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^{13}C nuclear magnetic resonance in donor- and acceptor-type intercalation compounds

M. Suganuma and U. Mizutani
Department of Crystalline Material Science, Faculty of Engineering, Nagoya University, Nagoya 464, Japan

T. Kondow
Department of Chemistry, Faculty of Science, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

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The ^{13}C nuclear magnetic resonance was measured in pure graphite and its intercalation compounds of potassium and rubidium (donor type) and of bromine and nitric acid (acceptor type). The measurements were performed at room temperature and 77 K with the use of a Varian WL-112 cw spectrometer. The linewidth of the ^{13}C resonance was very broad and field dependent in the case of pure graphite because of its anisotropic magnetic susceptibilities. The linewidth for the donor-type compounds increased with decreasing concentration of the intercalant alkali metals and was found to be field independent. On the contrary, the linewidth for the acceptor-type compounds changed with the static field applied. These results are discussed in terms of the heterogeneous charge-distribution model. The ^{13}C Knight shift with respect to pure graphite was very small for all intercalation compounds studied. The result strongly suggests that the electrons or holes produced by intercalation are of p character in the vicinity of the carbon nuclear sites.

I. INTRODUCTION

The electronic structure of graphite intercalation compounds has recently become the subject of great interest because of a variety of the electronic properties characteristic of two- or three-dimensional metallic systems. Such unique properties are certainly the result of the peculiar structure of graphite intercalation compounds, in which a spatial inhomogeneity in the charge distribution should be present in the direction along the c axis, as a result of charge transfer between the carbon and intercalant layers. Raman scattering experiments[1,2] indicate that there exist two different types of carbon layers in compounds having stage numbers $n \geq 3$: The carbon layer C_b bounded by an intercalant layer I and the interior carbon layer C_i bounded only by carbon layers. However, different features are apparent in the charge distribution between the donor- and acceptor-type compounds, as indicated by measurements of the degree of ionization of an intercalant and by the concentration dependence of the various electronic properties.[3-5] From measured Knight shifts, Carver has determined the degree of ionization of the cesium atom in various cesium intercalation compounds.[6] Very recently, Conard *et al.*[7] measured the ^{13}C Knight shift using a pulse spectrometer and analyzed the degree of charge transfer in various graphite intercalation compounds.

In the present study, ^{13}C nuclear magnetic resonance (NMR) measurements were performed on a continuous-wave spectrometer for several donor- and acceptor-type graphite intercalation compounds. The results are compared with those by Conard *et al.* and considered in terms of the line shape and the Knight shift. These measurements provide information concerning the character of electrons in the carbon layer and the difference in electronic structure between the two different type intercalation compounds.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

Spectroscopic graphite powder, grade SP-1, supplied from the Union Carbide Corp., served as a starting material for synthesizing various graphite intercalation compounds. The graphite particle sizes were found using an optical microscope to range from 10 to 100 μm. Various intercalants were introduced, including potassium, rubidium, bromine, and HNO_3 molecules. Stage-1 and -2 alkali-metal–graphite intercalation compounds were prepared using the dual-furnace method.[3] Higher-stage compounds were prepared by diluting the corresponding stage-1 compound with the necessary amount of pure graphite. Each compound was annealed under vacuum at 280 °C for several days. After homogenization, a sample was transferred into a Pyrex glass tube 12 mm in diameter and 90 mm long in a pure argon atmosphere for NMR measurements. The samples were transferred in a well-controlled dry box (Vacuum/Atmospheres Co., U.S.A.) in an atmosphere having average oxygen and H_2O concentrations of about 2 ppm. The average weight of each NMR specimen was 1.5 g. Each compound was analyzed by x-ray diffraction to confirm the desired phase.

The Br_2-graphite intercalation compounds were fabricated by exposing the well-degassed powdered graphite to the vapor of liquid bromine for several days. The resulting $C_{16}Br_2$ compound was then debrominated in air for various periods of time in order to obtain residue compounds of different compositions. The bromine uptake was determined from the weight increase of each specimen. The stage-2 and -3 HNO_3-graphite intercalation compounds were prepared by directly immersing pure graphite in nitric acid of different concentrations.[8] The structure of the HNO_3-intercalation compounds was also identified using the x-ray diffraction technique and the interplanar distance, corresponding to the length of a C_b-I-C_b unit, was found to be 7.8 Å for both stage compounds. Once prepared, the Br_2- and HNO_3-intercalation compounds were sealed in Pyrex glass tubes under the respective gas atmospheres for NMR measurements.

B. NMR measurements

The NMR examinations were carried out using a Varian Wideline CW Spectrometer WL-112. For measurements at room temperature, the sample was mounted in a conventional tuned crossed-coil probe WL-230. The measurements at liquid-nitrogen temperature were performed using a homemade Blume-type rf head connected to a Varian rf unit. The rotary saturation method was used to calibrate the rf magnetic field H_1.[9]

Since the natural abundance of ^{13}C is only 1.1%, the NMR signal is very weak. In undertaking these measurements, the signal-to-noise ratio was enhanced by employing a Varian C-1024 time-averaging computer. Measurements on graphite intercalation compounds and pure graphite required the accumulation of signals for at least 12 h (50 scans) and 24 h (100 scans), respectively. In each scan, the computer was triggered by a proton NMR signal so as to eliminate the effect of any magnetic field drift during the long experimental runs. The ^{13}C NMR signals were recorded at rf frequencies of 9.000 00, 6.000 00, and 3.000 00 MHz in magnetic fields of 8.4, 5.6, and 2.8 kG, respectively.

The derivative curve of the dispersion mode, rather than that of the absorption mode, was recorded because of an unavoidable saturation effect described below. A dispersion derivative curve should normally be observed as shown in Fig. 1(a). However, the curve for graphite intercalation compounds, as well as for pure graphite, is often heavily distorted for several reasons as follows. (1) A fairly long spin-lattice relaxation time, T_1, has been reported for pure graphite and some alkali-metal intercalation compounds.[6] For instance, the value of T_1 for pure graphite is approximately 2 min even at room temperature. Thus, a small rf field H_1, of the order of a few mG, is already strong enough to cause saturation and to substantially reduce the signal intensity in the absorption mode. Nevertheless, the dispersion mode is still observable, although its derivative curve is deformed as shown for a typical example in Fig. 1(b). (2) The dispersion derivative curve may be asymmetrically deformed due to the skin effect, which occurs in proportion to the electrical conductivity of a solid. This is schematically illustrated in Fig. 1(c). The skin depths of pure graphite and C_8K at a frequency of 9 MHz, for example, can be estimated from the conductivity data at room temperature[10] to be 100 and 5 μm, respectively. This requires the use of a powdered specimen, composed of particles several tens of μm in size. (3) NMR measurements on a randomly oriented powdered specimen should give rise to line broadening caused by the anisotropy of the electronic structure.

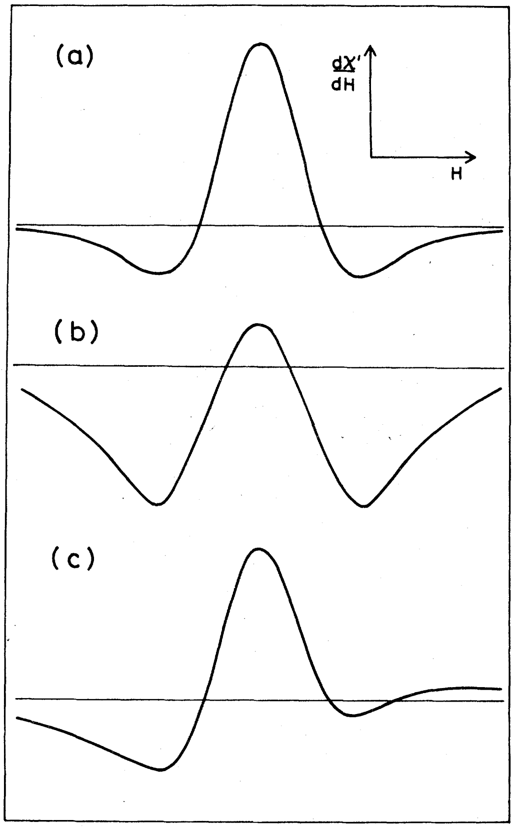

FIG. 1. NMR dispersion derivative curves: (a) typical; (b) deformed by the saturation effect; and (c) deformed by the skin effect.

III. RESULTS

A dispersion derivative curve for pure graphite was measured using an rf field, H_1, of 50 mG and the result is shown in Fig. 2. The presence of strong saturation apparently suppressed the characteristic central resonance peak shown in Fig. 1(a). An attempt to minimize saturation was unsuccessful because the reduction in H_1 to a few mG resulted in a poor signal-to-noise ratio and reproducible data were not obtained. However, the linewidth and position of the minimum in the dispersion derivative curve were found to be independent of the strength of H_1. The linewidth changed more or less proportionally to the applied static field, H_0, without altering the position of the minimum.

The NMR spectra for a series of rubidium-graphite intercalation compounds were obtained at room temperature and are shown in Fig. 3. The results indicate that both saturation effect and linewidth gradually increase as the alkali-metal content decreases. However, the H_0 dependence of the linewidth is absent for the compounds of all stages, in sharp contrast with the results for pure graphite. ^{13}C NMR measurements were also made on the potassium-graphite intercalation compounds, C_8K and $C_{24}K$, at room and liquid-nitrogen temperatures. The results are similar to those of the rubidium compounds. The spectra at liquid-nitrogen temperature were essentially

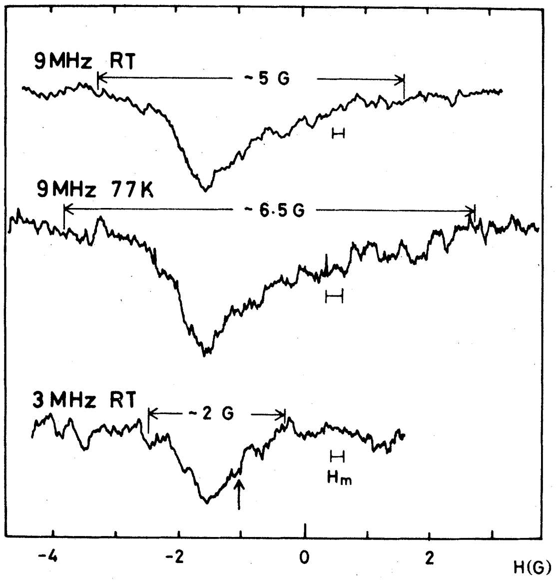

FIG. 2. The ^{13}C NMR dispersion derivative curves for pure graphite. The origin of the abscissa is set at the resonance field of TMS. The bottom curve measured at 3 MHz is displaced so that its peak coincides with those of the other two curves. Hence, the resonance field of TMS is also displaced by the same amount and indicated by the arrow. The peak-to-peak width of the modulation field, H_m, is marked by ⊢⊣. The rf field, H_1, was set at 50 mG.

TABLE I. The ^{13}C NMR data in graphite intercalation compounds. The Knight shift is determined with respect to tetramethylsilane (TMS) and its sign is defined to be positive when the shift occurs in a magnetic field lower than that for TMS. The linewidth is determined from the dispersion derivative curves, as shown in Figs. 2–4. The value in parentheses denotes the linewidth measured at 3 MHz. *S*, *M*, and *W* stand for strong, medium, and weak, respectively.

Specimen		^{13}C shift (ppm) Present results	Conard *et al.* (Ref. 7)	Linewidth (G) 9 MHz	6 MHz	Characteristics Saturation	Anisotropy
Graphite	RT	179 ± 10	155	5	4(2)	*S*	*S*
	77 K	180 ± 15	· · ·	6.5	· · ·	*S*	*S*
Donor type	C_8Rb	76 ± 5	80	1.4	· · ·	*W*	*W*
	C_8K	81 ± 5	65	1.4	1.3	*W*	*W*
	$C_{24}Rb$	131 ± 4	· · ·	1.4	1.4	*S*	*W*
	$C_{24}K$	128 ± 4	122	1.3	1.4	*S*	*W*
	$C_{36}Rb$	122 ± 5	121	1.6	· · ·	*S*	*M*
	$C_{48}Rb$	123 ± 5	· · ·	2.0	(2.1)	*S*	*S*
Acceptor type	G-Br_2 (mole % Br_2)						
	6.2	154 ± 10	155	3.2	2.8	*S*	*S*
	4.3	155 ± 10	· · ·	3.6	2.8	*S*	*S*
	1.6	155 ± 10	· · ·	3.6	· · ·	*S*	*S*
	0.28	155 ± 10	· · ·	5	3.7	*S*	*S*
	$C_{10}HNO_3$	160 ± 10	155	3	2	*S*	*S*
	$C_{15}HNO_3$	155 ± 10	155	3	2	*S*	*S*

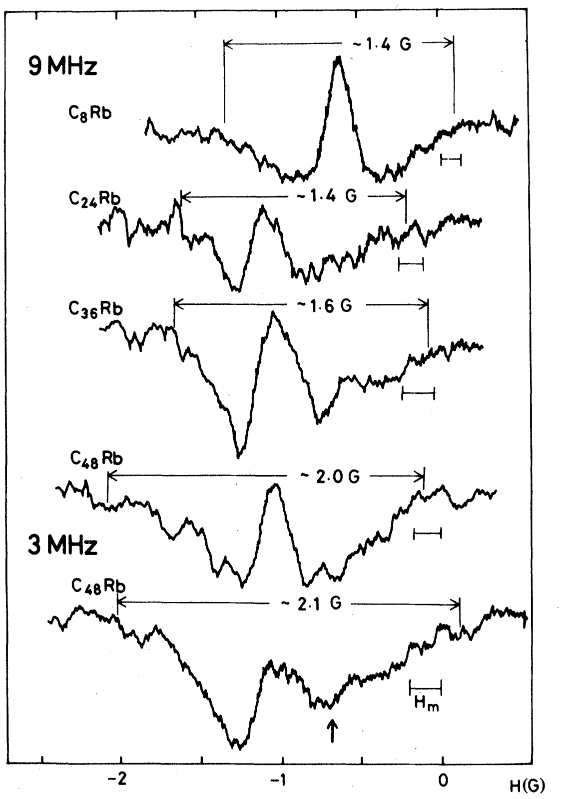

FIG. 3. The ^{13}C NMR dispersion derivative curves of rubidium-graphite intercalation compounds. The curve for 3 MHz is displaced so that its central peak coincides with those of the curves for 9 MHz. Hence, the resonance field of TMS is also displaced as indicated by the arrow. The rf field was set at 5 mG in all cases.

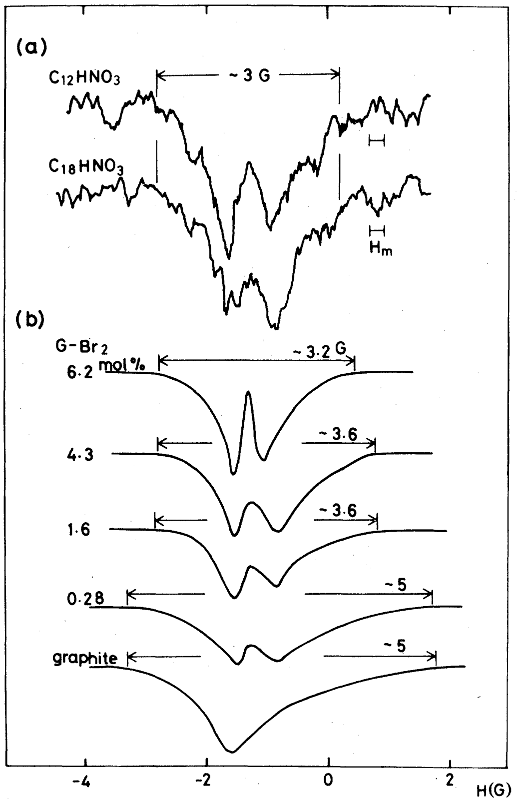

FIG. 4. The ^{13}C NMR dispersion derivative curves of (a) HNO_3 graphite and (b) Br_2-graphite intercalation compounds. The curves for Br_2 compounds are shown in smoothed form to clarify the change in the line shape with the Br_2 concentration. The rf field H_1 was set at 5 mG for HNO_3- and Br_2-rich compounds. As the Br_2 concentration decreased, a large H_1 field was required to maintain a good signal-to-noise ratio (see Sec. III in text).

the same as those at room temperature, although the ordering in the alkali-metal layer is known to occur below 98 K in $C_{24}K$.[11] The NMR spectra for Br_2- and HNO_3-graphite intercalation compounds were measured at room temperature and are shown in Fig. 4. All spectra are saturated. The linewidths for all the acceptor-type compounds studied here behave in a manner similar to that for pure graphite and varies almost proportionally to H_0.

The origin of the abscissa in Figs. 2 to 4 is located at the NMR signal of tetramethylsilane (TMS), which is often used as a reference for ^{13}C NMR measurements.[12] The ^{13}C Knight shift in pure graphite could not be precisely determined because of the absence of the central resonance peak. This value is roughly estimated by assuming the observed minimum to be the center of the resonance, since the minimum is apparently independent of such experimental parameters as H_0 and H_1. The present results are summarized in Table I, together with the data by Conard *et al.*[7] For ease of comparison, both sets of the Knight-shift data are shown with respect to TMS. This was made on the assumption that the Br_2 and HNO_3 compounds exhibit essentially no Knight shift with respect to pure graphite and that the Knight shift obtained by Conard *et al.* for the acceptor-type compounds is set equal to 155 ppm. It can be seen that both sets of data including those for pure graphite are quite consistent, although different NMR techniques were employed.

IV. DISCUSSION

A. Line shape

1. *Pure graphite*

A comparison of Fig. 2 with Figs. 3 and 4 clearly shows that the spectrum of pure graphite is highly saturated and broadened. Its unique dispersion derivative curve is probably caused by the saturation effect due to its unusually long T_1, coupled with the line-broadening effect mentioned in Sec. II. The wide linewidth, compared with those obtained for graphite intercalation compounds, was already pointed out by Carver[6] as well as Conard *et al.*[7] Line broadening for powdered graphite is attributed to the presence of the strongly anisotropic magnetic susceptibility; the $\chi_{\parallel}$ component, parallel to the *c* axis, is about -21.5×10^{-6} emu/g at room temperature and the magnitude increases with decreasing temperature, while the $\chi_{\perp}$ component is only -0.5×10^{-6} emu/g and is more or less temperature independent.[13] As a result, the effective field at the ^{13}C nuclear site should be different, depending on whether the applied field H_0 is parallel or perpendicular to the *c* axis of pure graphite. Therefore, the anisotropy should cause line broadening in the case of a powdered specimen and also variation in the linewidth with H_0 as well as temperature, which is indeed observed in the present experiment. However, it has not been possible to simulate by computer the observed dispersion derivative curve based on the model described above for randomly oriented powdered graphite in the presence of the saturation effect.

2. *Donor-type intercalation compounds*

The NMR spectra in Fig. 3 indicate that the dispersion derivative curves of the stage-1 compounds C_8K and C_8Rb are best represented by the ideal case of Fig. 1(a), indicating a relatively short T_1 at room temperature. However, the saturation effect gradually develops as the stage number increases. Carver has reported an increase in T_1 at liquid-helium temperatures toward the value of pure graphite, for ascending stages of cesium-graphite intercalation compounds. The present results, even at room temperature, indicate the same tendency as the T_1 measured by Carver.[6]

The linewidths for the rubidium-graphite intercalation compounds are seen in Table I to increase as the alkali-metal content decreases. Contrary to pure graphite and the acceptor-type compounds, the linewidth is almost independent of the applied field H_0. This suggests that the model proposed by Carver for pure graphite does not account for line broadening in higher-stage rubidium-graphite intercalation compounds. In higher-stage compounds, recent measurements of several physical properties including the results of Raman scattering[1,2] low-energy optical transitions,[14] and magnetoreflection[15] strongly suggest a heterogeneous charge distribution along the *c* axis. Charge transfer occurs essentially in the C_b-I-C_b units, while the C_i layer remains almost identical to a pure graphite layer. Very recently, low-temperature specific heats were measured for the rubidium-graphite intercalation compounds by the present authors.[16] It was observed that both the electronic and lattice specific heats can be better understood in terms of the heterogeneous charge-distribution model, rather than the rigid-band model based on uniform charge distribution. The present results, consistent with the data by Conard *et al.*[7] lend further support to this model, if the contributions to the central resonance peak and line broadening can be attributed to the ^{13}C nuclei in the C_b and C_i layers, respectively. The same interpretation has been put forward by Conard *et al.*[7] The lack of the field dependence of the linewidth suggests that some electrons spill over into the C_i layers. The electron concentration is high enough to destroy the anisotropy of the magnetic susceptibility[17] and, in turn, the H_0 dependence of the linewidth.

3. *Acceptor-type intercalation compounds*

As shown in Fig. 4, the NMR spectra for Br_2 and HNO_3-graphite intercalation compounds are highly saturated. Thus, the spin-lattice relaxation time, T_1, for these compounds is probably longer than that for lower-stage donor-type compounds. The characteristic features of the line shape for the acceptor-type compounds may be summarized as follows: (1) similar H_0 dependences of the linewidth are observed; (2) the central resonance peak is always visible; (3) the linewidths for stage-2 and -3 HNO_3 compounds are essentially identical, although the former does not possess the C_i layer, while the latter does; (4) the linewidth for Br_2 compounds is also independent of the Br_2 concentration, except for the very dilute 0.28-mole% Br_2 compound.

In the present experiment, normal HNO_3-graphite intercalation compounds having an interplanar distance of 7.8 Å were employed. Batallan *et al.*[18] has observed the stage-dependent magnetothermal oscillations for residual-type HNO_3 compounds having an interplanar distance of 6.8 Å. This difference in the interplanar distance may determine whether or not the electronic properties are stage dependent.

The lack of stage or concentration dependence of the linewidth is in good agreement with the results by Conard *et al.*[7] They drew the conclusion that charge transfer is small and that the Fermi level remains essentially unchanged from its position in pure graphite. The observed field dependence of the linewidth is in accord with this conclusion and is probably associated with the presence of a pure graphite-like layer. However, the narrow linewidth, as compared to that of pure graphite, and the presence of the central resonance peak should be taken as evidence of the existence of graphite layers which are greatly perturbed by the intercalant layers. Hence, charge transfer, though perhaps much smaller than for the donor-type compounds, is sufficient to cause a drastic change in the various physical properties such as the NMR line shape, electrical conductivity,[4] and magnetic susceptibility.[19]

B. Knight shift

The Knight shifts with respect to an NMR signal for TMS are summarized in Table I. The values are in good agreement with those by Conard *et al.*[7] As pointed out in Sec. III, the center of the resonance cannot be precisely determined for pure graphite. Nevertheless, the observed Knight shifts for all graphite intercalation compounds are extremely small, as compared with that for pure graphite. Carver has studied the ^{133}Cs Knight shift in cesium-graphite intercalation compounds of various stages and concluded that the cesium atom is partially ionized in C_8Cs and completely ionized in higher-stage compounds.[6] As a consequence, the electrons released from alkali metals should be distributed over the carbon layers and should lead to an increase in the electron density, particularly, in the C_b layers. Therefore, the negligibly small ^{13}C Knight shift in the donor-type intercalation compounds can be explained only if the majority of electrons transferred into the carbon layers resides in the *p*-character band and does not contribute to a positive Knight shift. Ohno *et al.*[20] recently made a self-consistent band calculation for C_8K, taking into account the charge transfer between the carbon and potassium layers. Their calculation shows that the *p*-like electrons are dominant in the vicinity of the carbon layer, although a small amount of 4*s*-like electrons appear to be also present. The band calculation, however, does not clearly indicate if the 4*s*-like electrons exist at the ^{13}C nuclear site. It is worthwhile mentioning that the Knight shift for higher-stage donor-type compounds remains independent of the stages. This indicates that only the C_b-I-C_b units are responsible for the occurrence of the central resonance peak and that its position is not affected by the presence of the C_i layers. Therefore, the behavior is consistent with the heterogeneous charge-distribution model.

In acceptor-type intercalation compounds, charge transfer occurs in the opposite direction and the electrons in the carbon layer should be partially depleted. Accordingly, the Fermi level should be lowered relative to that for pure graphite. The decrease in the Fermi level would leave the majority of electrons in states of *p* character, on the basis of the E-k relationship calculated for pure graphite.[21] Hence, the Knight shift, associated with the C_b-I-C_b units, is expected to be essentially the same as that for pure graphite.

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