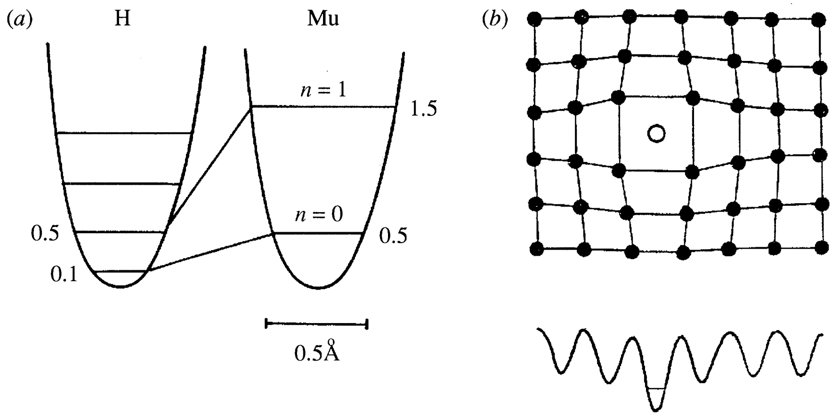

Figure 7. The relative importance of zero-point or confinement energy and vibrational excitation for hydrogen and muonium (*a*). The values indicated, in eV, are representative of covalently bonded hydrogen and muonium; values for non-bonding interstitial sites are somewhat lower. The principle of self-trapping via elastic distortion or lattice relaxation is illustrated in (*b*): with the heavy atoms 'frozen' in this configuration, the muon cannot tunnel to an adjacent site, but must wait for a configurational change.

may account for the puzzlingly low value of the hyperfine constant for $\mathrm{Mu}_{\mathrm{T}}^{0}$, which cannot be reproduced by *ab initio* calculations at the T-site alone.)

Much greater are the isotope effects where long-range mobility or diffusion is concerned. A comparison of the mobilities of isotopes is usually invaluable in testing a dynamical model, but an isotopic mass ratio of 1:9 is unprecedented and provides an unusually severe test. Figure 7 summarizes the features to be kept in mind. In its ground vibrational state, muonium is already behaving like 'hot hydrogen' – roughly on a level with the first excited state of protium in a harmonic well. On the other hand, the separation to the first excited state being so much higher, the occupancy of excited levels at normally accessible temperatures is negligible for muonium, so that their thermal excitation plays little role in muonium mobility. Tunnelling, however, is greatly facilitated for the lighter particle, so that muonium is a prime candidate for observation of quantum diffusion.

(*b*) *Quantum diffusion*

Tunnelling is in competition with localization induced by phonon scattering or lattice imperfections. This competitition can lead to a number of different regimes where the mobility either increases or decreases with temperature (Prokof'ev, this volume; Schober, this volume). Data for the diffusion of $\mathrm{Mu}_{\mathrm{T}}^{0}$ in the semiconductor GaAs, reported in figure 8, show a striking minimum in the variation of mobility with temperature (Kadono *et al.* 1990). This typifies the behaviour expected of a particle which becomes *self-trapped*, deepening the potential well which it ocupies via the elastic distortion, as in figure 7*b*. All coherence of the motion is destroyed and the particle moves step by step in a random walk. As the temperature is raised to the point where the lattice vibrations are of appreciable amplitude, the tunnelling probability is increased by favourable instantaneous configurations – the fluctuations digging a path, so to speak, between adjacent sites. This is *phonon-assisted tunnelling* (Flynn & Stoneham 1970; Kagan & Prokof'ev 1992); it

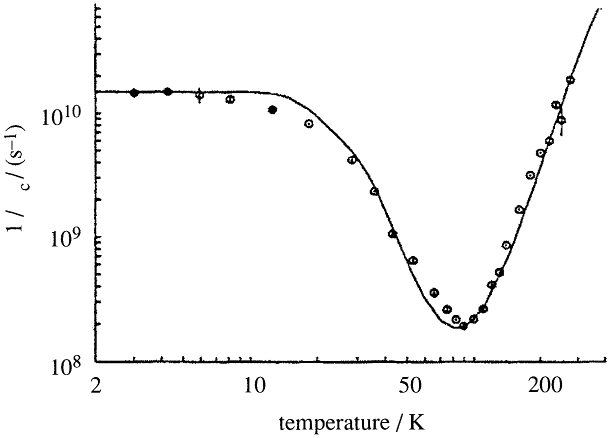

Figure 8. Hop rate for $\mathrm{Mu}_{\mathrm{T}}^{0}$ in GaAs deduced from muon spin relaxation data (Kadono *et al.* 1990) and illustrating two regimes of quantum diffusion.

results in the more familiar thermally activated hopping but can be distinguished from classical over-the-barrier motion by an unusually low activation energy.

Muon spin relaxation provides the source of information on the muonium hop rate: motion through the lattice causes a modulation of the local field experienced by the muonium atom and induces transitions between the coupled muon–electron spin states.† Precise values of the hop rate may have to be revised in the light of a more thorough modelling of this relaxation mechanism (Cox & Sivia 1994) but the basic phenomenon is clear. Data for neutral muonium in insulators such as the alkali halides (Kadono 1990) also show the effect, as do earlier data for muons in metals (Hartmann *et al.* 1980) although here the low-temperature behaviour is complicated by a strangely sluggish (non-adiabatic) response of the screening charge (Kondo 1985).

Whereas neutral $\mathrm{Mu}_{\mathrm{T}}^{0}$ is highly mobile, the cage-centred ion $\mathrm{Mu}_{\mathrm{T}}^{-}$ appears to be static, or very nearly so, up to high temperatures: spectra such as that shown in figure 5 (which would be washed out by diffusion) are detectable up to at least 500 K (Estle *et al.*, unpublished work). The neutral bond-centred state $\mathrm{Mu}_{\mathrm{BC}}^{0}$ also appears to be static according to existing data.‡ This is an extreme example of self-trapping. Preliminary data for the positive charge state, $\mathrm{Mu}_{\mathrm{BC}}^{+}$, show mobility setting in above about 200 K. In view of the evidence for charge exchange, diffusion at high temperature could well involve a succession of interchanges between $\mathrm{Mu}_{\mathrm{T}}^{0}$ and $\mathrm{Mu}_{\mathrm{BC}}^{+}$, so that these findings have interesting implications for the nature of hydrogen transport states.

(At very high temperatures, it may well be inappropriate to present a picture of such well-defined geometries. Simulations of the trajectory of a proton through a hot lattice (Buda *et al.* 1989) and of the quantum uncertainty of a muon's

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† The nuclear moments are large and abundant in GaAs, making this a very suitable host; in view of the success of this experiment, it would be worth examining Si and Ge carefully, to see if the rare dipolar isotopes cause sufficient longitudinal relaxation to permit a similar determination of muonium mobility.

‡ A useful signature for $\mathrm{Mu}_{\mathrm{BC}}^{0}$ is a distinctive dip in the *repolarization curve* reported in a companion paper (Davis *et al.*, this volume); it would be worthwhile examining the width of this feature for any sign of motional narrowing signalling the onset of mobility.

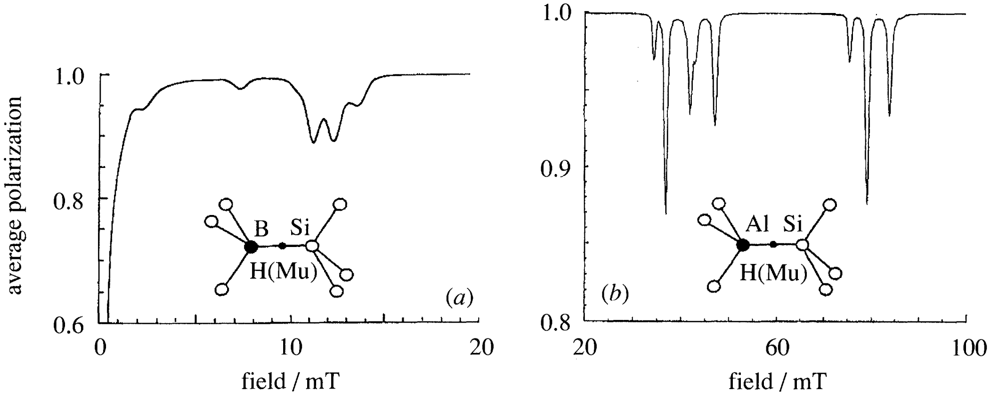

Figure 9. Simulated level crossing resonance spectra for the muonium-substituted passivation complex {B,Mu} (*a*) (Maric *et al.* 1991) and {Al,Mu} (*b*) (Meier, unpublished work) in Si.

position (Ramírez & Herrero 1994) are instructive here and exemplify current interest in the diffusivity of hydrogen in semiconductors.)

7. Passivation

While μSR spectroscopy has been invaluable in discovering the nature of isolated hydrogen defect centres, it has so far contributed little to the study of the pairing of hydrogen with other defects or dopants. Atomic hydrogen being particularly reactive, the hydrogen normally present in semiconductors does not remain in isolated states. μSR is able to study the states reached on the microsecond timescale following implantation before the muonium has had time to seek out and associate with other centres.

(Muonium certainly moves fast enough to encounter impurities within the muon lifetime if these are present at levels higher than about $10^{15}\mathrm{cm}^{-3}$. Clear examples are the absence of any $\mathrm{Mu}_{\mathrm{T}}^{0}$ signal in irradiated or Czochralski silicon (Patterson 1988). In fact the nature of the interaction with the vacancies on the one hand and the oxygen impurity on the other has never been studied explicitly; these problems deserve renewed investigation in the light of current ideas (Jones, this volume; Estreicher 1994).)

Particularly important is the manner in which hydrogen can pair with dopant atoms, negating their electronic function by removing the electrically active levels from the energy gap. Trace quantities of hydrogen impurity can seriously degrade device performance by this phenomenon, which is known as *passivation*. The proposed geometry for passivation complexes with acceptors in silicon places the hydrogen atom in an approximately bond-centre position immediately adjacent to the acceptor atom, as in the inserts to figure 9. This inspires the notion that the muonium counterparts could be studied by level crossing resonance (Cox *et al.* 1990*a*, *b*). Characteristic spectra of the type shown in figure 9 are expected (Maric *et al.* 1991; Meier, unpublished work).

Attempts to detect such spectra have so far proved inconclusive. It may be that the muonium does not trap at the expected site on the required timescale, in which case a systematic search at various dopant concentrations and temperatures may be rewarded. Or perhaps the measurement is spoiled by some local effect such as rapid spin-lattice relaxation of the acceptor depolarizing the approaching muonium, or rapid reorientation of the complex by tunnelling; in these cases some trick such as uniaxial stressing of the sample would be required. The prize for success would be a valuable check on the calculated electronic structure, and the first of its kind using a local probe spectroscopy.

8. Conclusion

With due regard for the effects of zero-point energy, the local electronic structures of hydrogen and muonium defect centres are very similar, as probed by measurements of hyperfine and quadrupole interactions. Muonium therefore provides an invaluable model for hydrogen when such spectroscopic studies of hydrogen itself prove impossible. As regards mobility, muonium and hydrogen differ considerably, but in systems where the diffusivities of both may be measured, comparison provides a particularly severe isotope test of dynamical models, with the availability of a light isotope favouring observation of quantum motion, i.e. modes of diffusion involving tunnelling.

Many of the puzzles concerning hydrogen in materials, and its effect on physical properties, reflect the lack of a microscopic model of the sites which protons, hydrogen atoms or hydride ions occupy in a lattice (or amorphous structure) or of the dynamical and chemical processes which they undergo. It is in providing such models that studies of implanted muons have made the greatest impact. The surprising variety of the states which hydrogen can adopt in semiconductors, and the complexity of the interplay between charge state and crystallograhic location, could scarcely have been appreciated without the aid of these μSR experiments. The results serve to illustrate the importance of muonium studies in building up a full picture of the properties of hydrogen in semiconductors, as well as the potential for other materials.

References

Abragam, A. 1984 *C.r. Acad. Sci. Paris* **299**, 95–100.

Bech Nielsen, B., Bonde Nielsen, K. & Byberg, J. R. 1994 *Mater. Sci. Forum* **143–7**, 861–866.

Brewer, J. H., *et al.* 1973 *Phys. Rev. Lett.* **31**, 143–146.

Brewer, J. H., Crowe, K. M., Gygax, F. N. & Schenck, A. 1975 *Muon physics*, vol. 3 (ed. V. W. Hughes & C. S. Wu), pp. 3–139. New York: Academic Press.

Briddon, P. R. & Jones, R. 1990 *Hyp. Int.* **64**, 593–602. (See references therein.)

Buda, F., Chiarrotti, G. L., Car, R. & Parinello, M. 1989 *Phys. Rev. Lett.* **63**, 294–297.

Chow, K. H., *et al.* 1995 (In the press.)

Chow, K. H., *et al.* 1993 *Phys. Rev.* B **47**, 16004–16007.

Claxton, T. A., *et al.* 1990 *Hyp. Int.* **65**, 913–926.

Claxton, T. A. & Cox, S. F. J. 1994 *Hyp. Int.* **87**, 917–922.

Cox, S. F. J. 1987*a* *J. Phys.* C **20**, 3187–3319.

Cox, S. F. J. 1987*b* In *Proc. Int. Symp. Muons and Pions in Matter (Dubna)*, pp. 153–164.

Cox, S. F. J. & Sivia, D. S. 1994 *Hyp. Int.* **87** 971–976.

Cox, S. F. J. & Symons, M. C. R. 1986 *Chem. Phys. Lett.* **126**, 516–525.

Cox, S. F. J., Briddon, P. R. & Jones, R. 1990*a* *Hyp. Int.* **64**, 603–612.

Cox, S. F. J., Buttar, D. & Smith, J. A. S. 1990*b* *Hyp. Int.* **65**, 987–992.

Davis, E. A., Singh, A. & Cox, S. F. J. 1991 *J. Non-Crystalline Solids* **137–8**, 17–20.

Estreicher, S. K. 1994 *Mater. Sci. For.* **148–9**, 349–392. (See references therein.)

Flynn, C. P. & Stoneham, A. M. 1970 *Phys. Rev.* B **1**, 3966–3978.

Gorelkinskii, Yu. V. & Nevinnyi, N. N. 1987 *Sov. Tech. Phys. Lett.* **13**, 45–46.

Gorelkinskii, Yu. V. & Nevinnyi, N. N. 1991 *Physica* B **170**, 155–167.

Hartmann, O., *et al.* 1980 *Phys. Rev. Lett.* **44**, 337–340.

Holme, B., Bonde Nielsen, K. & Bech Nielsen, B. 1991 *Phys. Rev. Lett.* **66**, 2360–2363.

Johnson, N. M., Herring, C. & Van de Walle, C. G. 1994 *Phys. Rev. Lett.* **73**, 130–133.

Kadono, R. 1990 *Hyp. Int.* **64**, 615–634.

Kadono, R., *et al.* 1990 *Hyp. Int.* **64**, 635–640.

Kagan, Yu. & Prokof'ev, N. V. 1992 In *Modern problems in condensed matter science* (ed. A. J. Legget & Yu. Kagan), vol. 34, pp. 41–143. North Holland.

Kiefl, R. F., *et al.* 1987 *Phys. Rev. Lett.* **58**, 1780–1783.

Kiefl, R. F., *et al.* 1988 *Phys. Rev. Lett.* **60**, 224–226.

Kondo, J. 1985 *Physica* B **125**, 279–285.

Kreitzman, S. R. 1990 *Hyp. Int.* **95**, 1055–1070.

Mainwood, A. & Stoneham, A. M. 1984 *J. Phys.* C **17**, 2513–2524.

Major, J., *et al.* 1992 *ISIS A. Rep.* (RAL-92-050), A363.

Maric, Dj. M., *et al.* 1991 *J. Phys. Condens. Matter* **3**, 9675–9686.

Morenzoni, E. 1992 *Z. Phys.* C (*Particles and Fields*) **56**, S243–S249.

Morenzoni, E., *et al.* 1994 *Phys. Rev. Lett.* **72**, 2793–2796.

Odermatt, W., *et al.* 1988 *Phys. Rev.* B **38**, 4388–4393.

Patterson, B. D. 1988 *Rev. mod. Phys.* **60**, 69–159. (See references therein.)

Ramírez, R. & Herrero, C. P. 1994 *Phys. Rev. Lett.* **73**, 126–129.

Schenck, A. 1985 *Muon spin rotation spectroscopy.* Bristol: Hilger.

Schneider, J. W., *et al.* 1994 *Phys. Rev. Lett.* **93**, 557–560.

Van de Walle, C. G., Denteneer, P. J. H., Bar-Yam, Y. & Pantelides, S. T. 1989 *Phys. Rev.* B **39**, 10791–10808.

Walker, D. C. 1983 *Muon and muonium chemistry.* Cambridge University Press.

Westhauser, E., *et al.* 1986 *Hyp. Int.* **32**, 589–592.

Discussion

R. C. NEWMAN (*IRCSM, Imperial College, London, U.K.*). In the lecture it was implied that hydrogen was not soluble in semiconductors except when it was in the form of clusters or complexes with other atoms or defects. At low temperatures, isolated H atoms have been detected in proton-irradiated Si via the AA9 EPR spectrum, although these defects anneal at $T < 200$ K and it would appear that complexes form. It is interesting to ask why other workers have in general failed to reproduce the early Russian results and why corresponding measurements have not been reported for Ge, GaAs, GaP, InP, etc.

However, at high temperatures H atoms are dissolved in low concentrations when Si (and Ge) are heated in H_2 gas and this topic is addressed in my own paper. It is nevertheless true that the high concentrations up to 10^{20} cm^{-3} occur only when strongly bound complexes form.

S. F. J. COX. The fact that paramagnetic states of muonium are more easily detected than their hydrogen counterparts is almost certainly a question of timescale as well as one of sensitivity. The microsecond timescale of μSR spectroscopy does not allow the muonium to reach other impurities by diffusion and bind to them, which would give diamagnetic complexes. Nor does it allow thermodynamic equilibrium to be reached by exchange of electrons with distant impurities, which would leave empty or doubly occupied levels in the gap. If negative-U character is confirmed, paramagnetic states should be unstable under all circumstances, and one might say that their detection by μSR has been rather lucky! H atoms would in that case reach equilibrium among themselves according to $2H^0 \rightarrow H^+ + H^-$. It is significant that detection of the AA9 centre by EPR required illumination to generate the singly occupied level, perhaps according to the process $H^+ + e^- \rightarrow H^0$. The signal is not seen without light on the sample. (The annealing temperature is also comparable to the temperature at which Mu^0_{BC} loses an electron by ionization.) This EPR observation has in fact now been repeated in the West (note the reference to Bech Nielsson *et al.*, drawn to my attention by R. Jones and also cited in his paper). There is still no EPR observation of an isolated cage-centred state analogous to Mu^0_T (at least in semiconductors; the trapped atom state is of course well known in oxides and halides); perhaps this might be prepared by hole trapping at the negative (hydride) ion: $H^- + h^+ \rightarrow H^0$, or sought in other materials. The bond centre may no longer be the more stable location for the neutral interstitial in other materials. It is noteworthy that Mu^0_T and Mu^0_{BC} are well known in Ge, GaAs and GaP (although with no information on relative stability) but have not yet been detected in muon spin rotation spectra for InP (nor indeed in InAs, InSb or GaSb). It is worth considering II–VI materials too: Mu^0_{BC} is not expected when the ionicity is high but Mu^0_T is visible in ZnS and ZnSe, though not in CdS or CdTe; studies have yet to be performed on ZnTe and CdSe.

R. A. Catlow. (*Royal Institution, London, U.K.*). I find the results Dr Cox presented on quartz to be particularly interesting. One might expect the majority of the muons to bind to the lone pairs of the bridging oxygens to form O–μ groups. However, it appears that muonium dominates. Presumably this must be a consequence of the initial radiolysis process in wich muonium is formed. But it is still perhaps surprising that muonium does not bond to hole states created by radiolysis.

S. F. J. Cox. Muonium formation must be in competition with electron–hole recombination and the detection of the signal implies that the muonium has escaped the influence of other paramagnetic radiolysis products. The encounter Professor Catlow suggests with holes might simply depolarize the muon so that the product could not be observed, although in fact there is very little ‘missing’ muon polarization in SiO_2 spectra. SiO_2 gives about the highest yield of muonium per incident muon of any material. Perhaps the large band gap prevents μ^+ slowing to the point where it can stick to the electron lone pairs (i.e. the muon cannot lose its last 10 eV or so of energy by electronic collisions, as has been suggested in frozen rare gases).

There are numerous cases of delayed muonium formation ($\mu^+ + e^- \rightarrow Mu$) and in reactive media muonium can be a precursor to diamagnetic products. But there is no clear example of muonium assisting recombination ($[\mu e + h \rightarrow \mu)$ – unless this contributes to the charge exchange process in semiconductors described in the paper by R. L. Lichti – or forming a bound exciton state ($[\mu e + e \rightarrow [\mu ee]$).

E. A. Davis (*University of Leicester, U.K.*). I should like to draw attention to a poster presented at this meeting on muon implantation into Se and $Se_{90}Ge_{10}$.

These are glasses in which there are no cage-like sites or sp^3 bonds – the traditional sites for muonium in tetrahedral crystalline semiconductors. However, there are lone-pair electrons at the Se atoms and these may indeed be involved in the formation of muonium, which is formed with a high yield per incident muon.

A. M. Stoneham (*Harwell Laboratory, Oxfordshire, U.K.*). Dr Cox pointed to the muon as an analogue of the proton. I believe I remember some systems where it is the analogue of an electronic hole. In fluorides the hole combines with two fluorides giving a molecular negative ion. The positive muon seems to give a very similar diatomic species; I think the positron does so too.

S. F. J. Cox. It is true that the positive muon attracts two fluorine ions strongly (in alkali fluorides such as NaF). The magnetic dipole interaction between the muon and the two fluorine nuclei gives a distinctive signature in the zero-field μSR spectrum (see, for instance, Brewer *et al.* 1986; Noakes 1993). But this is a triatomic molecular ion analogous to the species (FHF): the muon's role is that of a hydrogen nucleus in a 3-centre hydrogen bond, with the electrons remaining paired and the whole entity diamagnetic. $(F_2)^-$, on the other hand, is a 2-centre paramagnetic species, and hardly comparable.

M. Symons (*Department of Chemistry and Biological Chemistry, University of Essex, U.K.*). I would like to comment on the possible formation of Mu^- anions, which are the equivalent of H^- or 'hydride' ions. These are only found as stable species in metal hydrides such as NaH, or as 'U-centres' in alkali halides, when H^- replaces the halide ion. These are well characterized by an intense ultraviolet band whose energy is a function of the lattice, but falling in the 200–300 nm region. It would be most interesting if there were some way of detecting such a band for Mu^-, or indeed for H^- in silicon.

At this stage perhaps I can also comment from a chemical viewpoint on H^+ (Mu^+ or μ^+) and $H^{\cdot}$ ($Mu^{\cdot}$) centres. The key point is that, whereas H^- and $H^{\cdot}$ are real 'stand-alone' entities, at least in first order, H^+ isn't, unless it has very high kinetic energy. Thus, it always seeks out electrons and forms a bond. If there are 'lone-pairs' available, as in SiO_2, there is no problem, but it will form a bond, come what may! In contrast, $H^{\cdot}$ can add to double bonds, extract hydrogen as in reaction (D 1), etc., but it can readily be trapped as such:

$$X\text{–}H + H^{\cdot} \rightarrow X^{\cdot} + H_2. \tag{D 1}$$

Additional references

Brewer *et al.* 1986 *Phys. Rev.* B **33**, 7813.

Noakes *et al.* 1993 *J. Phys. Chem. Solids* **54**, 785.