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A SOLID STATE ^{13}C -NMR STUDY OF DIAMONDS AND GRAPHITES

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Abstract

The ^{13}C -NMR spectra of gem quality and industrial diamonds show two resonances with the more intense resonance at high field. Two resonances are also shown in ^{13}C -NMR spectra of various graphites however, the low field resonance is of greater intensity than the high field resonance in the graphites. The resonances are very broad and they are assigned to graphite type (sp^2) carbon and diamond type (sp^3) carbon.

INTRODUCTION

The application of the ^{13}C nuclear magnetic resonance to the study materials in the solid state has been relatively limited.^{1,2} The spectra ordinarily give very broad lines caused both by chemical shift anisotropy as well as the overlap of many different resonances. Several techniques^{3,4} have been developed to overcome this

problem the most notable being high speed spinning at the magic angle which removes the anisotropy. Relatively simple organic molecules, e.g. adamantane, have been fairly extensively investigated by these resonance enhancement techniques.⁵ Several studies on coal have been reported; usually two resonances are observed which are assigned to the aromatic and non-aromatic components of coal, respectively. The resonance of diamond and graphite have also been reported.⁶ Diamond shows a single peak well above tetramethylsilane (TMS) with apparently a very long relaxation time (the spectrum was obtained by accumulating four pulses over three days). The relaxation time of graphite has been determined to be 90 ± 10 sec.⁷ The graphite resonance is about 35ppm from CS₂ (158ppm below TMS) and the sample was a polycrystalline Madagascar sample. More exotic sample, wood, ivory, etc. have also been examined.⁸ In this paper we report the ¹³C-NMR spectra of graphites and diamonds. For the first time two resonances are observed in the spectra of these systems.

EXPERIMENTAL

The ¹³C-NMR spectra were obtained using a JEOL FX-60 spectrometer operating in the external lock mode under high resolution conditions. A flip angle of about 30° was used with TMS as an external reference by tube substitution. Spectra were obtained using either 4 or 8K data points over a spectral width of 10,000 Hz. The scan repetition rate was varied between 0.6 and 1.6 sec; spectra usually required 100,000 to 200,000 pulses.

X-Ray diffraction scans were carried out on a Phillips Electronics X-ray diffractometer using copper radiation with a graphite monochromator at a scan rate of 2°/min. X-Ray fluorescence measurements were obtained on a Phillips Electronics vacuum path X-ray fluorescence spectrometer. A tungsten target tube and LiF(200) analyzing crystal were employed.

The graphite and diamond samples were all commercially obtained and were used as received. Three different sources of graphite were used. The industrial diamonds were kindly provided by the General Electric Company and were graded as to diamond quality. Gem quality diamonds were obtained from a local jeweler and were not graded according to perfection.

RESULTS

Graphites. Eight different samples of graphite have been examined by X-ray fluorescence (for iron, cobalt and nickel), X-ray diffraction, as well as NMR spectroscopy. Five of the samples (A-E) were obtained from Asbury Graphite Mills and were approximately graded by them as to degree of graphitization; three samples (A, B, E) were said to be highly graphitized while the other two (C,D) were much lower in degree of graphitization. Two samples (F-G) were from Ultracarbon Corporation and were stated to be highly graphitized. The eighth sample (H) was an electrode grade graphite from Johnson Matthey.

Since it was observed that some of the graphites could be picked up by a magnet, the magnetic susceptibilities and the approximate iron content of all graphite samples was determined. By the Guoy balance technique all of the graphite samples appear to be diamagnetic. This must mean that the diamagnetism of the graphite far outweighs the paramagnetism or ferromagnetism of the impurities. The X-ray fluorescence data agrees with these results; four of the samples, (E-H), show a low (1-3 ppm) iron content, while the other four all show high (perhaps 0.5-1%) iron.

X-Ray diffraction results further segregate the graphite samples. Five of the samples (A, E-H) show essentially only graphite diffraction maxima while two (C,D) show many non-graphite maxima. The last sample (B) is intermediate and also shows maxima which are attributable to a-quartz and calcite.

The NMR spectra also segregate the graphites into two classes. Some graphite samples (A, E-G) show essentially only one resonance which is centered at about 170 ppm below TMS and is very broad with a tail (caused by

chemical shift anisotropy) which extends well down towards TMS. Two samples (C, D) show two resonances one at about 170 ppm below TMS (assigned as above to graphite) the other about 50 ppm above TMS rising out of the aromatic tail and seemingly a large amount of the total sample (Fig. 1). The other samples also all show two resonances but the upfield resonance is far less than in samples C and D. Samples B and E (Fig. 2) show only a very small nonaromatic resonance which may well be attributable to anisotropy while sample H (Fig. 3) shows a definite peak which is; however, much smaller than that in samples C and D. The fluorescence, diffraction and NMR data are summarized in Table 1.

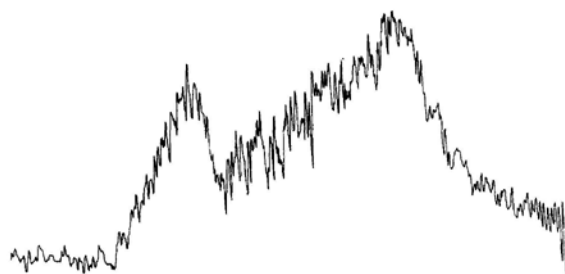


Fig. 1. ^{13}C -NMR spectrum of graphite sample C over a 10,000 Hz sweepwidth (665 ppm), peaks are approx. 170ppm and -50ppm from TMS.

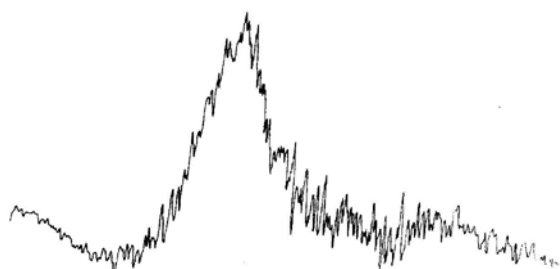


Fig. 2. ^{13}C -NMR spectrum of graphite sample B over a 10,000 Hz sweepwidth, the major peak is approx. 170 ppm from TMS.

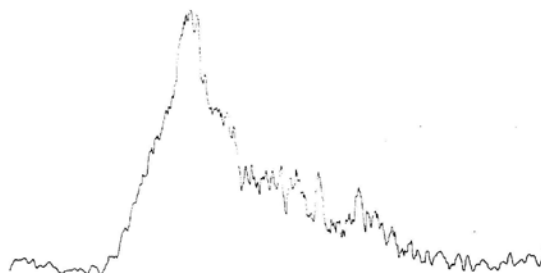


Fig. 3. ^{13}C -NMR spectrum of graphite sample H over a 10,000 Hz sweepwidth (665 ppm), the major peak is approx. 170ppm from TMS.

Table 1. Summary of X-ray fluorescence (XRF), X-ray diffraction (XRD) and ^{13}C -NMR data on the graphites used

Graphite Sample	XRF ^a	XRD ^b	NMR ^c
A	High Fe	1	none
B	High Fe	2	very small
C	High Fe	8	major
D	High Fe	6	major
E	Low Fe	1	very small
F	Low Fe	1	none
G	Low Fe	1	none
H	Low Fe	1	small

^a X-Ray Fluorescence Results

^b Number of unassigned peaks

^c Amount of non-aromatic resonance

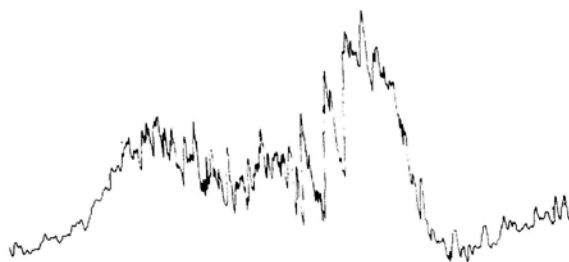


Fig. 4. ^{13}C -NMR spectrum of gem quality diamonds over a 10,000 Hz sweepwidth (665 ppm), peaks are approx. 170ppm and -50ppm from TMS.

In keeping with what has been observed for coals⁹ the downfield resonance is assigned to the aromatic carbons while the upfield resonance must represent some kind of a nonaromatic impurity in the graphite. The great breadth of the resonances (typical half-width is 1000-1500 Hz) and the lack of knowledge of relaxation times prevents any attempts at even an approximate determination of the relative amounts. The reported aromatic ^{13}C -NMR chemical shift is in the same range as previously observed and is further downfield than simple known aromatic compounds as has previously been reported.⁶ The high-field ^{13}C -NMR resonance is also further upfield than simple model compounds (e.g. hydrocarbons).

The ^{13}C -NMR spectrum of an intimately mixed (one to one by weight) sample of pure silicon carbide and graphite sample C was obtained. The silicon carbide shows only a low field resonance at approx. 21 ppm while the graphite is as reported above. The spectrum of the mixture shows three peaks, one corresponding to the chemical shift of silicon carbide and the other two resonances at the graphite position. Approximate integration of the spectrum obtained agreed with the known amounts of the two components.

Diamonds. The spectrum of gem quality diamonds is shown in Fig. 4. The major resonance is centered near 50 ppm above TMS with a smaller, broader feature near 170 ppm below TMS. Industrial grade diamonds spectra are shown in Figs. 5-7. The major resonance in each is centered near 40ppm above TMS with the minor resonance near 180ppm below TMS. In all cases the upfield (major) resonance is due to diamond type carbon atoms while the other resonance is due to a presumed aromatic type impurity. The three industrial diamonds are; respectively, a smooth, very tough crystal which resists shock (smallest aromatic impurity), Fig. 5; a generally smooth surfaced crystal designed for metal bond requirements; and an irregular rough surfaced diamond for resin bond applications. These last two exhibit about the same amount of non-diamond impurity (Figs. 6 and 7). Again the lines are quite broad with half-widths of about 1,000 to 1500Hz. All spectra are taken over a 10,000 Hz sweepwidth.

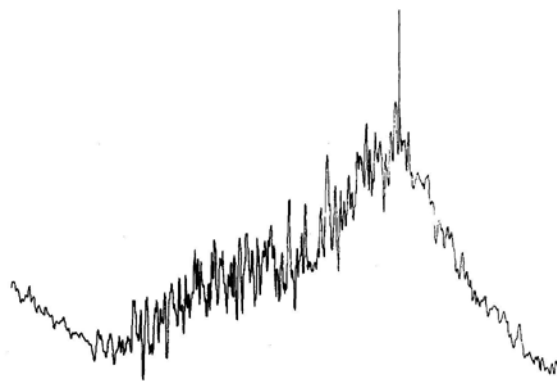


Fig. 5. ^{13}C -NMR spectrum of industrial diamonds-G. E. type MSD over a 10,000 Hz sweepwidth (665 ppm), peaks are approx. 140 ppm and - 80 ppm from TMS.

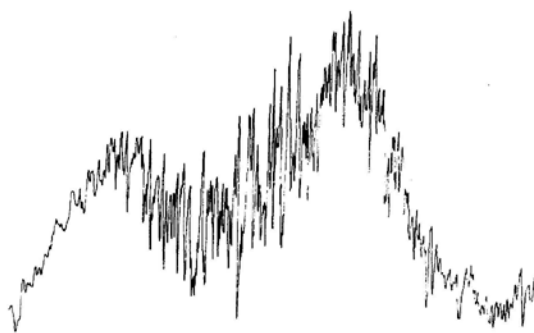


Fig. 6. ^{13}C -NMR spectrum of industrial diamonds-G. E. type RVG over a 10,000 Hz sweepwidth (665 ppm), peaks are approx. 180 ppm and - 40 ppm from TMS.

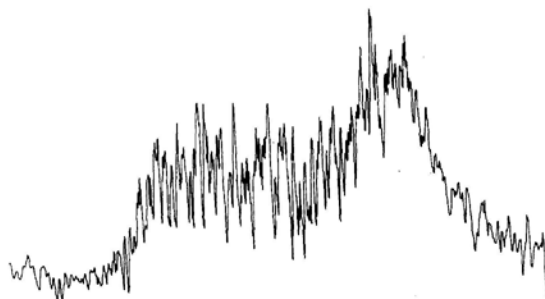


Fig. 7. ^{13}C -NMR spectrum of industrial diamonds-G. E. Type MBG-II over a 10,000 Hz sweepwidth (665 ppm), peaks are 180 ppm and - 40 ppm from TMS.

DISCUSSION

The width of all resonances is relatively large (typical width at half-height is about 1,000-1,500 Hz) and this width may be due to the combined effects of the overlap of unresolved resonances and chemical shift anisotropy. This technique does not allow the quantitative determination of the kinds and relative amounts of carbon atoms which are present in graphites and diamonds. Qualitative agreement is obtained for the diamonds between the expected quality of the diamond based on end use requirements¹⁰ and the degree of perfection of the materials. The industrial diamonds are all ferromagnetic while the gem quality diamonds presumably are diamagnetic. The very long relaxation time of diamond, which has been suggested by VanderHart and Retcofsky⁶ by their experimental conditions for obtaining their very high quality diamond spectrum (which we have reproduced) indicates that the diamond resonance is completely saturated and the more quickly relaxing aromatic resonance is consequently observed. The difference between VanderHart and Retcofsky's spectrum and Fig. 4 is presumably due to relaxation (and saturation) phenomena. Relaxation times in the industrial diamonds are undoubtedly much shorter due to the presence of ferromagnetic impurities. If these impurities equally affect all parts of the sample then the spectra are truly representative of the amount of impurity.

The graphite data shows no apparent correlation with iron content; one high iron sample shows only the aromatic resonance while two of these show a very large nonaromatic resonance. The quality of the spectra is also apparently unaffected by the presence of iron. The same broad features of the spectra are observed whether iron is or is not present. There is, however, apparently a correlation with the diffraction data. The samples which show a large amount of diffraction which cannot be assigned to graphite also show a large nonaromatic resonance; those which show essentially only diffraction from graphite show only, or predominately, the aromatic resonance. Thus graphites C and D must have a lower degree of graphitization. This is qualitatively seen from the X-ray diffraction data and their ^{13}C -NMR spectra. The spin lattice relaxation time of the non-aromatic resonance is no doubt quite different from that of the aromatic resonance. The apparently large amount of non-aromatic resonance in these graphites may well be due to the short delay between pulses.

The silicon carbide-graphite experiment indicates that this mixture gives a ^{13}C -NMR spectrum in proportion to the amounts of carbide and graphite carbons. The semiquantitative nature of this experiment gives rise to the real possibility of determining the types and approximate amounts of carbon atoms in a variety of insoluble carbon-containing compounds. We are actively pursuing this possibility.

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