

MSR Studies in the Progress Towards Diamond Electronics

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Abstract. The recent development of device quality synthetic diamond dramatically increases the potential of diamond as a wide band gap semiconductor. A remaining obstacle is the lack of shallow n-type dopants. Molecular dopant systems have been shown theoretically to lead to the shallowing of levels in the band gap. Some of these systems involve defect-hydrogen complexes. This, and other phenomena, motivate the study of the chemistry and dynamics of hydrogen in diamond. Much information on this topic has been obtained from Muon Spin Rotation (MSR) experiments. These experiments view the muonium ($\text{Mu} \equiv \mu^+e^-$) atom as a light chemical analogue of hydrogen. Data on isolated muonium in diamond is reviewed, and evidence on formation of N-Mu-N (a shallow dopant candidate), the trapping of Mu at B-dopants, and fast quantum diffusion of muonium are discussed.

Key Words: diamond, diffusion, dopants, muonium.

1. Introduction

Diamond has for a long time been known to have a theoretical performance as an electronic material with figures of merit (FoM) for various active electronic applications that can exceed those of silicon by one to four orders of magnitude, depending on the application [1–4]. In fact, it is advantageous for extreme electronic applications, such as high power, high temperature, and high frequency devices. Of particular significance are the high breakdown field and combined charge carrier mobility together with the highest room temperature thermal conductivity and extremely low intrinsic resistivity. Diamond is also radiation hard. Besides these properties that are directly relevant to device performance, diamond also exhibits a range of other excellent optical, physical, thermal, mechanical and chemical properties. For example, the spectral transparency is the widest of any material. The low thermal expansion coefficient together with the previously mentioned high thermal conductivity renders it very resistant to thermal stresses.

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The main reason for the slow development of applications has been the small size, cost and defected nature of natural and synthetic material. True grain boundaries, dislocations and significant concentrations of inhomogeneously incorporated single substitutional nitrogen are recognised as important defects. Recently, however, the situation regarding sample quality and size has improved, both with respect to the high pressure high temperature (HPHT) synthesis and the chemical vapour deposition (CVD) synthesis of diamond. For example, away from the seed, HPHT diamonds appropriately processed attain X-ray rocking curves close to the Darwin line width [5]. Single crystal (SC) CVD diamonds exhibit charge carrier lifetimes in the microsecond range, more than two orders of magnitude better than selected nitrogen free natural diamonds [6]. Charge collection distances are therefore larger than typical device dimensions.

The realisation of device quality diamond dramatically increases the potential to exploit this material as a wide band gap semi-conductor. A reasonably shallow p-type dopant exists, this being the boron acceptor with an activation energy of 0.37 eV. There is not yet a shallow n-type dopant. Nitrogen forms a very deep donor with an activation energy of 1.7 eV. It is possible that phosphorous yields an acceptor level with an activation energy of 0.52 eV, however, it readily complexes with the vacancy, and activation levels are very low. Other possibilities for elemental dopants have been considered theoretically and experimentally, but they are not yet reliably established [7, 8]. There are effectively only intrinsic or unipolar electronic devices. The possibility of shallow molecular dopant systems in diamond is intriguing. Several of these have been predicted, see for example [9–11]. Complexation of certain defects appears to be favourable in diamond, and it is expected that this can be exploited to produce carefully selected molecular species.

There is therefore an active interest for research which increases the understanding of factors leading to improved diamond quality and developing shallow n-type dopants. In this regard, hydrogen plays an important role. For example, diamonds are always contaminated with hydrogen. Hydrogen is known to passivate acceptors and donors, and possibly also other compensating centres themselves. There may be a mechanism by which it can facilitate the formation of extended defects. Hydrogen surface termination leads to surface conductivity. There is at least one electrically active hydrogen defect (H1). Finally, hydrogen complexation with certain impurities is expected to lead to the shallowing of donor states (see [7, 11] and references therein).

Much of the information on hydrogen in diamond has come from Muon Spin Rotation/Relaxation/Resonance (MSR) studies, and this method also provides the only unambiguous data [11, 12]. These experiments view the muonium ($\text{Mu} \equiv \mu^+e^-$) atom as a light chemical analogue of hydrogen. Chemical information is related to the spectroscopy of the muonium states formed. Caveats apply due to the lighter mass of muonium in comparing dynamical information.

This work will briefly review the situation for isolated muonium in diamond. Following this several recent experiments are of interest. A possible shallow molecular dopant system is N-H-N [9] and a candidate for this system has been observed in MSR experiments. The passivation of the boron dopant in diamond by hydrogen has been observed in electrical measurements. MSR measurements in p-type diamond evidence trapping behaviour which is consistent with passivation. These processes involve diffusion. It is therefore of interest to discuss studies of the fast quantum diffusion of muonium in diamond.

2. Isolated muonium in diamond

There is not yet any information on isolated hydrogen in diamond, and therefore MSR studies are especially important here. The population of different isolated muonium states formed in diamond are affected by the sample quality. In the purest of diamonds (HPHT samples with the concentration of nitrogen $C_N < \text{ppm}$), the following species are observed, where f is the prompt formation fraction.

Mu_T : Muonium at the tetrahedral interstitial site ($f_{\text{Mu}_T} \approx 70\%$).

Mu_{BC} : Bond centered muonium ($f_{\text{Mu}_{BC}} \approx 20\%$).

μ_D⁺ : The muon in a diamagnetic environment ($f_{\mu_D^+} \approx 10\%$).

In this case there is no missing fraction ($f_{MF} \approx 0$). The hyperfine (hf) interaction of Mu_T is isotropic with a hf constant $A = 3711 \text{ MHz}$. This is 83% of the vacuum muonium value which is amongst the largest measured in any material. This species is known to diffuse rapidly, as in defected diamond, it has a rapidly relaxing amplitude.

The hf interaction of Mu_{BC} is anisotropic with 111 axial symmetry. The fermi contact and dipolar hf coupling constants are small and of opposite sign, $A_s = -205 \text{ MHz}$ and $A_p = 186 \text{ MHz}$ respectively [13]. The nuclear hf coupling constants for the nearest and next nearest neighbours have also been measured [14]. Taken together this indicates that the unpaired electron spin density is dominantly localised on the two carbon neighbours (92%) somewhat analogous to a muonated radical. The correspondence to theoretical models which include relaxation and electron correlations is good (see [11, 14] and references therein). The neighbouring carbon atoms relax away from each other by about 40%. This may be seen rather as a rehybridisation of the valence orbitals of these carbon atoms from sp^3 to sp^2 so that less energy is required than an elastic distortion. The temperature stability of this species (measured up to 1080 K) as well as the preservation of anisotropy and the very narrow line widths are indicative of an immobile state.

There is a thermally activated first order transition from Mu_T → Mu_{BC} at 450 K. The Arrhenius prefactor for this is compatible with the optical phonon

frequency so that only one hop is required. Mu_{BC} is therefore the most stable form of isolated muonium in diamond.

In comparing the situation to hydrogen, one expects to be able to identify both H_T and H_{BC} . However, zero point energies would be lower so that the barrier for the transition $\text{H}_T \rightarrow \text{H}_{BC}$ would be higher. In addition, the time-window for MSR is about 12 μs wide immediately following implantation of muons at a concentration so low that they would not be expected to interact with each other. In contrast, later and longer time windows for H measurements, together with the mobility of H_T suggest that it traps competitively with other defects and impurities present in the diamond. In addition, auto-trapping configurations are possible (H_2^* e.t.c.). Nonetheless, despite searches, H_T and H_{BC} have not yet been seen in diamond.

3. N-H complexes – possible shallow molecular dopants

Transverse Field (TF)- μSR measurements on nitrogen-rich type Ia diamond containing aggregated A- and B-centres of up to 1000 ppm exhibit a substantial missing fraction (MF), a reduced and rapidly spin relaxing Mu_T fraction and no Mu_{BC} [15–17]. An A-centre is formed by two adjacent nitrogen atoms at substitutional sites [18], and a B-centre is believed to be formed by four nearby nitrogen atoms at substitutional sites surrounding a vacancy [19–21]. The spin relaxation rate of the Mu_T state has been interpreted as due to diffusion and trapping at these nitrogen-aggregated centres [14, 15]. The MF was conjectured to be a muonium state associated with nitrogen aggregates, and may therefore be revealed in Longitudinal Field (LF)- μSR measurements. This turned out to be the case. In fact almost 100% recovery of the spin polarization was possible already at a field of 0.4 T for the extrapolated initial muon fraction [22–24]. The corresponding TF- μSR data for this sample were used to assist in extracting the components due to Mu_T , Mu_{BC} and μ^+ from the net LF- μSR repolarisation curve. The field quenching behaviour of the remaining 60% (previously missing) fraction was then revealed as shown in Figure 1. The new configuration was termed Mu_X and would represent muonium trapped in some way at an A or B-centre. The hf interaction symmetry is just less than axial, and its parameters are given as $A_s = 4158(1500)$ MHz, $A_p = 248(130)$ MHz and $\delta A = -28(50)$ MHz.

Various muonium complexes with A and B centres have been explored theoretically. A likely candidate is the muonium trapped in the ‘bond centre’ position of the A-centre. Neutral hydrogen was found to be more stable within an A-centre than within the bond-centred site by about 2.4 eV [25]. In addition, the hydrogen, though centrally located between the nitrogen atoms in the A-centre, has a small off axis displacement which may account for the observed less than axial symmetry of the hf parameters at this site.

The N-H-N system is a possible shallow molecular dopant [9]. Future experiments will be optimised to study the structure and possible ionisation of this system.

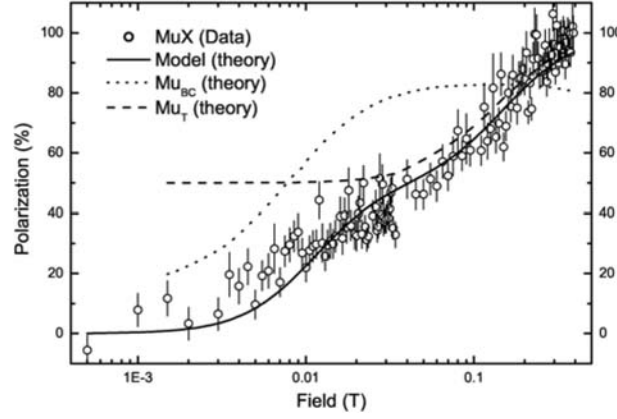


Figure 1. Repolarisation curve for muonium configuration Mu_X , in nitrogen-rich diamond. The known behavior (from TF- μ SR measurements) for Mu_T and μ_D^+ have been removed. Curves for Mu_T and Mu_{BC} are included for comparison. (Asymmetries referenced to 100% for each species).

4. Muonium interactions in p-type diamond

As has been mentioned before, low nitrogen content diamonds are expected to exhibit a large non-relaxing Mu_T fraction. Natural semi-conducting diamond has sufficiently low nitrogen and other defects that a significant proportion of boron acceptors are uncompensated. The boron acceptors would therefore be expected to be the dominant trap in such a diamond. TF- μ SR measurements were conducted in a natural semi-conducting diamond which contained 0.28 ppm uncompensated boron acceptors. The external magnetic field was 7.5 mT and the temperature was varied in the range 3-300 K. The spin relaxation rate λ_{Mu_T} for the Mu_T component, was determined in the usual way [26], and is displayed in Figure 2.

The relaxation rate is high at low temperatures, and has a power law fall off from 100-300 K. Its final value is consistent with the relaxation expected for a pure diamond. The relaxation is explained by rapid diffusion of the Mu_T followed by deep trapping at a defect where the muon(ium) experiences a substantially different hyperfine environment. This is a T_2 mechanism where the muon ensemble dephases due to different arrival times at the traps. Effectively, the relaxation rate is proportional to the diffusion constant $D_c(T)$. The faster diffusion at lower temperatures has been discussed elsewhere in the context of quantum diffusion. What is relevant here is clear evidence of the interaction of Mu_T with the boron dopants, following diffusion [27, 28].

5. Quantum diffusion of muonium in diamond

The rapid diffusion at low temperature, seen in the previous section, led to a continuing study of the motional behavior of the tetrahedral interstitial muonium (Mu_T) in diamond. The presence of traps in the previous study complicate

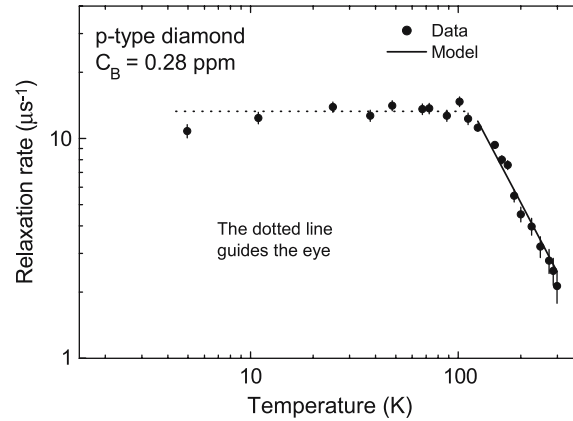


Figure 2. Spin relaxation rate of Mu_T , as a function of temperature, in p-type semi-conducting type IIb diamond.

extraction of the diffusion constant as the trap radius is itself also temperature dependent. Clearly, one needs to observe the motion of the Mu_T in a pure diamond. This requires a pure synthetic diamond consisting dominantly of ^{13}C . Mu_T diffusion experiments were carried out using both the TF- μSR and LF- μSR methods. In the previous case, and in the following two cases, the **relaxation mechanism** by which the diffusion constant is related to the relaxation rate λ_{Mu_T} is summarised.

TF- μ SR: diffusion, deep trapping; This has been explained above. The sample must have defects. Faster relaxation corresponds to faster diffusion. This is a T_2 mechanism.

TF- μ SR : motional narrowing; The sample is pure, the diffusion is against a background of randomly oriented ^{13}C nuclear moments. A static or trapped ensemble experiences different local fields and each member of the ensemble precesses at a slightly different rate, leading to the dephasing of the spin polarisation of the ensemble. If the Mu_T is sufficiently mobile, such that it averages the local field to a single well-defined value on a time scale which is short compared to the period of its precession, then the ensemble does not dephase. In this mode, faster diffusion leads to smaller relaxation of the spin polarisation. This is a T_2 mechanism.

LF- μ SR: induced transitions; The sample is pure, the diffusion is against a background of randomly oriented ^{13}C nuclear moments. This is equivalent to illumination of the Mu_T by radio-frequency radiation with a Lorentzian power spectrum, centered at zero with a width dependent on the diffusion constant. This effective radiation field induces transitions in the hyperfine levels of the Mu_T ,

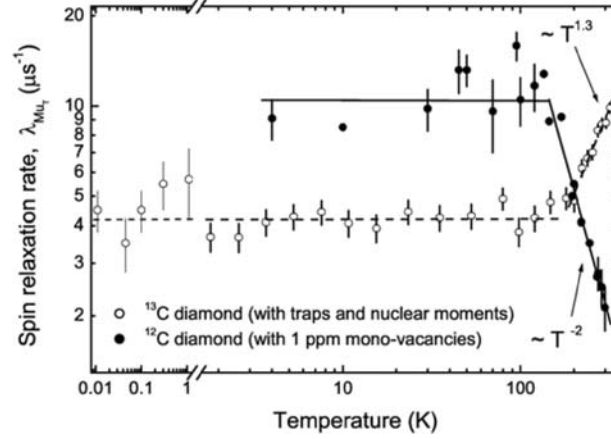


Figure 3. Spin relaxation rate of Mu_T , as a function of temperature, in diamond as described in the text.

which depolarize the Mu_T ensemble. There is not a monotonic relation between the relaxation rate and the diffusion constant. This is a T_1 mechanism.

Light particle diffusion in diamond would be expected to proceed through different mechanisms in different temperature regimes. This would be fast quantum diffusion of Mu_T in a relatively delocalised Bloch state at low temperatures and fast classical over-barrier hopping at high temperatures. The intermediate regime is associated with slower quantum diffusion due to phononic mechanisms that cause a loss of coherence (see [29, 30] and many references therein). Ideally, one would observe a minimum in the diffusion constant between these two regimes. The lower temperature side of this minimum is related to a two-phonon mediated tunneling between adjacent interstitial sites of the small polaron represented by the weakly self-trapped Mu_T due to its own local lattice distortion. This section is expected to follow a negative power law temperature behaviour. The higher temperature side of this minimum is related to effects like the fluctuational preparation of the barrier (FPB) and the polaron effect (PE), which are single phonon mediated and have an Arrhenius-like signature even though they are still related to quantum tunneling. In diamond, the period of quantum diffusion is expected to be maintained to rather high temperatures [12].

The relaxation rate data for the first two mechanisms mentioned above is presented in Figure 3. It is clear that the diffusion constant would be high in both cases, and then follow a power law decrease in the region 100–300 K. It is expected that the ^{13}C sample is not perfectly pure as the relaxation rate is not sufficiently low in the rapid diffusion regime. There would be therefore a mixture of the two mechanisms for this sample. In addition, the temperature dependence of the trap radius would weaken the power law behaviour in the 100–300 K regime for both measurements. These two measurements of the relaxation rate,

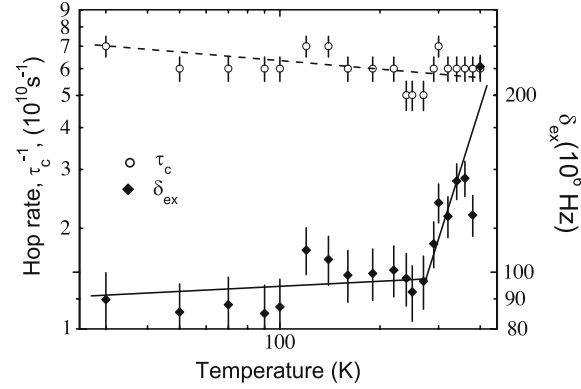


Figure 4. Hop rates, τ_c^{-1} , and nuclear hyperfine interaction, δ_{ex} , of Mu_T in ^{13}C diamond, as a function of temperature. Dotted and solid lines guide the eye.

with very different mechanisms, therefore seem to corroborate each other. Further details of the experiment can be found in [27, 29].

The relaxation rate data for the third mechanism mentioned above is presented in Figure 4. To produce this data, conventional LF- μ SR time spectra were recorded at various temperatures (ranging from 10 K to 400 K) and magnetic fields (ranging from 20 mT to 0.4 T). The extraction of the diffusion constant from the relaxation rate is not unique unless the fitting of the temperature dependence of the time differential muon asymmetry is done simultaneously for different magnetic fields. This fitting is performed using the Redfield analysis method [32]. Moreover the choice of the magnetic fields must be carefully made. The procedures used to select the fields and extract the inverse correlation time τ_c^{-1} (which is proportional to the diffusion constant) are discussed in detail in [31]. This mechanism has the more reliable model for the extraction of the diffusion constant, and it is also quantitative in the inverse correlation time, τ_c^{-1} . An additional parameter extracted is the nuclear hf parameter, δ_{ex} , which is a measure of the combined effect of all the nuclear spins in the vicinity of the muonium interacting with the muon via the correlated electron.

One notes from Figure 4 that the inverse correlation time τ_c^{-1} is essentially constant at the rather high value of $6 \times 10^{10} \text{ s}^{-1}$. This is inconsistent in its temperature behaviour with classical diffusion, and its magnitude confirms the very fast diffusion appropriate for a quantum mechanism. However, the power law behaviour from 100–300 K seen in the previous two types of measurement is not evident. Instead, the nuclear hf parameter, δ_{ex} , appears to display a power law behaviour. The phenomena resembles that observed in NaCl [32], which was attributed to dynamical effects. The measurements could not be pursued to higher temperatures in order to continue to map out the diffusion behaviour due to the onset of the thermal conversion of $\text{Mu}_T \rightarrow \text{Mu}_{BC}$.

6. Conclusions

Hydrogen chemistry and dynamics in diamond are important in understanding the material in the context of ultra-high quality diamond as well as electronic diamond. Here, MSR studies have been essential. The isolated forms of muonium in diamond have been reviewed. Recent measurements elaborate the frontiers of these studies where the data is consistent with the formation of possible shallow molecular dopants, as well as the direct observation of passivation. Finally, it appears that diamond does indeed support the quantum diffusion of muonium up to at least room temperature, the highest temperature for this diffusion mode of any material.

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