A molecular radical model for hydrogen and muonium in graphite

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Abstract
Detection of muon spin relaxation in graphite above room temperature, together with reports of a temperature-dependent muon Knight shift, suggest that the muon state in graphite is not electronically diamagnetic, as previously supposed. The involvement of a molecular radical formed by the chemical reaction and bonding of interstitial muonium is proposed. These considerations should, with due regard for isotope effects, apply similarly to hydrogen and are supported by simulations of hydrogen addition to a graphene fragment. Density functional calculations provide hyperfine parameters as well as a visualization of the singly occupied molecular orbital. This allows interpretation of the data in terms of the temperature-dependent occupancy of this orbital and its rate of exchange with conduction electrons.

Positive muons stopped in graphite retain their full spin polarization. For this reason, graphite has traditionally been used as a control sample in μSR[6] and related experiments to calibrate muon polarization and decay asymmetry. Explicitly, the muons suffer no loss of polarization on implantation due to muonium formation: their muon spin-rotation signal in a transverse magnetic field has the appearance of simple Larmor precession and takes its maximum possible amplitude. In this respect, muons in graphite give similar precession signals to those stopped in non-magnetic metals such as aluminium or silver where, again, the muon spin-rotation signal has full initial amplitude. In metals, the absence of muonium formation is attributed to effective screening of the muon charge: the Yukawa potential, which replaces the unscreened Coulomb potential, either completely suppresses the binding of electrons in hydrogen-like states or else squeezes these to such shallow levels that they are in resonance with conduction band states and rapidly exchanged (see e.g. Stoneham 1975). In other words, there is no paramagnetic moment centred on implanted muons in simple metals, just as there is none centred on the

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[6] Muon spin rotation, relaxation and resonance.

screened-proton state of interstitial hydrogen. In graphite, however, the conduction electron density is much lower than in metals. At around 3×10^{18} cm^{-1} it is well below the threshold at which bound states should appear—the threshold is $\sim 3 \times 10^{22}$ cm^{-1}, approximately equivalent to the free-electron density in Sr or Ba, according to the criterion of Estreicher and Meier (1983). This consideration, together with the report that the muon Knight shift in graphite is temperature dependent (Chakhalian *et al* 1997), led us to examine the possibility that localized paramagnetic states are involved.

The fact that the muon spin-rotation signal has a unique frequency, close to but not in fact identical to the Larmor frequency of a free muon, implies that any contributing paramagnetic state has a lifetime much shorter than its inverse hyperfine constant (see e.g. Ivanter and Smilga 1969). That is, its spin exchange or charge exchange with the graphite conduction electrons is rapid. The intermittent or fluctuating hyperfine interaction, whose time average we suppose to be the main cause of the frequency shift in transverse field, should then also provide a source of muon spin relaxation which is equally effective in transverse or longitudinal magnetic fields[7]. Figure 1 shows our data for longitudinal relaxation rate in high-purity pyrolytic graphite, from measurements in a field applied parallel to the initial muon polarization (Cox *et al* 1998, 2000). In such experiments there is no precession or oscillatory evolution of polarization and we observe only a slow decline which can be fitted to a simple exponential, $P(t) = \exp(-t/T_1)$. Here we use the magnetic resonance notation for spin–lattice relaxation although the primary interaction of the muon spins is with the conduction electrons—as it is for the Korringa mechanism of nuclear spin relaxation in metals.
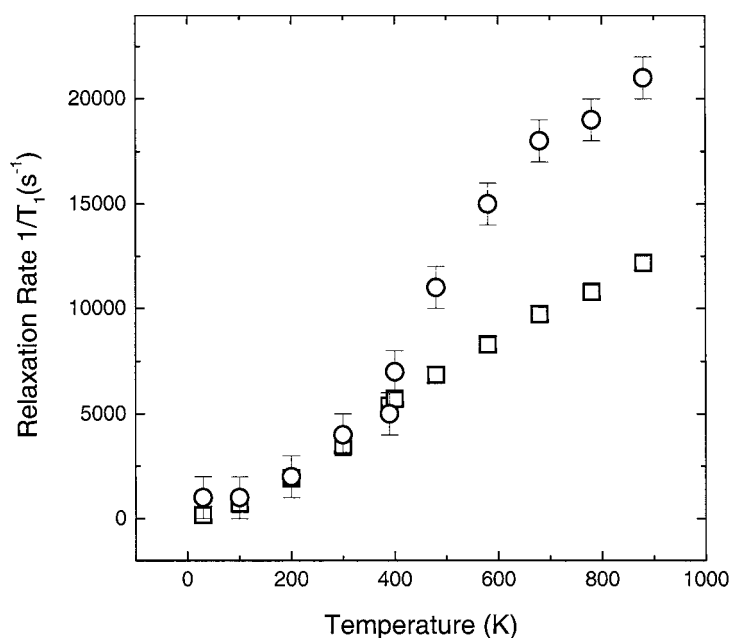

Figure 1. The temperature dependence of the muon spin-relaxation rate in graphite (circles), measured in a longitudinal field of 10 mT, together with the expectations of the Korringa formula (squares).

[7] Although nuclear magnetism is weak in graphite, with the result that the dipolar fields contribute little to the $1/T_2$ relaxation in transverse fields, we concentrate on $1/T_1$ relaxation in longitudinal fields; muon diffusion is not an issue in Korringa relaxation, provided that the electron exchange is faster than the muon hop rate.

We begin by comparing our relaxation-rate data with the prediction of the celebrated Korringa (1950) formula, which relates nuclear spin–lattice relaxation rate $1/T_1$ to Knight shift K in simple metals:

$$\frac{1}{T_1} = \frac{4\pi kT}{\hbar}\left(\frac{\gamma_n}{\gamma_e}\right)^2 K^2. \tag{1}$$

(An alternative derivation of this formula is given in the accompanying paper by Blundell and Cox (2001).) Figure 1 includes this prediction, evaluated from equation (1) using interpolated values of the muon Knight shift in graphite, now available above room temperature (Chakhalian and Kiefl 1999). To be explicit, we have used the isotropic component of the Knight shift, measured by these authors in a transverse magnetic field at TRIUMF; this varies between 380 ppm at low temperature and a broad maximum of 640 ppm around 600 K. Our own longitudinal-field relaxation data were taken with the EMU instrument at the ISIS Facility, where the pulsed nature of the ISIS source greatly facilitates detection of such slow relaxation: below room temperature the relaxation rates are at the limit of measurement, consistent with the absence of any report on this topic in the early μSR literature. Above room temperature, the rise in relaxation rate and the departure from the Korringa law are both rather striking[8].

In the following, we pursue a model of charge exchange on a localized paramagnetic centre, i.e. the rapid and repeated capture and loss of conduction electrons at or near the muon site. The frequency shift due to the intermittent hyperfine interaction should be proportional to the electronic polarization of the paramagnetic state and to the occupancy p_0 of that state— i.e. the average time spent in it. Assuming an isotropic hyperfine or Fermi-contact interaction of the form $hA\boldsymbol{I}\cdot\boldsymbol{S}$ between the muon spin $\boldsymbol{I}$ and the localized electron spin $\boldsymbol{S}$, we obtain

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

For the relaxation rate, we adapt an expression derived for charge exchange on muonium centres in semiconductors due to Chow *et al* (1993):

$$\frac{1}{T_1} = Wp_0\frac{2(\pi A)^2}{(2\pi A)^2 + (\gamma_e B)^2 + W^2}. \tag{3}$$

Here W is the inverse lifetime of the paramagnetic state, so Wp_0 may be thought of as the cycle rate and the remaining term in equation (3) as the proportional loss of polarization per cycle. In an accompanying paper we use the same equations ((2) and (3)) to interpret μSR data for hot silicon (Cox *et al* 2001). For graphite we expect to be in the fast-exchange limit at all temperatures and accessible fields, so $W \gg 2\pi A, \gamma_e B$ and the dependence on magnetic field B is suppressed, leading to the asymptotic expression

$$\frac{1}{T_1} \approx 2p_0(\pi A)^2/W. \tag{4}$$

Experimentally, we indeed find no variation in relaxation rate with field up to 100 mT; higher fields remain to be explored. Note that equation (3) is equally applicable to spin exchange: setting p_0 constant at unity and W equal to the electron spin-flip rate, it reduces to the expression for muon spin relaxation in a paramagnetic centre derived by Senba (1991). Equation (4) is likewise identical to the expression for fast spin exchange derived earlier by Ivanter and Smilga (1969). Spin exchange with $p_0 = 1$ cannot be the whole story for graphite, however, or the

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[8] In fact it is no surprise that the Korringa relationship, which was derived for the host nuclei of Pauli paramagnets at low temperature, should break down for interstitial muons in a semimetal. A version which uses a more appropriate density-of-states function around the Fermi level is under development by Chakhalian and Kiefl (1999).

frequency shift would follow Curie's law and vary as $1/T$: this dependence is evidently masked by the behaviour of p_0, which must *increase* with temperature.

It is noteworthy that by eliminating the hyperfine constant A between equations (2) and (4), a relationship is obtained between relaxation rate and paramagnetic shift, which is parametric in the cycle rate Wp_0 and which may be compared with the simpler Korringa relationship of equation (1).

We now consider the nature of the paramagnetic centre in graphite. If this were atomic muonium, the fraction of time spent in its neutral state would vary with temperature according to the lower set of results in figure 2. These are obtained by setting $A = 4.5$ GHz—the free-muonium hyperfine constant—in equation (2); p_0 then rises rapidly from a negligible value at cryogenic temperatures to 1% around room temperature, then more gradually to 5% near 800 K. (These values may be regarded as lower limits, since the hyperfine constant is often somewhat reduced for muonium as an interstitial defect.)
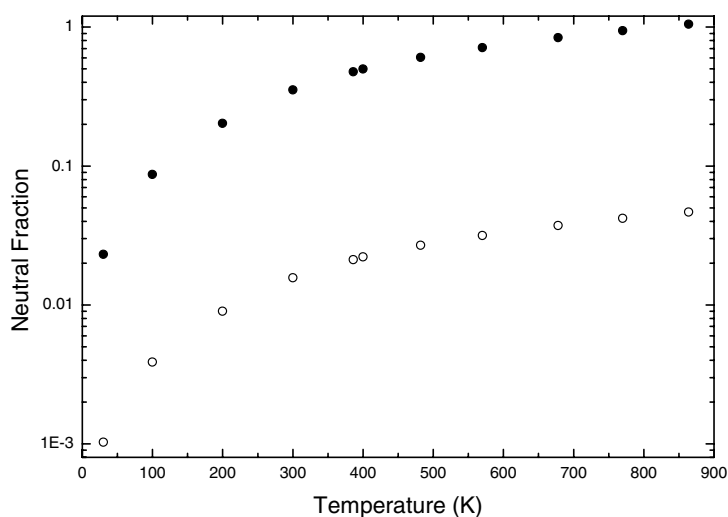

Figure 2. The paramagnetic fraction p_0 inferred from equation (2) and the muon Knight-shift data of Chakhalian and Kiefl (1999) assuming that the paramagnetic species is either (a) atomic muonium (lower points) or (b) the molecular radical of figure 4—see later (upper points).

Given the particular structure of graphite, however, where the bonding between layers is weak with the result that within the layers there is partial double-bond character, we envisage that muonium will react chemically by addition. Considering one of the Kekulé structures of a graphitic sheet, the reaction breaks one double bond, saturating the carbon atom at one end—the point of addition—and placing the unpaired spin at the other—in a dangling bond, so to speak. Superposition of all such contributing structures then suggests that most of the spin density will be distributed over the three equivalent carbon atoms adjacent to the point of addition, as sketched below (figure 3), presumably with a further degree of delocalization resulting from bond alternation.

That is, we envisage formation of a molecular radical, as is common for the reactions of atomic hydrogen or muonium with a variety of unsaturated organic compounds (see e.g. Walker 1983, Roduner 1988)[9]. The closest parallel with more complex structures is perhaps with

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[9] Initial muonium formation followed by chemical reaction and charge exchange is a formal description; of course, initial fixation of the thermalized muon in a manner akin to protonation, followed by electron capture, would lead to the same radical species.
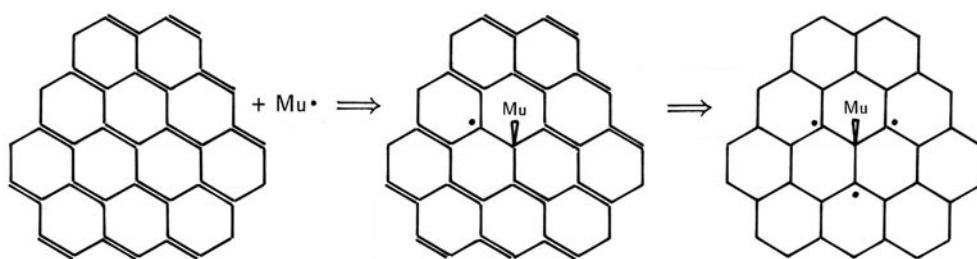
Figure 3. Sketch of muonium (or hydrogen) addition to a graphitic sheet and the intuitive distribution (dots) of the unpaired electron spin.

muonium addition to C_{60} fullerene, for which the spin-density distribution is known from various computational methods (e.g. Percival and Wlodek 1992, Claxton and Cox 1993) and from experiment (Percival *et al* 1995). The essential difference in graphite is that the spin states of the unpaired electron are short-lived, because of exchange with conduction electrons, so no hyperfine spectrum is visible.

This expectation is confirmed by AIMPRO calculations for the muonium or hydrogen adduct of a graphene fragment, $C_{62}H_{20}$. AIMPRO is a density functional cluster code that operates within the local spin-density approximation (Jones and Briddon 1998) and has been used to model similar carbon–impurity systems accurately, both on fullerenes (Eggen *et al* 1996) and on graphite itself (Leary *et al* 2000). Structures undergo a full unconstrained relaxation and the electron distribution by atom is calculated using Mulliken population analysis (Mulliken 1955). Figure 4 shows the singly occupied molecular orbital (SOMO) carrying the unpaired spin in the neutral species. A similar orbital becomes doubly occupied on capture of a second electron.
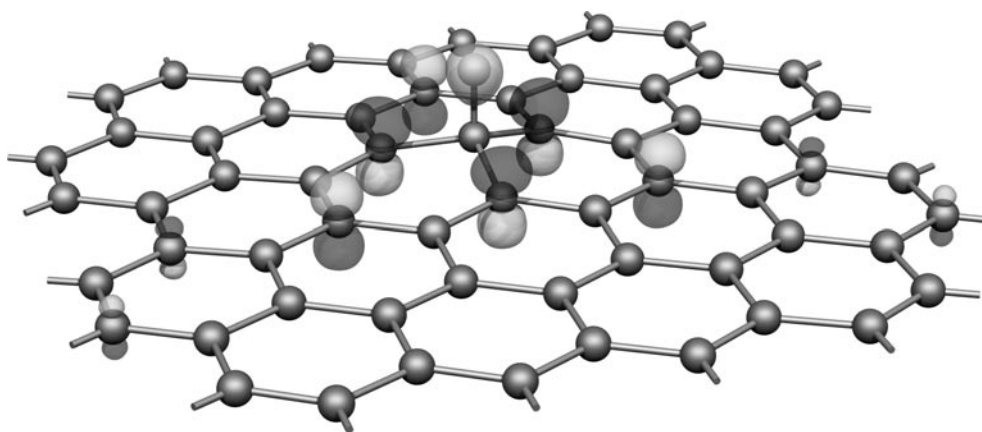

Figure 4. An AIMPRO representation of the singly occupied molecular orbital resulting from hydrogen or muonium addition to a graphene fragment.

Without correction for zero-point energies or isotope effects, these calculations give the s-wave spin density on the muon or proton at equilibrium geometry as 4.4% of the free-atom (muonium or hydrogen) values. In the usual units, this corresponds to a μSR hyperfine

constant of 200 MHz or an ESR[10] proton splitting of 2.2 mT. Setting $A = 200$ MHz in equation (2), the frequency-shift data of Chakhalian *et al* (1997), Chakhalian and Kiefl (1999) can be analysed for the paramagnetic fraction p_0 to give the upper results shown in figure 2, these rising from 1% near 100 K and saturating close to unity near 800 K. This increase will be somewhat attenuated, and the final value lower, if there is any significant structural change with temperature: the muonium is rather weakly bound, so the average C–Mu bond length and corresponding hyperfine constant will both increase with temperature, but these effects have yet to be calculated.

While the graphene fragment is not small, its symmetry makes it a semiconductor with a HOMO–LUMO gap of about 1.0 eV[11]. With the hydrogen atom added, the AIMPRO calculations place the SOMO just below mid-gap. In bulk graphite there is no such energy gap so we cannot estimate the position of the defect with respect to the Fermi level. In other words, we cannot predict whether the diamagnetic species in dynamic equilibrium with the neutral radical is the positively or negatively charged molecular ion. Ionization of the negative ion at high temperatures leaving the orbital of figure 4 singly occupied is an appealing interpretation: Chakhalian and Kiefl (1999) describe this as 'shaking off' the electrons which screen the magnetic moment (which they envisage as atomic muonium). The following argument, however, puts a $0/-$ charge cycle in some doubt. Using the upper values of p_0 in figure 2, our relaxation data of figure 1 may be analysed via equation (4) for the transition rate W. We find the interesting result that W is almost constant above room temperature at a value close to 40 ps^{-1}, corresponding to a lifetime of the paramagnetic state of 0.025 ps. This result argues against equilibrium with the negative ion since, if W were an electron capture rate, it should increase with temperature, reflecting both the density and thermal velocity of conduction electrons. For equilibrium with a positive ion, on the other hand, W would correspond to an ionization rate of a shallow neutral centre, saturated at its prefactor value. Details of the charge-exchange cycle in this semimetal evidently remain an open question, as they do in semiconductors such as silicon at high temperature (Cox *et al* 2001).

In conclusion, we find significant spin–lattice relaxation for positive muons implanted into graphite. We attribute this and the reported temperature dependence of the muon Knight shift to intermittent hyperfine interaction in a localized paramagnetic centre. The short-lived bound state could be muonium, resembling interstitial atomic hydrogen, but we favour a molecular radical model in which the electron spin is delocalized over carbon atoms close to the point of addition. The data require a temperature-dependent paramagnetic fraction, tending to unity towards 800 K for our molecular radical model, although rapid electron exchange precludes spectroscopic characterization. AIMPRO calculations support the radical model, providing details of the SOMO and of the muon or proton hyperfine coupling. Pending small corrections for isotope effects, the instantaneous spin density on the muon or proton is some 4% of its value in atomic muonium or hydrogen. This result, together with the muon spin-relaxation data, implies a lifetime of the neutral state of about 0.025 ps above room temperature.

Acknowledgments

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[10] Electron spin resonance.
[11] In the centre of the sheet (before placement of the hydrogen atom) the C–C bond lengths are all 1.410 ± 0.005 Å.

References

Blundell S J and Cox S F J 2001 *J. Phys.: Condens. Matter* **13**

Chakhalian J, Dunsiger S R, Kiefl R F, MacFarlane W A, Sonier J E, Hitti B and Fischer J 1997 *Hyperfine Interact.* **106** 245

Chakhalian J and Kiefl R F 1999 private communication of *TRIUMF Report on Experiment E758*; also presented orally by J Chakhalian at *8th Int. Conf. on Muon Spin Rotation, Relaxation and Resonance (Les Diablerets, Switzerland, 30 August—3 September 1999)*

Chow K, Kiefl R F, Schneider J W, Hitti B, Estle T L, Lichti R L, Schwab C, DuVarney R C, Kreitzman S R, MacFarlane W A and Senba S 1993 *Phys. Rev.* B **47** 16 004

Claxton T A and Cox S F J 1993 *Chem. Phys. Lett.* **207** 31

Cox S F J, Charlton M and Cottrell S P 1998 *ISIS Annual Report: Experiment RB9182*

Cox S F J, Charlton M, Donnelly P A, Schenck A and Amato A 2001 *J. Phys.: Condens. Matter* **13**

Cox S F J, Cottrell S P, Charlton M, Donnelly P A, Blundell S J, Smith J L, Cooley J C and Hults W L 2000 *Physica* B **289–290** 594

Eggen B R, Heggie M I, Latham C D, Jones R and Briddon P R 1996 *Science* **272** 87

Estreicher S K and Meier P F 1983 *Phys. Rev.* B **27** 642

Ivanter I G and Smilga V P 1969 *Sov. Phys.–JETP* **28** 796

Jones R and Briddon P R 1998 *Semicond. Semimet.* A **51** 287

Korringa J 1950 *Physica* **16** 601

Leary P, Ewels C P, Heggie M I, Jones R and Briddon P R 2000 *Phys. Status Solidi* **217** 429

Mulliken R S 1955 *J. Chem. Phys.* **23** 1833

Percival P W, Addison-Jones B, Brodovitch J-C, Ji F, Thewalt M L W and Anthony T R 1995 *Chem. Phys. Lett.* **245** 90

Percival P W and Wlodek S 1992 *Chem. Phys. Lett.* **196** 317

Roduner E 1988 *The Positive Muon as a Probe in Free Radical Chemistry (Springer Lecture Notes in Chemistry vol 19)* (Berlin: Springer)

Senba M 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** 3531 (first-order term in equation (44))

Stoneham A M 1975 *Theory of Defects in Solids* (Oxford: Clarendon) ch 9

Walker D C 1983 *Muon and Muonium Chemistry* (Cambridge: Cambridge University Press)