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## Paramagnetic defects in hydrogenated amorphous carbon powders

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### Abstract

Hydrogenated amorphous carbon materials typically contain high concentrations of paramagnetic defects, the density of which can be quantified by electron paramagnetic resonance (EPR). In this work EPR measurements near 9.5, 94, and 189 GHz have been performed on polymeric and diamond-like hydrogenated amorphous carbon (a-C:H) powder samples. A similar single resonance line was observed at all frequencies for the two forms of a-C:H studied. No contributions to the spectrum from centres with resolved anisotropic  $g$ -values as reported earlier were detected. An increase in linewidth with microwave frequency was observed. Possible contributions to this frequency dependence are discussed.

Hydrogenated amorphous carbon (a-C:H) materials exhibit a wide range of physical properties due to the coexistence of both  $sp^3$  and  $sp^2$  bonded carbon sites, allowing flexibility in the ratio and range of possible configurations. It has been proposed that the inclusion of  $sp^2$  sites within a continuous random network of  $sp^3$  sites would result in the formation of ring structures, and that these rings can fuse, forming clusters [1]. A ubiquitous feature of a-C:H materials is the presence of a high concentration of paramagnetic centres, typically in the range  $10^{18}$ – $10^{21}$   $\text{cm}^{-3}$ , as determined by electron paramagnetic resonance (EPR). Conventional EPR spectra recorded near 9.5 GHz yield a single structureless line, providing little direct insight into the nature of the defect centres. Evidence for different microscopic configurations can, however, be inferred from variations in linewidth with deposition conditions [2]. It has been reported [3] that EPR measurements performed at the higher frequency of 94 GHz allow the spectral averaging effects arising from exchange interactions to be overcome, so allowing

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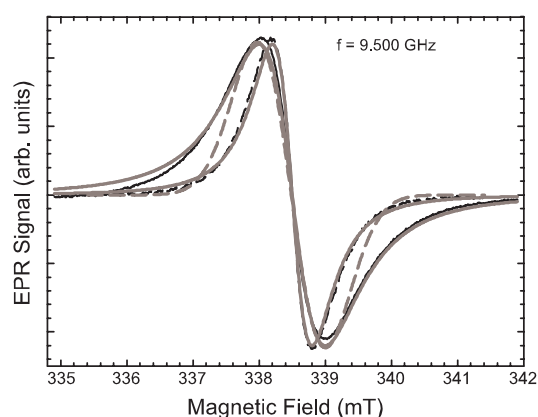
contributions to the spectrum from paramagnetic centres with anisotropic spin Hamiltonians to be resolved. The presence of resolved features in an EPR powder pattern spectrum can often be identified as resulting from  $g$ -value and or nuclear hyperfine interaction anisotropy and can provide chemical and structural insight on the defect. The spectra from a-C:H thin films grown on silicon showed contributions from two centres giving axial powder patterns that were attributed to localized  $\pi$  states on nanosized  $sp^2$  graphite-like carbon clusters of two different sizes [3]. In this paper we report EPR measurements on a-C:H materials performed at frequencies near 9.5, 94, and 189 GHz, and find no evidence for the resolution of such axial powder-pattern spectra.

If  $sp^2$  sites could be excluded, then the formation of a continuous random network of  $sp^3$  sites, with bond length and angle variations consistent with energy minimization, would characterize the structure of a-C:H. Inclusion of  $sp^2$  sites greatly extends the range of possible structures. It has been proposed that these sites would pair, forming sixfold rings, and that these rings could fuse to create aromatic clusters [1]. Later, total-energy calculations suggested the presence of smaller  $sp^2$  clusters, and showed that these would tend to be formed from alkene (olefinic), chainlike, groups [4–6]. Evidence for the presence of both aromatic and alkene clusters has come from Raman spectroscopy [7].

There is a clear trend, albeit with considerable scatter, in the relation between optical gaps and paramagnetic defect densities for amorphous carbon materials [8]. The lowest paramagnetic defect densities are reported for low  $sp^2$  content, high optical gap, in material termed *polymeric*. While the  $sp^3$  fraction is high, so is the hydrogen content, giving a soft material. The reduction of the optical gap correlates with a reduction in hydrogen content and an increase in  $sp^2$  carbon content, giving a harder, *diamond-like*, material. Diamond-like a-C:H exhibits a high paramagnetic defect density. The variation in optical gap is assumed to be controlled by the configuration of the  $sp^2$  sites [9, 10]; increasing their content is accompanied by variations in cluster size density and bond distortion.

The 9 GHz band EPR spectra from these materials contains a single line with a near-Lorentzian lineshape. Deviations toward a Gaussian lineshape have been reported for some high- $sp^3$ , high-hydrogen, polymeric samples. The linewidth has been observed to reduce with increasing  $sp^2$  content through the diamond-like phase region, while the spin concentration, after an initial rise, remains approximately constant. The observation suggests that the associated structural changes result in the clustering of paramagnetic entities, allowing exchange interactions between centres to become increasingly effective, thereby giving rise to increased exchange narrowing. Barklie *et al* [2] have made a systematic study of EPR linewidth and lineshape variations in a-C:H, which has provided further evidence on the role of exchange and the presence of spin centre clustering. There has been general acceptance that the omnipresent paramagnetic centres observed in amorphous carbon materials are probably associated with the  $sp^2$  regions. However, no direct evidence on the nature of the centres was obtainable from 9 GHz band spectra, for example from  $g$ -value anisotropy or hydrogen hyperfine structure.

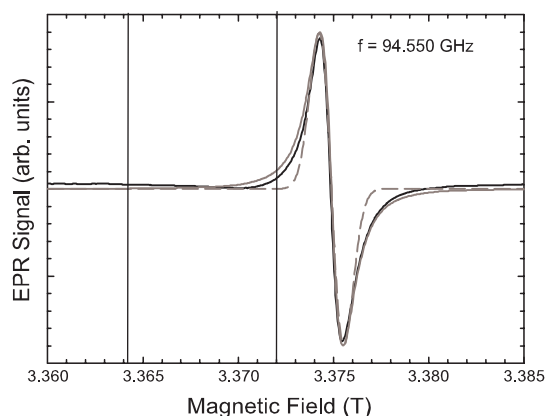
Recent EPR measurements [3] made near 9.5, 35, and 94 GHz on thin films of a-C:H, namely a polymeric, a diamond-like, and a sample intermediate between the two, all deposited on silicon samples, seem to show clearly resolved  $g$ -value anisotropy in the 94 GHz spectrum. Two centres exhibiting different axial  $g$ -anisotropies were reported. The appearance of resolved features in the high-frequency spectrum was attributed to the dominance of the resulting increased resonance magnetic field anisotropy over the effect of the exchange interaction. Using a previous study on the relation between  $g$ -value anisotropy and crystallite size for heat-treated carbon blacks [11], the results were interpreted as providing evidence for the existence of two cluster sizes, both less than 5 nm.



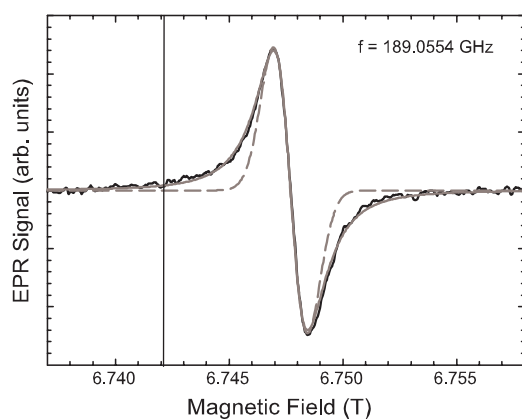
**Figure 1.** 9.5 GHz EPR spectra from polymeric (solid) and diamond-like (dash) a-C:H with best fit Gaussian (grey dash) and Lorentzian (grey solid) lineshape functions.

The samples used in this study were deposited from methane using a plasma-enhanced chemical vapour deposition system. The samples were deposited on large-area glass which provided convenient quantities of powder materials. The measurements reported here were made on polymeric and diamond-like samples. The use of powder samples avoided the possibility of detecting spurious EPR signals from the substrate or the film–substrate interface. EPR studies near 9.5 GHz were performed using a Bruker EMX spectrometer. The microwave frequency was measured, and the magnetic field monitored using an NMR magnetometer. High-frequency EPR measurements were performed with a quasioptical spectrometer operating near 94 and 189 GHz, using a non-resonant sample cavity and a frequency-locked oscillator [12]. Care was taken with the high-frequency measurements to analyse absorption spectra. Either the microwave phase was systematically adjusted or the experimental mixed phase spectra were corrected using a Hilbert transform method. Care was also taken to avoid line broadening due to either power saturation or over-modulation. Average spin density measurements were made near 9.5 GHz using a series of solid, and toluene solution, DPPH standard samples.

The 9.5 GHz EPR spectra for the polymeric and diamond-like samples are shown in figure 1, with best fit Lorentzian and Gaussian lineshapes. The polymeric sample exhibits a wider line (see figure 4) and shows slight departures from a Lorentzian. The paramagnetic defect densities were determined to be  $1.4(3) \times 10^{19} \text{ cm}^{-3}$  and  $1.0(2) \times 10^{20} \text{ cm}^{-3}$  for the polymeric and diamond-like samples, respectively. The  $g$ -values were found to be 2.0025(2) for both samples. The properties of the EPR spectra for the two types of a-C:H are consistent with previous reports [2, 8]. A near-94 GHz EPR spectrum from the polymeric a-C:H sample is shown in figure 2. It is closely Lorentzian and has an increased linewidth compared to the 9.5 GHz spectrum as shown in figure 4. The spectrum from the diamond-like sample was closely Lorentzian. Neither of the 94 GHz spectra showed evidence for the previously reported [3] defect centres with resolved axial  $g$ -value features thought to arise from a bimodal size distribution of  $sp^2$  nanoclusters. The expected positions of these features, calculated from the reported  $g_{\parallel}$  values [3], are shown in figure 2. Measurements were also made near 189 GHz. The spectrum from the polymeric sample is shown in figure 3. The linewidth again increases (see figure 4) and the lineshape is closely Lorentzian. The diamond-like sample also showed a Lorentzian spectrum with a linewidth increased with respect to that at 94 GHz as shown in figure 4. No evidence for spectra with resolved  $g$ -anisotropy was found from either sample; the



**Figure 2.** 94 GHz EPR spectrum from polymeric a-C:H with best fit Gaussian (grey dash) and Lorentzian (grey solid) lineshape functions. The expected positions of  $g_{\parallel}$  features at 2.0045 and 2.0092 are shown.



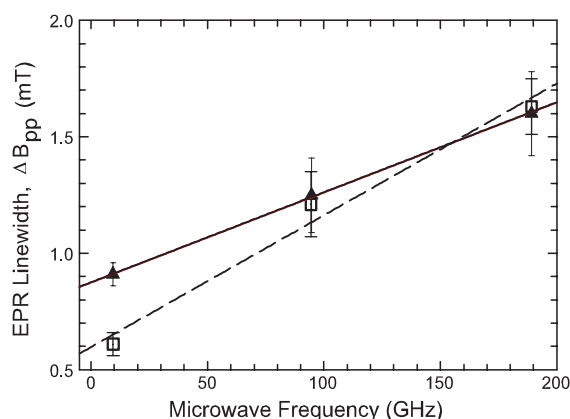
**Figure 3.** 189 GHz EPR spectrum from polymeric a-C:H with best fit Gaussian (grey dash) and Lorentzian (grey solid) lineshape functions. The expected position of a  $g_{\parallel}$  feature at 2.0045 is shown.

detailed narrow-field-range 189 GHz polymeric sample spectrum shown in figure 3 illustrates this with the expected position of the relevant  $g_{\parallel}$  feature marked. Measurements on both samples were also made at 10 K and the spectra found to be similar in form to those recorded at room temperature.

The axial powder pattern spectra observed by von Bardeleben *et al* [3] were assumed to result from the a-C:H film and were attributed to nanosized  $sp^2$  graphite-like carbon clusters with two characteristic sizes. No physical model has been developed to support the sharply bimodal distribution of cluster sizes required. The results presented here do not exclude the possibility that paramagnetic centres arise from  $sp^2$  containing clusters, but they provide no evidence for a distribution of cluster sizes.

We now turn to the observed variation in linewidth with microwave frequency shown in figure 4.

The diamond-like sample has a characteristically high spin concentration which, if the centres are uniformly distributed, should alone result in a dipolar-broadened contribution to



**Figure 4.** Peak-to-peak first-derivative average linewidths for polymeric (solid triangles) and diamond-like (open squares) a-C:H plotted against microwave frequency.

the linewidth,  $\Delta B_{pp(\text{dipolar})}$ , of 0.8 mT [13], greater than the 0.6 mT width observed at 9.5 GHz. From a study of the variation in relaxation times,  $T_1$  and  $T_2$ , in a-C:H samples it has been established that this reduction is due to exchange narrowing [2]. From this study it can be inferred that the exchange frequency,  $\omega_e$ , for the diamond-like sample studied here is likely to be less than  $1 \times 10^{10} \text{ rad s}^{-1}$ . The dependence of the linewidth on microwave frequency,  $\omega_0$ , for an exchange-narrowed paramagnetic system can be described by the expression [14]

$$\Delta B_{pp} = \frac{\Delta B_{pp(\text{dipolar})}^2}{J_{\text{ex}}} \left[ 1 + \frac{5}{3} \exp\left(-\frac{1}{2} \left(\frac{\omega_0}{\omega_e}\right)^2\right) + \frac{2}{3} \exp\left(-2 \left(\frac{\omega_0}{\omega_e}\right)^2\right) \right], \quad (1)$$

where  $J_{\text{ex}}$  is the exchange coupling constant in magnetic-field units. For the magnitude of exchange energy and the range of microwave frequencies relevant here, equation (1) predicts a frequency-independent linewidth. The presence of centres with axial  $g$  tensors would result in an increase in linewidth with frequency. However, the expected  $\omega_0^2$  dependence is inconsistent with figure 4. Furthermore, the magnitude of the anisotropy required to account for the 189 GHz linewidth should result in clearly resolved distortions from a simple Lorentzian. It is necessary to introduce additional line-broadening mechanisms: for example contributions from random distributions in the spin Hamiltonian parameters values, specifically  $g$  strain effects, and the possibility of frequency dependence of the relaxation time  $T_2$ . The former gives a broadening linear with microwave frequency. Recent multi-frequency EPR studies of model paramagnetic systems have reported increased line broadening with increasing microwave frequency [15–17]. The detailed mechanisms responsible have not been identified with certainty.

The polymeric sample gives a 9.5 GHz linewidth of 0.91 mT, greater than the dipolar-broadened width of 0.11 mT calculated assuming a uniform distribution of paramagnetic centres. The observed linewidth has been attributed to unresolved hydrogen superhyperfine structure resulting from the significantly increased hydrogen content [2]. A small departure from a Lorentzian lineshape is seen in figure 1. At high frequencies it is harder to know the true lineshape with certainty, despite the precautions outlined earlier. However, there is evidence in figure 3 that the departure from Lorentzian is less at 189 GHz. This may result from competing line-broadening mechanisms in this frequency range. A linear dependence of linewidth on microwave frequency is observed for the polymeric sample in figure 4. Random variations in local environment can contribute a distribution of  $g$ -values,  $g$ -strain, and can be modelled using a normal distribution. The model has been used to successfully account for the

linear increase in broadening with microwave frequency observed for spectra from vanadyl ions in glasses [18]. The high-frequency linewidths are similar for both the diamond-like and polymeric samples. However, these data do not exclude the possibility that the increase in linewidth with frequency for the diamond-like sample is also linear as shown in figure 4. If this arises from  $g$ -strain broadening a larger site-to-site variation in  $g$ -values for the diamond-like compared to the polymeric sample would be inferred. Studies over a wider range of microwave frequencies are required to clarify this possibility.

The results presented here were taken on powder a-C:H samples. Measurements on substrate-supported a-C:H thin films can be complicated by the presence of paramagnetic centres within the substrate. Further, recent low-temperature, high-frequency, EPR measurements have observed anisotropic effects originating from demagnetizing fields for such samples [19, 20]. The 9.5, 94, and 189 GHz EPR results presented here show no contributions from centres with axial  $g$ -values. A single Lorentzian or near-Lorentzian line was observed at all frequencies from both diamond-like and polymeric a-C:H samples. These results do not support the recently proposed bimodal  $sp^2$  cluster size model for paramagnetic centres in a-C:H.

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