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The electrical activity of hydrogen and muonium in silicon at high temperatures

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Abstract

Above 500 K in silicon, isolated hydrogen defect centres scatter intrinsic charge carriers strongly by momentary formation of the neutral atomic ground state, located at the tetrahedral cage centre. This is inferred from the analogous behaviour of muonium, via distinctive muon spin rotation and relaxation signals. A consistent interpretation of a surprisingly large shift of the muon Larmor frequency and the strong transverse and longitudinal spin relaxation rates is achieved in terms of charge-state transition rates into and out of the neutral paramagnetic state. The nature of the charge cycle and the interplay with the crystallographic site are discussed and the electrically active level in the energy gap is determined.

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This work seeks to model the electrical activity of hydrogen impurity in silicon above room temperature—specifically, in the range of 500–900 K. The principal effect here is a strong scattering of charge carriers, mediated at least in part by momentary formation of the neutral atomic state in its 1s configuration, located at the tetrahedral cage centre (the T-site). Various possible (0/+) and (−/0) charge cycles are considered, including trapping and detrapping of electrons by the positive ion, mimicking the interstitial proton with or without site change to the bond-centre (BC) site, a similar capture and loss of holes by the hydride-ion analogue without site change, and alternate capture of electrons and holes, i.e. recombination.

We infer the behaviour from data, not on the hydrogen centres themselves, but on their muonium counterparts, examining how the μSR signals (muon spin rotation and relaxation) depend on temperature and applied magnetic field. Whereas at cryogenic temperatures the muonium spin states are long-lived, so that the 4-frequency hyperfine spectra are readily interpreted in terms

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of crystallographic site and local electronic structure, at high temperatures the rapid sequence of charge-state transitions requires interpretation of the muon's response to intermittent hyperfine interaction. The principal effect is a fierce depolarization or relaxation of the muon spin. The longitudinal relaxation (i.e. the response in magnetic fields applied parallel to the initial muon polarization) was originally studied in some detail by Chow et al. [1]. Their work first drew attention to the so-called charge exchange régime above room temperature, identifying this as repeated capture and loss of charge carriers at the muon site. Predicting an associated paramagnetic shift of the Larmor precession signal, Cox et al. [2] later examined the transverse-field response and found the frequency shift to be unexpectedly large. Their interpretation in terms of an effective hyperfine field, proportional to the time fraction spent as neutral muonium and to the Boltzmann polarization of the muonium electron, implied a neutral fraction close to unity above 700 K but was unable to achieve a consistent interpretation of the longitudinal relaxation.

In Fig. 1 we present new data for all the observables, including for the first time the corresponding transverse-field relaxation rates, showing that they differ from the longitudinal rates from the onset region up to the relaxation peak around 700 K but become equal as both rates decrease to higher temperature. Most importantly, we have found that the frequency shift is not linearly proportional to the applied field, as would be expected of Boltzmann polarization at these temperatures. This is shown in Fig. 2. It is not, therefore, a straightforward paramagnetic shift. The Boltzmann contribution proves instead to be small compared with a purely dynamic term whose field and temperature dependence is determined by the transition rates into and out of the neutral state, relative to the electron Larmor and hyperfine frequencies. One can say that the 4 muonium frequencies, which are now unresolved and would collapse identically to the muon Larmor frequency in the limit of short neutral-state lifetimes, contribute in different proportions at intermediate lifetimes, generating the shift.

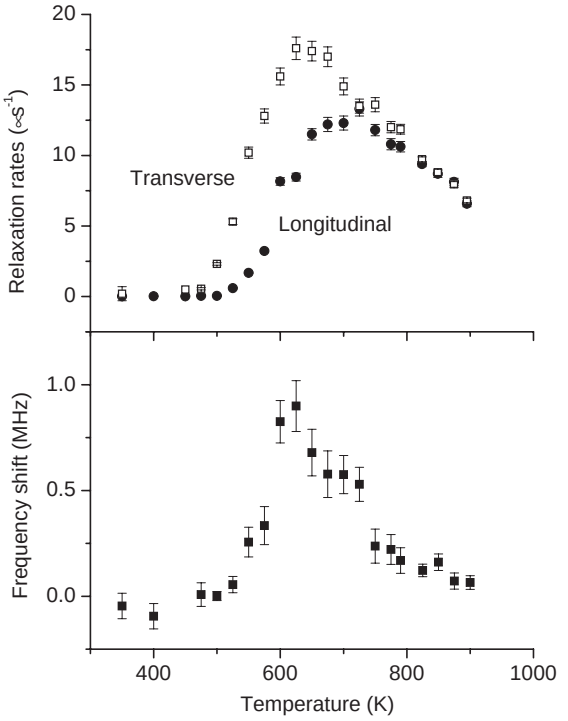

Fig. 1. Temperature dependence of muon spin relaxation rates at 2 kG and of muon spin rotation frequency, relative to the muon Larmor frequency (27 MHz, also at 2 kG).

In the light of the new data we are obliged to retract the earlier conclusion of high neutral fraction but instead are able to give a consistent interpretation of all three observables, the frequency shift and the two relaxation rates, extracting temperature dependences for the responsible charge-state transition rates. This is underpinned by two new treatments of the muon response in the charge-exchange régime. Numerical simulations (due to JS Lord) follow evolution of the density matrix through the sudden changes of the Hamiltonian and are sufficiently fast to be used in fitting the data. Another approach (due to N Gidopoulos, to be described in more detail elsewhere) follows the evolution of wavefunction and examines the nature of the loss of coherence for the various possible charge-state transitions, checking and confirming the density-matrix method.

The onset region around 400 K probably represents capture and loss of electrons without site change at the bond centre, cycling between

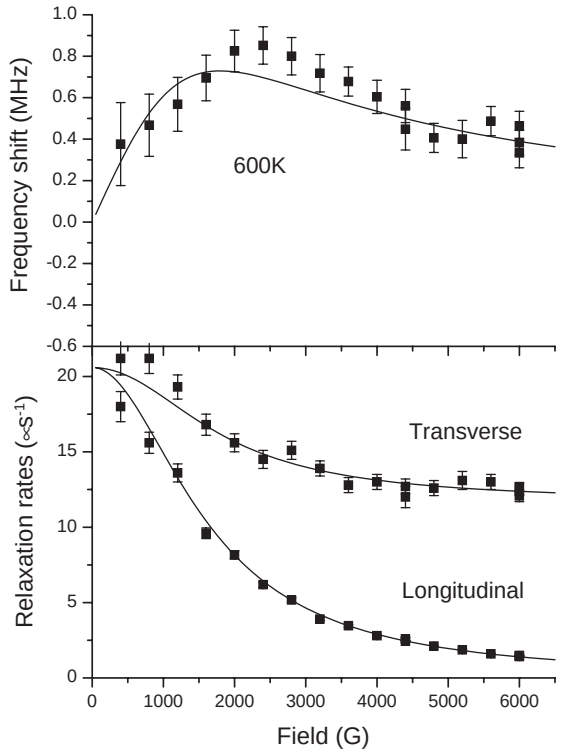

Fig. 2. Global fits to the 600 K data set of field dependences, yielding the two transition rates (see Fig. 3).

Mu^{+}_{BC} and Mu^{0}_{BC} (Here we use the nomenclature for site and charge state that has now commonly been adopted, for hydrogen as well as for muonium [3,4].) A small negative shift of the frequency here is entirely consistent with the small negative contact interaction in Mu^{0}_{BC}, itself due to spin polarization of valence electrons, but relaxation is weak here and we make no attempt to fit the data below 500 K. Above this temperature the frequency shift becomes positive and the relaxation considerably stronger. Neither can then be explained in terms of Mu^{0}_{BC} parameters; both instead require the much larger hyperfine constant appropriate to Mu^{0}_{T} in its ground state, as Chow et al. [1] had already noted from their longitudinal-field data. It does not appear necessary to invoke any new neutral state specific to high temperatures. Examples of global fits to the field dependences of all three observables at a particular temperature are given in Fig. 2. Field scans at successive temperatures give temperature dependences for the transition rates and resultant neutral fraction, as shown in Fig. 3. The latter is seen to rise only to 5% at 900 K, more in line with the original values [1].

The question is now whether the dominant charge cycle above 500 K is still with the positive ion and whether, in this case, it involves a site change at each transition, i.e. between Mu^{+}_{BC} and Mu^{0}_{T}. The alternative is that the charge cycle has switched from $0/+$ to $-/0$ to involve the negative ion, in which case it could proceed without site change at the cage centre, between Mu^{0}_{T} and Mu^{-}_{T}. Explicitly, we consider the following alternatives:

$$Mu^{+} + e \rightleftharpoons Mu^{0}, \quad (1)$$

$$Mu^{+} \rightleftharpoons Mu^{0} + h, \quad (2)$$

$$Mu^{-} + h \rightleftharpoons Mu^{0}, \quad (3)$$

$$Mu^{-} \rightleftharpoons Mu^{0} + e, \quad (4)$$

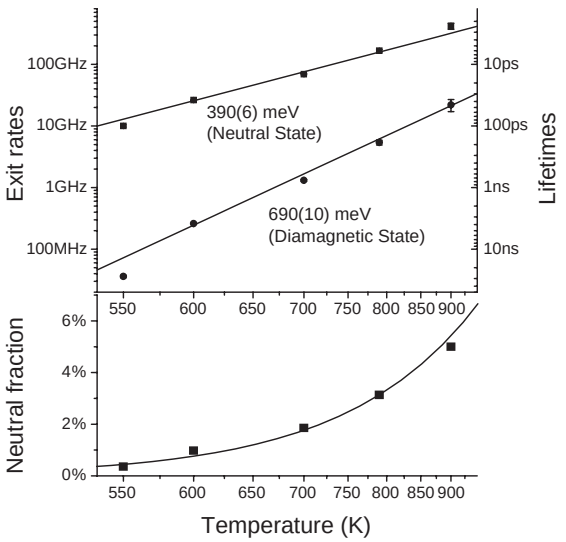

Fig. 3. Temperature dependences of the transition rates (the corresponding lifetimes are shown at right) and resultant T-site neutral fraction. Within the lifetimes denoted as diamagnetic, i.e. ionic, additional charge cycles which are too fast or involve too small a hyperfine coupling to affect the muon spin are not excluded; these would enhance the overall neutral fraction and carrier scattering.

$$Mu^0 + e \rightarrow Mu^-, \quad Mu^- + h \rightarrow Mu^0, \text{etc}, \tag{5}$$

$$Mu^+ + e \rightarrow Mu^0, \quad Mu^0 + h \rightarrow Mu^+, \text{etc}. \tag{6}$$

Eqs. (1)–(4) represent repeated capture and loss of the same carrier type; Eqs. (5) and (6) represent alternate capture of the two types, i.e. recombination.

Arrhenius plots of the two transition rates in Fig. 3 give activation energies of 690 ± 10 meV for entry into and 390 ± 6 meV for exit from the neutral atomic state. Interestingly, these sum almost exactly to the high-temperature bandgap: the possible significance of this, namely defect-related carrier generation—the inverse of recombination, will be pursued elsewhere. In the present discussion, we note simply that the larger value is just over half the bandgap and take this to represent the availability and capture rate of thermally excited carriers. (In due course, the temperature dependences of thermal velocity and density of states will have to be factored into any capture rate, but we do not at this stage wish to impose a model prematurely.) The smaller value plays the role of an ionization energy of the neutral state. On this basis, processes (1) and (3) can be retained as candidates but all the others can reasonably be excluded. Process (1) corresponds to trapping and detrapping of electrons at the positive ion, as assumed by Chow et al. It would appear to define a $0/+$ donor level in the upper half of the energy gap, namely at 390 meV below the conduction-band minimum. An alternative which is worth exploring is process (3), occurring without site change at the cage centre, i.e. the T-site. The neutral-state lifetime is in this case limited by hole ionization, defining a $0/-$ transition level in the lower half of the gap, 390 meV above the valence-band. (It is not the thermodynamic acceptor level, but is experimentally the more accessible parameter [5].) From RF resonance data at lower temperature, Hitti et al. [6] identified this transition as 560 meV below the conduction band. Taking the indirect bandgap to be close to 1 eV around 700 K, this interpretation is reasonably consistent and cannot be excluded from the present data alone. Evidence against it—but in favour of an electronic $0/+$ cycle—comes from comparing data on samples of different doping. Our new data in Figs. 1–3 are for lightly doped p-type Si ($[B] = 10^{14}$ cm^{-3}). The onset temperature for the strong relaxation and positive frequency shift is some 30 K higher than in the original data for nominally pure Si [1,2], although otherwise the data are quite similar. In more heavily doped p-type material the onset temperature is pushed up further (to around 550 K with $[B] = 10^{16}$ cm^{-3}) and the peak relaxation is substantially reduced [7]. (In n-type material with $[P] = 10^{16}$ cm^{-3} we have preliminary data indicating the relaxation to be so much enhanced that it can scarcely be measured at these temperatures.)

If Eq. (1) does represent a mode of electrical activity at high temperature, in pure and moderately p-type silicon, two comments must be made. The first is that the apparent donor depth of 390 meV is quite distinct from the value of 210 meV determined for muonium below room temperature. This latter is a true $0/+$ donor level, defined by ionization without site change of Mu^0_{BC} [3,6]. The depth of the corresponding level for hydrogen has most recently been given as 175 meV [4]. (The small difference is readily accounted for in terms of the different harmonic potentials for the positive and neutral centres, and the different zero-point energies of muon and proton.) The second point is that, although the high-temperature charge cycle undoubtedly involves Mu^0_T, the apparent donor depth of 390 meV cannot then be reconciled with a single-site ionization energy—the hyperfine constant involved here is some 40% of the free atom value, implying a much higher binding energy. It could instead represent the energy barrier for site change to the bond-centre site (where ionization would be extremely fast at these temperatures) and indeed this value is almost identical to the barrier height deduced from RF resonance data closer to room temperature [3,6]. Contrary to the view of Chow et al. [1], who invoked a temperature-dependent potential energy surface which constrains the positive ion to the T-site at high temperature, this interpretation implies site change at each charge-state transition. Explicitly, it appears that the charge-exchange cycle which dominates the muon response in silicon switches from Eq. (7) to Eq. (8) around 500 K,

with a concomitant change of donor level from a true value (an electron binding energy) of 210 meV for process (7) to an effective value (a site-change barrier) of 390 meV for process (8):

$$Mu^{+}_{BC} + e \rightleftharpoons Mu^{0}_{BC}, \quad (7)$$

$$Mu^{+}_{BC} + e \rightleftharpoons Mu^{0}_{T}. \quad (8)$$

Although molecular dynamics simulations seemed to show protons avoiding the bond-centre site at high temperatures [8], the maximum trajectory time followed was 0.7 ps only, compared with the much longer timescales involved here: the average repeat periods for the overall cycle (Fig. 3) are in excess of 50 ps below 900 K, 1 ns below 700 K. Given the importance of optical phonons in Si at these temperatures, assisting in stretching the bonds, it may be that the bond-centres are momentarily accessible on these longer timescales. The possible role of oxygen or other impurities in catalysing bond-centre trapping has also been suggested [4].[1]

It is worth emphasizing that while Eq. (8) appears to be the simplest process compatible with the μSR data, it is not unique. Other charge cycles could well be operative. For instance, it is possible that process (7) continues together with process (8) or that there is momentary capture into excited neutral states at either site. Such additional processes are too fast, or the hyperfine interactions involved are too small, to affect the muon spin, though they may well contribute to carrier scattering. The essential requirement of the μSR data is that a charge cycle exists whereby the cage-centred atom reaches its ground state with the entry and exit transition rates of Fig. 3 so that, with small corrections to the energy barriers involved, hydrogen must exhibit a similar behaviour. The corresponding neutral fraction is a lower limit, not counting the contribution of scattering in and out of more weakly bound states. By inference, the high-temperature electrical activity of isolated interstitial hydrogen, at temperatures where passivation complexes are dissociated, is undoubtedly significant.

The experimental work was performed at the Swiss Muon Source, Paul Scherrer Institute, Villigen, Switzerland.

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