

Local coordination of carbon atoms in amorphous carbon

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Amorphous carbon has been studied by ^{13}C and ^1H NMR with the techniques of static single-pulse excitation, magic-angle spinning, and cross polarization with magic-angle spinning. A spin-lattice relaxation time of 0.7 s was obtained for ^{13}C by progressive saturation. Two different components are seen in the NMR spectrum of ^{13}C in the static sample. These were resolved using a tensor fitting routine with Gaussian broadening functions. The downfield component corresponds to “ sp^2 -like” carbon atoms, which comprise 93.6% of the total signal. This component was fit to an axially symmetric shift tensor with $\sigma_{\parallel} = -28$ ppm, $\sigma_{\perp} = 209$ ppm, and $\bar{\sigma} = 130$ ppm. The remaining upfield component is assigned to “ sp^3 -like” carbon atoms. These were fit to a symmetric shift tensor with $\bar{\sigma} = 62$ ppm. The concentration of the dangling bonds, as inferred from spin counting by ESR, is about $2 \times 10^{20} \text{ cm}^{-3}$. About two thirds of the carbon atoms are not seen in the static NMR measurement because of the high concentration of the unpaired electrons, which leads to severe inhomogeneous line broadening. These carbon atoms are detected under magic-angle spinning by the sidebands, which spread over a range of 2000 ppm. The first moment is located at $130 (\pm 5)$ ppm. The upper limit of the fraction of hydrogenated carbon is estimated to be 1.5%.

I. INTRODUCTION

Considerable current interest exists in the structure of amorphous carbon as well as disordered phases formed in thin-film processes. The latter encompass nanocrystalline carbon as well as mixtures of amorphous and crystalline phases. Recently, several fundamental calculations have been performed on the structure of amorphous carbon ($a\text{-C}$, throughout this paper).¹⁻³ These studies differ from more schematic models of $a\text{-C}$, which presume local structures that are graphitelike,⁴⁻⁷ i.e., systems with connected planar hexagonal rings. Experimental studies of the radial distribution function (RDF) of well characterized $a\text{-C}$ films have demonstrated that the fundamental models are more correct in not exhibiting ordered hexagonal ring structures.⁸ While these hexagonal units appear to be present in certain nanocrystalline forms of C, including glassy C, their order is not consistent with the observed RDF of $a\text{-C}$.

The experimental RDF of $a\text{-C}$ also demonstrates, as did earlier studies, that the average coordination number of C exceeds 3. The form of the RDF precluded, however, an accurate estimate of the fraction of threefold, sp^2 -type and fourfold, sp^3 -type sites. Information about the fraction of threefold to fourfold sites is of importance both for comparison with theoretical models as well as for estimating the relative structural disorder in bond distances and angles for each site. The RDF of $a\text{-C}$ suggests, for example, that bond length fluctuations of threefold sites are substantially greater than that of $a\text{-Si}$ and $a\text{-Ge}$ systems of predominant fourfold coordination. While this radial disorder is qualitatively consistent with

a molecular dynamics model for $a\text{-C}$,³ certain aspects of the radial distribution differ from this theory. Additional information relevant to the properties and structural topology of $a\text{-C}$ clearly require an improved estimate of the fraction of fourfold sites.

One means of inferring information about the fraction of threefold to fourfold sites involves the use of NMR. Although it had been suggested that a substantial concentration of hydrogen may be required to obtain appropriate relaxation times for detection of ^{13}C by NMR,⁹ it appears that the primary experimental limitation has been the preparation of a thin-film sample of sufficient size to contain enough ^{13}C at natural abundance to be detectable by NMR. In the present study a combination of static, magic-angle spinning and cross polarization with magic-angle spinning (CPMAS) NMR yields $\sim 6.5\%$ fourfold bonding. This value is below that estimated by detailed theoretical structure studies.¹⁻³ The results thus emphasize that the electronic and vibrational properties of $a\text{-C}$ are primarily determined by distorted threefold environments.

II. EXPERIMENT

Amorphous carbon was prepared by rf sputtering on a 99.99% pure graphite target in a high vacuum system of base pressure 1×10^{-7} Torr. A 5-in.-diam cathode was sputtered at a power of 400 W at an Ar pressure of 8 mTorr. Substrates of Cu were placed in good thermal contact with a liquid nitrogen cooled plate to prevent film ordering due to heating. Such ordering is observed in the Raman spectra of films deposited on uncooled substrates

as two distinct microcrystalline peaks. In contrast, *a*-C studied here exhibits a very broad high-frequency band as well as additional low-frequency scattering. Amorphous carbon films were removed from the substrate by using dilute HCl acid and cleaned thoroughly in deionized water. RDF measurements on this sample yielded a network density 1.08 times that of graphite. A macroscopic density 0.89 times that of graphite, in contrast, is due to film microporosity.

Because the sample was prepared without the deliberate introduction of hydrogen, most carbon atoms are not hydrogenated, and one can expect that the sample has a high density of dangling bonds (or radicals). The paramagnetic interaction with the single electrons of those dangling bonds and the chemical-shift interaction will dominate the nuclear spin-spin and the spin-lattice relaxation. Amorphous carbon in the studies reported here was probed using several transient techniques in NMR including single pulse static and MAS experiments on ^{13}C and ^1H , and cross polarization with magic-angle spinning, using two homebuilt spectrometers operating at 220 and 100 MHz for ^1H (55.4 and 25.15 MHz for ^{13}C), respectively. All NMR experiments were performed at room temperature. Single pulse excitation of ^{13}C was performed at 55.4 MHz using a static sample (100 mg) to extract the principal components of the chemical-shift tensors and the fractional ratio of the components in different chemical environments. In this experiment, a 5- Ω resistor was connected in series with the resonance coil, which reduced the recovery time of the spectrometer to 2 μs after the 7- μs $\pi/2$ pulse.

Residual hydrogen content of the sample was examined by ^1H NMR at the resonant frequency of 220 MHz. Both evacuated (at 90°C and 10^{-6} Torr for 5 h) and unevacuated samples were measured to discriminate between protons in weakly adsorbed compounds such as water and hydrogens bonded to the amorphous carbon. The 90° pulse length was 3 μs . The recovery time was 3 μs after the pulse.

MAS and CPMAS experiments were performed at the ^{13}C resonance frequency of 25.15 MHz, using 32 mg of samples. A CPMAS spectrum of ^{13}C was obtained to determine possible chemical functionalities of the roughly 1.5% of hydrogenated amorphous carbon atoms. A spinning speed of 4.4 kHz and a proton B_1 field of 50 kHz for cross polarization and proton decoupling were used. Throughout this work, all resonance line positions were determined with respect to tetramethylsilane (TMS). The δ scale is used with positive numbers being downfield. The unpaired electron spin concentration was determined by comparison of ESR intensities of the amorphous carbon with that of a standard sample of diphenylpicrylhydrazyl.

III. RESULTS AND DISCUSSION

A spin-lattice relaxation time of 0.7 s for ^{13}C was determined for amorphous carbon at a resonant frequency of 55.4 MHz. The method of progressive saturation with maximum delay of 60 s between the scans was used. The ^{13}C - ^{13}C and ^{13}C - ^1H dipole-dipole interactions are not expected to be important for relaxation because of the low

abundance of ^{13}C nuclei and the relatively low (~ 1.5 at %) concentration of hydrogen in the sample. The observed value of T_1 indicates that dipole interaction with unpaired electrons in dangling bonds dominates spin-lattice relaxation. ESR measurements yielded a concentration of unpaired electrons in the sample of $2 \times 10^{20}/\text{cm}^3$. It is noted, that in the earlier study of unhydrogenated *a*-C by Jansen *et al.*,⁹ T_1 of carbon was found to be sufficiently long to prohibit an acquisition of NMR spectra. However, in the latter study a concentration of unpaired electrons of only $10^{18}/\text{cm}^3$ was found. The relatively large concentration of dangling bonds observed in the samples studied in the present work is attributed to reduced atomic mobility on cooled surfaces as well as substantial plasma bombardment in the rf sputtering process.

Figure 1 shows the static NMR spectrum of ^{13}C in amorphous carbon resulting from 60 000 signal averages. A delay of 4 s was used between scans. The resonant frequency was 55.4 MHz. The broad spectrum shown in Fig. 1 can be described as a superposition of two components: a downfield component representing "*sp*²-like" carbon atoms with a relatively large (200 ppm) chemical-shift anisotropy, and a much less intense, upfield signal representing "*sp*³-like" carbon atoms. The MAS spectrum, taken at 25.15 MHz (50 000 accumulations with a 4-s delay) is given in Fig. 2. It is interesting to note that although magic-angle spinning resulted in a reduction in linewidth by a factor of almost three, the "resolution" in the MAS spectrum is not significantly improved. The overlapping of the isotropic peaks corresponding to the two carbon fractions results from severe residual broadening, presumably due to the interaction with unpaired electrons. Also, the distribution of bond lengths in amorphous carbon contributed to the broadening of the NMR line which could not be eliminated by MAS.

The spectra of Figs. 1 and 2 were used to estimate the

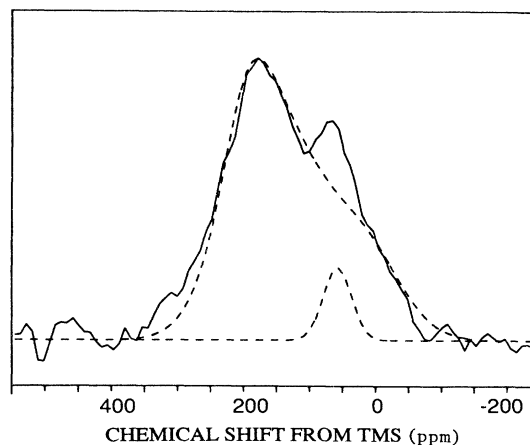


FIG. 1. NMR spectrum of ^{13}C in a static (nonspinning) sample. Solid line: experimental result. Dashed lines: fits to an axially symmetric shielding tensor ("*sp*²-like" carbon) and a symmetric shielding tensor ("*sp*³-like" carbon).

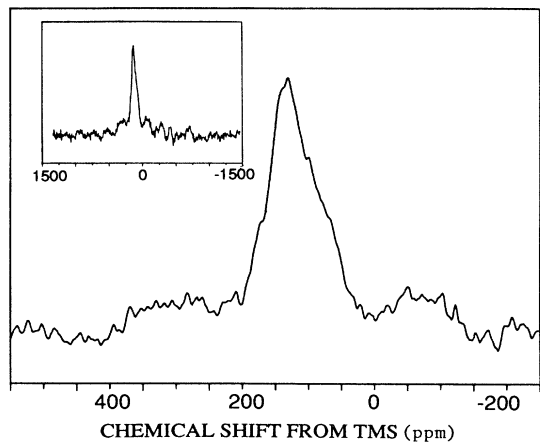


FIG. 2. NMR spectrum of ^{13}C in amorphous carbon under magic-angle sample spinning. Main figure: same spectral range as shown in Fig. 1. Inset: spectral range expanded to show spinning sidebands associated with inhomogeneous broadening of ^{13}C NMR by unpaired electrons, with concentration $2 \times 10^{20} \text{ cm}^{-3}$.

ratio of “ sp^2 -like” carbon to “ sp^3 -like” carbon in the sample. The two components were resolved in Fig. 1 (dashed lines) using a tensor fitting routine with a Gaussian broadening of 2.8 kHz. The component identified as “ sp^2 -like” comprises $93.6(\pm 1.5\%)$ of the total signal, and was approximated using an axially symmetric shift tensor with $\sigma_{\parallel} = -28$ ppm, $\sigma_{\perp} = 209$ ppm, and $\bar{\sigma} = 130$ ppm. The asymmetry of the tensor is higher than Resing’s result for graphite with $\sigma_{\parallel} = 0$ ppm, $\sigma_{\perp} = 178$ ppm, and $\bar{\sigma} = 119$ ppm.¹⁰ The isotropic chemical shift observed in the present work, however, is close to that observed by Resing for graphite. The shift due to a bulk susceptibility associated with $2 \times 10^{20}/\text{cm}^3$ unpaired electrons of spin $\frac{1}{2}$ would be 0.11 ppm downfield. The difference of 11 ppm between the present results and those for graphite must be therefore accounted for in terms of a contact shift, or distortion relative to the highly ordered graphite structure. The direction of shifts (upfield for σ_{\parallel} and downfield for σ_{\perp}) could indicate that the electron density perpendicular to the sp^2 plane is higher than that of graphite and the electron density in the sp^2 plane is lower than that of graphite. The second component in the spectrum of Fig. 1 may be interpreted in terms of a symmetric tensor with a line broadening of ~ 2.7 kHz, and an isotropic chemical shift $\bar{\sigma}$ of 62 ppm. This isotropic shift lies in the range observed for “ sp^3 -like” carbon atoms. The sp^3 carbon signal comprises $6.4(\pm 1.5)\%$ of the total intensity.

Note that the spectrum presented in Fig. 1 does not represent all carbon atoms in the sample. Spin counting was performed by integrating the intensity of ^{13}C spectrum from Fig. 1, and compensating the result for the loss due to recovery time. This result was compared to that of a reference sample, and indicated that only $28(\pm 5)\%$ of the total carbon atoms in the sample were

detected by NMR. The presence of unpaired electrons (*vide infra*) is the primary reason for the loss of observable intensity of the ^{13}C nuclei in the static experiment. The resonances of those nuclei for which the electron-nuclear dipolar interaction is large, compared to the width of the static NMR spectrum, contributed to the broad baseline spreading far beyond the range presented in Fig. 1 and could not be distinguished in this experiment. Also, since proton decoupling was not applied in single pulse experiments, Fig. 1 does not include the $\sim 1.5\%$ of carbon atoms that form C—H bonds (discussed later in this work).

The results of spin counting do not apply to the MAS spectrum of Fig. 2. An interesting feature of this spectrum is the presence of spinning sidebands (see the inset in Fig. 2) which spread over a range of more than 2000 ppm (50 kHz). The only inhomogeneous interaction which could give rise to such a broad pattern of sidebands is the coupling between ^{13}C nuclei and unpaired electrons (at a resonant frequency of 25.15 MHz a spinning speed of 5 kHz eliminates spinning sidebands due to chemical-shift anisotropy). As demonstrated by Nayeem *et al.*,¹¹ the powder pattern line shape of a static paramagnetic solid is affected by the anisotropic part of the dipolar interaction between an electron and a nucleus. Even in the presence of several unpaired electrons around a given nucleus, the net interaction is inhomogeneous, formally equivalent to that of a chemical-shift tensor, and thus responsible for the occurrence of sidebands in the MAS spectrum. It is, therefore, concluded that the sidebands represent most of those carbon atoms which were broadened outside the range of visibility in the static spectrum shown in Fig. 1. Since the acquisition of a spectrum with a considerable improved S/N was not possible due to the projected length of the experiment, the sidebands were not used to extract information concerning chemical functionalities of carbon involved. However, an analysis of the central peak yielded an estimate for the fraction of “ sp^2 -like” component of 93.1% and the fraction of “ sp^3 -like” component of 6.9%, with the isotropic peaks located at 130 and 65 ppm, respectively. These values agree to within experimental error with the results derived from analysis of the static spectrum. Our analysis showed that the integration of the intensity of the signal (including all sidebands) from carbon atoms close to unpaired electrons (invisible in Fig. 1) is 2.9 times that of the signal from the carbon atoms visible in Fig. 1. This result dovetails with that of the spin counting experiment. The first moment is located at $130(\pm 5)$ ppm, indicating that the major portion of those carbon atoms invisible in static measurement have sp^2 coordination. This is in agreement, to within experimental error, with the analysis of the static spectrum.

These NMR data are consistent with those of neutron diffraction experiments which indicated that there is a small fraction of fourfold bonds present in this sample.⁸ However, the value of $6.4 \pm 1.5\%$ for the fraction of fourfold sites in *a*-C is below that suggested by recent basic modeling studies.^{1,3,4} A first-principles, molecular dynamics model, based on the Car-Parrinello method, has 15%, fourfold bonds.³ While this model qualitatively

agrees with a relatively large fluctuation in bond lengths, the detailed peak positions and fourfold bonding fraction differ with respect to RDF and the NMR results. As this model was constrained to a density $\sim 20\%$ below that observed in RDF studies of the present sample, additional calculations at higher densities would be useful to determine if changes in bonding parameters occur. A hand-built model¹ of *a*-C and a model based on Monte Carlo calculation with an empirical pseudopotential² have 14% and $\sim 9\%$ fourfold bonding, respectively. The latter model, while yielding better agreement with the observed RDF peak positions and network density, does not exhibit the significant bond length and bond angle fluctuations.

Quantitative measurements of proton content were performed by comparison of NMR spectral areas of both evacuated and unevacuated samples with that of a reference. The result indicates that the sample consists of ~ 2.2 at % protons. Only half of those protons remained after evacuation. Neutron diffraction gives about 3 at % protons in the unevacuated sample.⁸ The difference may be due to the high density of radicals which cause some loss of proton signal relaxation to paramagnetic centers. Assuming that neutron diffraction data reflect all protons in the sample, an upper limit for the fraction of hydrogenated carbon atoms is 1.5%.

Figure 3 represents the CPMAS spectrum of amorphous carbon resulting from 200 000 accumulations taken with a delay of 2 s and a contact time of 1 ms. Since in the CP experiment, the polarization of ¹³C nuclei is achieved indirectly through the dipolar interaction with the neighboring protons, the spectrum from Fig. 3 represents only those ¹³C spins which are in the vicinity of protons (not more than 2–3 bond distances away). This is to say that the spectrum in Fig. 3 represents at most 1.5% of the carbon atoms in the sample. Hydrogenated carbon atoms were formed during the sample preparation, probably due to the residual H₂O or other proton containing compounds in the vacuum chamber. It is seen that even under high resolution conditions of CPMAS and proton decoupling a severe line broadening is observed. The main feature in the spectrum centered at ~ 140 ppm, which represents "*sp*²-like" hydrogenated carbon atoms, is close to Bustillo's CPMAS result (145 ppm) for *sp*² hydrogenated carbon atoms.¹² The spectrum in the region of 40–120 ppm is relatively flat, suggesting that in addition to the "*sp*²-like" C—H bonds there exist some "*sp*³-like" C—H bonds (resonances at 40–50 ppm) and a variety of intermediate C—H bonds. This could be the result of the structural distortion from pure *sp*² and *sp*³ symmetry in those C—H bonds. Such structural distortion will cause a distribution of ¹³C resonances. Again, it should be noted that the presence of paramagnetic centers associated with dangling bonds in the sample may cause additional broadening of the resonance lines in the CPMAS spectrum.

Note also that the resolution of the CPMAS spectrum is not improved compared to the static spectrum of Fig. 1, which, as indicated earlier, could be well fitted by two chemical-shift tensors. This observation may indicate that the bulk structures of "*sp*²- and *sp*³-like" carbon atoms unattached to protons are rather well defined. In

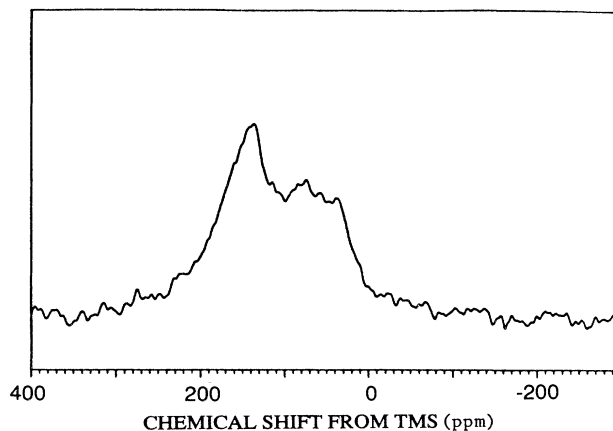


FIG. 3. NMR spectrum of ¹³C in amorphous carbon under conditions of cross polarization enhancement, and magic-angle spinning. This spectrum emphasizes the signal of the small fraction of those carbon atoms in the neighborhood of the 1.5 at % hydrogen in the sample.

contrast, the C—H carbon atoms, which are expected to be located at the edges of the amorphous carbon network, could exhibit more significant structural distortions. Since the dangling bonds are easily formed at the edges of the carbon network,⁵ it is reasonable to assume that those carbon atoms which give sidebands in Fig. 2 are also adjacent to structural distortions, which either are directly connected or very close to the dangling bonds.

IV. SUMMARY

NMR measurements have determined that the fraction of fourfold bonds is $\sim 6.4 \pm 1.5\%$ and the fraction of threefold bonds is $93.6 \pm 1.5\%$. These values are based on the static measurement for a sampling of $\sim 30\%$ of all ¹³C atoms in the sample. Two-thirds of carbon atoms are not seen in the static measurement because of the high concentration of unpaired electrons leading to severe inhomogeneous line broadening. Those "invisible" carbon atoms are detected by an MAS experiment with sidebands spreading over a range of 2000 ppm. The first moment of the sidebands is located at $130 (\pm 5)$ ppm in the MAS measurement. This indicates similar statistical distributions of bonding configurations within the neighborhood of paramagnetic defects for those carbon atoms visible in a static experiment, and those seen under MAS. The value $6.4 \pm 1.5\%$ is below that of various basic structural models, though near to the value of 9% obtained by Tersoff using an empirical pseudopotential.² The RDF and NMR spectra of *a*-C should provide important basic constraints on future, improved structural models. The NMR result also implies that the primary

character of the RDF of *a*-C is determined by threefold bonding configurations as are many of the physical properties of *a*-C films. The concentration of the dangling bonds is about $2 \times 10^{20}/\text{cm}^3$ which is responsible for the short T_1 (0.7 s) of carbon nuclei and broadening of the spectra. The upper limit of the fraction of hydrogenated carbon atoms is 1.5%.

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