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2001 J. Phys.: Condens. Matter 13 2155

(http://iopscience.iop.org/0953-8984/13/10/310)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 2155–2162 www.iop.org/Journals/cm PII: S0953-8984(01)17662-9

The neutral fraction of muonium in silicon at high temperatures

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Received 2 October 2000, in final form 19 January 2001

Abstract

Muon spin-rotation measurements on silicon above room temperature show the onset of a substantial paramagnetic shift from the muon Larmor frequency. The inferred fraction of the time spent as neutral paramagnetic muonium is close to unity above 600 K, so the capture rate of conduction electrons greatly exceeds the effective ionization rate. These findings are consistent with the configuration-coordinate model for the interplay between site and charge state, in which a site change is the bottleneck impeding electron loss. Difficulty is found, however, in obtaining parameters which also account for the available data on muon spin relaxation. Extensions of the model are suggested with the aim of determining the site-change energy for neutral muonium between the bond-centred and cage-centred sites—an elusive parameter necessary for determining whether or not interstitial muonium or hydrogen atoms constitute negative-U centres in silicon.

This paper concerns the interplay of crystallographic site and charge state for muonium in silicon at high temperatures and the inferences which may be drawn for the electrical activity of interstitial hydrogen. In particular we re-examine the régime of rapid capture and loss of electrons which gives rise to strong muon spin depolarization above 400 K (Chow *et al* 1993). Here muonium is the light isotope of hydrogen formed when positive muons are implanted into non-metallic materials. In semiconductors it can exist in all of its charge states: according to doping and temperature the muon may thermalize as the positive ion, mimicking the interstitial proton, or it may capture one or two electrons, forming defect centres analogous to the trapped hydrogen atom and the hydride ion. Thanks to the sensitivity with which it may be detected and characterized by the μSR techniques of *muon spin rotation, relaxation and resonance*, muonium provides an invaluable experimental model for hydrogen, in materials where hydrogen impurity is difficult or impossible to detect spectroscopically (see

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e.g. Cox 1987, 1995). This is the case for isolated hydrogen defect centres in silicon and other semiconductors for two reasons. Interstitial hydrogen is believed to be a negative-U centre, so its neutral paramagnetic state or states are only metastable; it is also so mobile and reactive that it is normally only observed paired with other defects or dopants, resulting in their electrical passivation.

Much of our insight into the behaviour of isolated hydrogen centres in semiconductors has come primarily from muonium studies. A feature of the experiments is that neutral paramagnetic states of muonium are formed with long enough lifetimes at low temperature for their sites and electronic structures to be established from their μSR spectra. These neutral centres can exist in both the tetrahedral cage-centre (T) and bond-centre (BC) sites depicted in the sketch below (figure 1). We denote these with the now commonly used notation, Mu^0_T and Mu^0_{BC}. The charged centres show a more pronounced site preference, the positive ion being stable only at the bond centre and the negative ion only at the cage centre—Mu^+_{BC} and Mu^-_T, respectively. The four analogous states of hydrogen are H^0_T, H^0_{BC}, H^+_{BC} and H^-_T; not all of these have been observed directly but the correspondence of respective energy levels, barriers and parameters relating to electrical activity between the muonium and protium systems is nonetheless quite well established (see e.g. Lichti 1995, Hitti *et al* 1999).

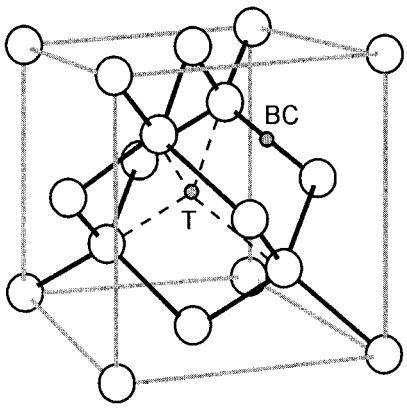

Figure 1. Chief interstitial sites for hydrogen and muonium in silicon.

Our own experiments use a sample of nearly intrinsic silicon at temperatures above the ionization threshold for both neutral muonium states. No paramagnetic signals are observed directly, therefore. The muon spin-rotation signal, in a magnetic field applied transverse to the incoming muon polarization, then corresponds to simple precession at or near the muon Larmor frequency; just above ionization we take it to represent Mu^+_{BC}, mimicking the interstitial proton. As the intrinsic concentration of conduction electrons rises with temperature, electrons encountering the muon can nonetheless be captured momentarily. Muonium is formed but quickly re-ionizes, in repeated cycles known loosely as *charge exchange*. (At no temperature accessible to the present experiments is the conduction electron density high enough to screen the muon charge and *preclude* muonium formation, as it does in metals.) Chow *et al* (1993) explain the muon depolarization or spin relaxation seen in a longitudinal magnetic field in these terms, i.e. as the result of intermittent hyperfine interaction with a succession of electrons of uncorrelated spin.

Given a small degree of electronic polarization p_e in finite magnetic fields, the intermittent contact interaction which is responsible for spin relaxation should, via its time average, also give rise to a small effective field acting on the muon spin. This field will be proportional both to p_e for the paramagnetic state and to the fraction p_0 of time spent in this state. Probably the muons

spend time in both paramagnetic states, but we assume that occupancy of the isotropic state Mu^0_T gives the dominant contribution, this having a much greater contact interaction $hA\boldsymbol{I}\cdot\boldsymbol{S}$ than Mu^0_{BC}. For the transverse-field precession signal, we therefore expect a paramagnetic shift of the muon Larmor frequency:

$$\delta f = \frac{1}{2} A p_e p_0 \tag{1}$$

or, equivalently, a proportional shift given by

$$\frac{\delta f}{f} \approx \frac{hA}{4kT}\frac{\gamma_e}{\gamma_\mu} p_0. \tag{2}$$

Equation (1) may be written directly as a perturbation term in the high-field approximation, but for sufficiently fast charge exchange it remains correct at all fields, as the weighted average of the four contributing frequencies corresponding to allowed transitions between the hyperfine coupled muon–electron spin states. In equation (2) we take the electron polarization to be given by the Boltzmann factor for an isolated paramagnetic centre, as we discuss below.

Our experiments were performed at the GPS instrument at PSI, on a near-intrinsic sample of crystalline silicon. The material is 'Topsil', with a net p-type carrier concentration at room temperature of $\approx 10^{11}$ cm^{-3}. This is from the same batch as was used by Chow *et al* (1993) for their longitudinal-field measurements of muon spin relaxation; it is also the material denoted 'P11' in the muon spin-resonance experiments of Kreitzman *et al* (1995) and Hitti *et al* (1999), whose dynamical parameters we use below. Data for the muon spin-rotation frequency and its variation with temperature are shown in figure 2(a). These measurements were made in a magnetic field of 6 kG, stable to several ppm, and were reproducible in several temperature sweeps. Some measurements in lower magnetic fields suggested that the proportional shift from the muon Larmor frequency was not exactly independent of field (as required by equation (2), if charge exchange is fast enough) but the field dependence remains to be detailed. In the following, we analyse the temperature dependence of our 6 kG data set. The small negative shift between about 300 and 450 K may represent a contribution from Mu^0_{BC} but the main feature, undoubtedly due to time spent as Mu^0_T, is the onset and striking rise of a positive shift above 500 K. This shift reaches values as high as 0.6% around 600 K. In figure 2(b), we present the corresponding values of neutral fraction p_0 inferred using equation (2). Here we have taken the hyperfine constant A to decrease linearly from 1935 MHz at 300 K to 1750 MHz at 800 K, extrapolating values measured spectroscopically below room temperature by Holzschuh (1983). The remarkable saturation of the neutral fraction near unity above 600 K justifies our use of the Boltzmann factor for electron spin polarization empirically: if p_e were equal to the much smaller band polarization, unphysically large values of p_0 would be obtained. In the following, we compare these data with the expectations of various models of the muonium-state dynamics.

According to the simplest model, p_0 is the equilibrium occupation of a single electrically active level:

$$p_0 = \left\{1 + \frac{1}{2}\exp\left(\frac{E_\mu - E_F}{kT}\right)\right\}^{-1}. \tag{3}$$

Although Chow *et al* (1993) found such a model to be consistent with their low-field relaxation data, their analysis implies a much smaller value of neutral fraction than we observe: their onset temperature is similar but their inferred value of p_0 rises to only 0.06 at 800 K. Our own values of close to unity are inconsistent with equation (3), or with other standard expressions for detailed balance on a single-defect level, whether this lies above or below the Fermi level. That is, our paramagnetic shift data cannot be fitted with a single-site ionization energy.

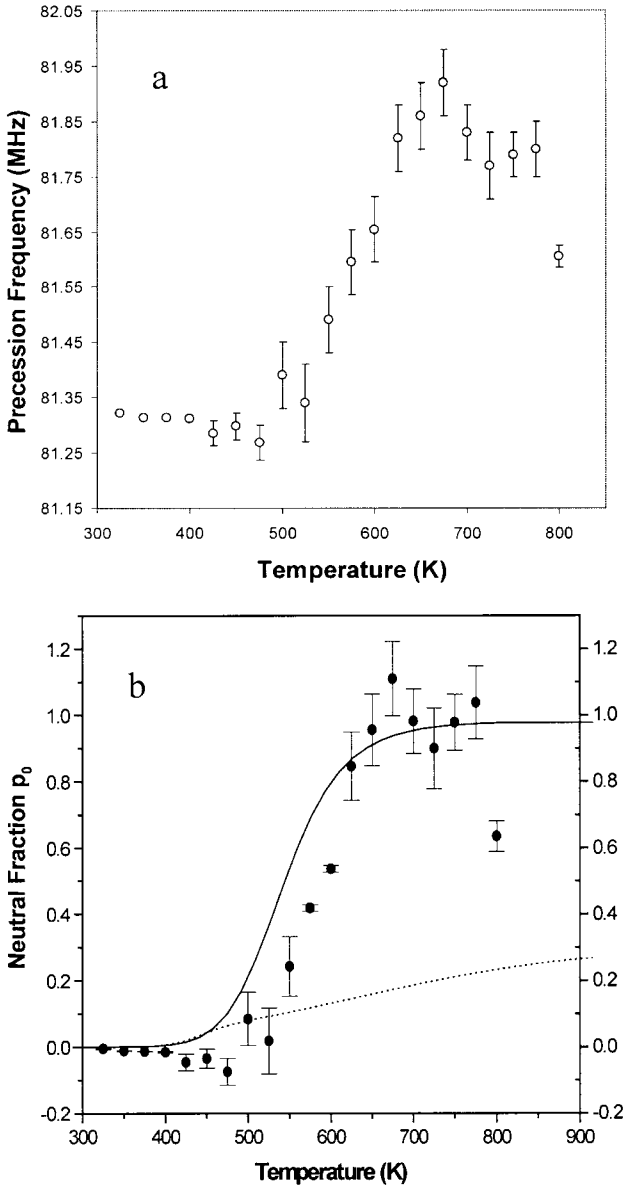

Figure 2. Temperature dependences of the muon precession frequency (a) in silicon at 6 kG and of the deduced neutral fraction (b) of muonium. The solid line is the prediction of equation (4) with the parameters of figure 4, but excluding transitions involving the negative ion; the dotted line includes the effect of these transitions.

If we consider instead an interplay of the three states Mu^{+}_{BC}, Mu^{0}_{BC} and Mu^{0}_{T}, using a configuration-coordinate model (Lichti 1995) with the most recent parameters obtained from RF resonance studies (Kreitzman *et al* 1995, Hitti *et al* 1999), we find predictions for neutral fraction following the solid line in figure 2(b). The full configuration-coordinate diagram and a sketch of the state transitions are given in figure 3, including the negative ion Mu^{-}_{T} which we do not expect to play a large rôle in an intrinsic or lightly p-type sample. For simplicity,

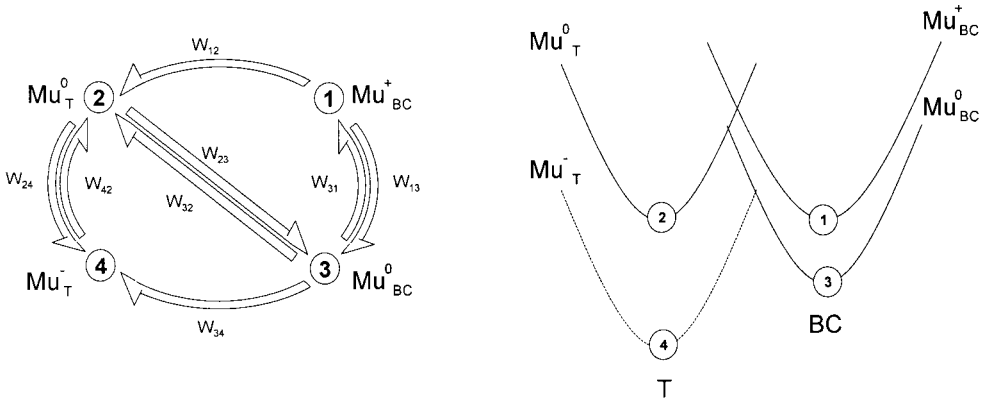

Figure 3. Site- and charge-state transitions and the configuration-coordinate diagram.

we label the states i, $j = 1$–4 as defined in figure 3 and denote the rate of transition between states i and j as W_{ij}. For our three-state model, solution of the population rate equations gives the following somewhat cumbersome expression for neutral fraction:

$$p_0 = (W_{13}W_{32} + W_{31}W_{12} + W_{12}W_{32})/(W_{12}W_{23} + W_{23}W_{31} + W_{31}W_{12} + W_{21}W_{13} + W_{13}W_{32} + W_{32}W_{21} + W_{12}W_{32} + W_{23}W_{13} + W_{31}W_{21}). \quad (4)$$

Hitti *et al* (1999) describe the nature of these transitions, i.e. electron capture W_{13} and loss W_{31} at the BC site; activated electron capture with site change W_{12} to the T site; and migration of the neutral state back to the BC site W_{23}. (They also introduce transitions to and from the fourth state Mu_T^- but we ignore these for the present. Their model has $W_{43} = W_{21} = 0$, as expected intuitively, and they also choose to neglect inverse site change of the neutral state, setting $W_{32} = 0$.) They give expressions for each transition rate in terms of Arrhenius parameters, conduction electron density and thermal velocity which we have calculated and plotted explicitly in figure 4, the better to visualize the relative values, competitions and crossovers.

There is no direct ionization of Mu_T^0 in this model: the state Mu_T^+ is not represented in the configuration-coordinate diagram, this branch of the energy surface being supposed inaccessible. With the parameters of figure 4, $W_{31} \gg W_{23}$ at all temperatures, so site change is the bottleneck impeding electron loss in the three-state charge cycle $\mathrm{Mu}_\mathrm{T}^0 \rightarrow \mathrm{Mu}_\mathrm{BC}^0 \rightleftharpoons \mathrm{Mu}_\mathrm{BC}^+ \rightarrow \mathrm{Mu}_\mathrm{T}^0$ *et seq*. Comparison of figures 2 and 4 shows that the neutral fraction rises through 50% as electron capture becomes faster than the two-stage process of electron loss. The quantitative expectations of this three-state model are close to our data and can be made to fit well with a small refinement of the parameters. Inclusion of transitions to and from the fourth state Mu_T^- (the analogue of the hydride ion) substantially reduces p_0 by exaggerating the occupancy of this state at high temperatures: this is shown by the dotted line in figure 2(b) and suggests that electron capture into this state has been overestimated in figure 4. However, we do note in figure 2 a tantalizing drop in neutral fraction at the highest temperature currently available to us. This could well indicate the onset of involvement of the negative state but the data point remains to be confirmed, and the measurements extended to higher temperatures and to doped samples.

The parameters of figure 4 were obtained chiefly by muon spin-resonance measurements at lower temperatures, where signals of the paramagnetic states are visible and their conversion to diamagnetic states via ionization or on doping could be followed explicitly (Kreitzman *et al*

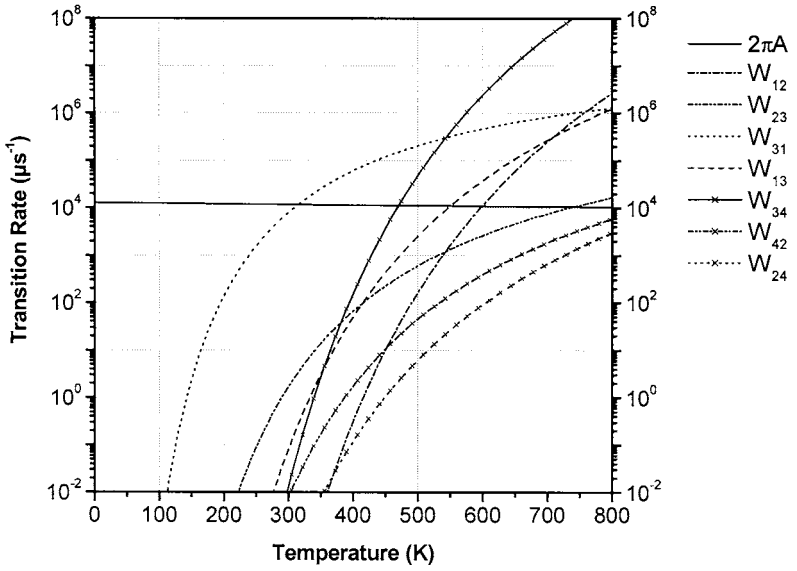

Figure 4. Transition rates for figure 3 deduced from parameters given by Hitti *et al* (1999).

1995, Hitti *et al* 1999). It appears that, except as regards the occupation of the negative state, they can also account for our neutral fraction data in the charge-exchange régime. This agreement may be fortuitous, however, since we have greater difficulty in establishing consistency with longitudinal-field relaxation data. In our own experiments, the partial rotation of the muon polarization with respect to the πM3 beam at PSI allowed us to analyse our data for the relaxation rate of longitudinal polarization as well as for the precession frequency of the transverse component. These high-field data are plotted in figure 5, where the low-field data of Chow *et al* (1993) are also reproduced.

We use the following expression for the relaxation rate, generalized from the two-state model given by Chow *et al* (1993) to our three-state model by incorporating equation (4) for neutral fraction:

$$\lambda = \{p_0 W\}\{2(1 + x^2 + W^2/(2\pi A)^2)\}^{-1}\alpha^{-1}. \tag{5}$$

Here p_0 again defines the average occupancy of $\mathrm{Mu}_{\mathrm{T}}^0$ (i.e. of state 2 in figure 3) and W is the total rate of exit from this state ($W = W_{23}$, simply, since we assume $W_{21} = W_{24} = 0$). The first bracketed term in equation (5) may therefore be thought of as the cycle rate and the second as the proportional loss of polarization per cycle. Alternatively, the expression may be rearranged to reveal a spectral density term at the electron–muon flip-flop frequency $A\sqrt{1 + x^2}$. Here the reduced field x is the magnetic field in units of the hyperfine field $2\pi A/\gamma_e$, so $x \approx 10$ in our 6 kG data and $x < 0.4$ in the low-field data of Chow *et al* (1993). The cycle rate $p_0 W$proves to be a monotonically increasing function of temperature, so the peaks in relaxation rate occur when the term $W^2/(2\pi A)^2$ relating the rate of exit from state 2 to hyperfine frequency becomes significant in the denominator: this condition may be deduced from figure 4, where the temperature-dependent (angular) frequency $2\pi A$ is also shown. The peak in relaxation rate should shift to higher temperature with increasing magnetic field, as confirmed by the two data sets of figure 5.

The third term α^{-1} in equation (5) is an ad hoc numerical factor which we are obliged to introduce. An indication that this is necessary can be seen from the dotted lines in figure 5:

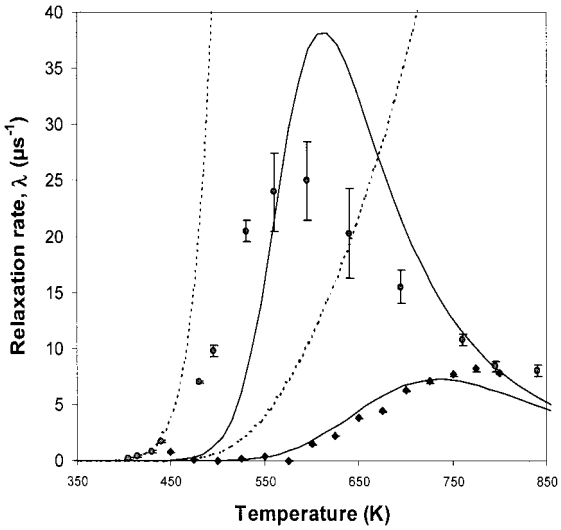

Figure 5. Muon spin-relaxation rates in a longitudinal field. The circles reproduce published low-field data (measured in 150–400 G by Chow *et al* 1993). The diamonds are our high-field data points (6 kG, this work). The lines are not fitted curves; they represent the corresponding low- and high-field predictions of equation (5), using the parameters of figure 4, with $\alpha = 1$ (dashed lines—low field left, high field right) and $\alpha = 35$ (solid lines, closer to the data sets).

these are simulations of λ from equation (5) using the parameters of figure 4, setting $\alpha = 1$. The left-hand dotted line goes together with the low-field data points (circles), the right-hand dotted line with our own high-field data points (diamonds). For both data sets the onset of relaxation is well modelled but the rates are vastly overestimated. Scaling with $\alpha = 35$ brings the rates into the correct range—these are the solid lines in figure 5—but does not model the field or temperature dependences satisfactorily.

From equation (5) it appears that the quantity λ/p_0 is a function of $W = W_{23}$ only. This quantity may therefore be analysed for the Arrhenius parameters of the site-change rate. With these established, it should be possible to refine the remaining parameters by fitting the p_0-data alone. However, it proves impossible to find a parameter set which also accounts for both the high- and low-field relaxation data, without values of α in the range 35–50. Even then, good fits could not be achieved over the whole temperature range.

We are currently pursuing several routes to resolving this difficulty. Within the three- and four-state models we are exploring different variants of the configuration-coordinate scheme, with different allowed transitions. In one of these we set $W_{12} = 0$ and introduce the reverse site change W_{32}; that is, we assume that electron capture precedes site change, eliminating the concept of activated capture. (The nature of activated capture is also discussed by Head and Lichti 2000). In another we retain all but one of the possible transitions, setting only $W_{21} = 0$. The virtue of these models is that, in principle, they offer the possibility of determining the elusive site-change energy between $\mathrm{Mu}^0_{\mathrm{BC}}$ and $\mathrm{Mu}^0_{\mathrm{T}}$, via the difference in activation energies for W_{32} and W_{23}. This parameter, so far undetermined, is crucial in deciding the order of the donor and acceptor levels of muonium in silicon, i.e. to resolving the negative-U question. With due regard for isotope effects, which will be relatively small since energy *differences* between the relevant sites and electronic configurations are not greatly sensitive to nuclear zero-point energy, any result for muonium should carry over, *mutatis mutandis*, for hydrogen (see e.g. Cox 1995).

It may be that at high temperatures the lattice cannot respond quickly enough to the instantaneous position of the fast-diffusing proton or muon, with the result that the bond-centre site becomes inaccessible (Kiefl 1999). Molecular dynamics simulations of proton trajectories in hot silicon (e.g. by Buda *et al* 1989) seem at first sight to support this suggestion but may be misleading, the simulation time windows being considerably shorter than the inverse rates of our charge-exchange cycle. If the bond centre does become inaccessible, the cycle $Mu_T^0 \rightleftharpoons Mu_T^-$ might then become more important as might also—at very high temperatures—the cycle $Mu_T^0 \rightleftharpoons Mu_T^+$. Other processes to be included within a three- or four-state model are hole capture, which may compete with electron loss via ionization, and also spin exchange on the Mu_T^0 state, since it could be the rate of spin flips W_{SF} with passing electrons rather than their capture and loss which limits the lifetime of its spin state. Spin exchange can easily be accommodated in equation (5) by writing $W = W_{23} + W_{SF}$ so that the larger of the two dominates. It is noteworthy that with $\alpha = 1$ and W equal to ionization rate, equation (5) reduces to the expression derived for two-state charge exchange by Chow *et al* (1993); with $\alpha = 1$ and $W = W_{SF}$ it reduces to the (first-order) expression for spin-exchange relaxation derived by Senba (1991).

In conclusion, we find that the muon spin-rotation signal in silicon exhibits a substantial paramagnetic shift at high temperatures. We infer that the neutral fraction is close to unity above 600 K, i.e. that the rate of electron capture is much greater than the rate of electron loss. This behaviour is well described by a three-state configuration-coordinate model for intrinsic Si in which the lifetime of the neutral state is set by site change from the cage centre to the bond centre, rather than by direct ionization of the deeper state. Our difficulty in obtaining simultaneous quantitative fits to longitudinal relaxation data with the same dynamical parameters raises doubts as to the overall consistency of the present three- or four-state models, however. Going beyond these, we hope to resolve the puzzle by introducing additional ingredients, namely by the involvement of vibrationally excited and delocalized or continuum states (see e.g. Oates *et al* 1978). By including the inverse site-change transition, $Mu_{BC}^0 \rightarrow Mu_T^0$, we hope also to obtain a value for the site-change energy and thence a resolution of the negative-U question.

Acknowledgments

Discussions with B Hitti, S R Kreitzman, R L Lichti and A M Stoneham are gratefully acknowledged.

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