Preferred Orientation of Ammonia in $KC_{24}(NH_3)_{4.3}$
Found by Proton NMR Spectroscopy

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Ammonia and other small molecules co-intercalate the alkali metal graphite intercalation compounds[1]. Possible effects of such intercalants on the degree of charge transfer from the alkali atoms to the graphite layers and on the stability of the compounds motivate the studies in the nuclear magnetic resonance spectroscopy (NMR) reported here. For the system $KC_{24}(NH_3)_{4.3}$ we present proton NMR spectra of the intercalated NH_3 and ^{13}C NMR spectra of the host graphite layers. The proton NMR spectra give an order parameter for the C_3 axis of ammonia with respect to the graphite c-axis. The ^{13}C spectra indicate stage and suggest changes in electron concentration.

Phase relations among the various components are complex[2]. A relatively simple section through the phase diagram involves compositions $KC_{24}(NH_3)_x$ where x can be conveniently and reversibly varied from ~2 (p NH_3~ 0.01 Torr) to 4.3 (6 atm). Virtues of this section are: a) even in the presence of excess NH_3 the alkalai atoms remain within the GIC; b) therefore the composition is simply controlled by the pressure of NH_3; c) the composition can be varied to achieve essentially pure stage I ternary (for which we present spectra here) as well as nearly pure stage II ternary (a residue compound), and various combinations of both stages[2].

Specimens were prepared by intercalating highly oriently pyrolytic graphite (HOPG) with potassium to Stage II as (verified by X-ray diffraction.) The principal sample was mounted in an axial, two chamber, 10 mm tube, such that excess liquid NH_3 could be condensed in the upper portion by slight cooling. NMR spectra were recorded on a JEOL FX60Q spectrometer (60 MHz ^1H, 15 MHz ^{13}C).

The proton NMR spectrum for the magnetic field B_0 normal to the graphite c-axis is shown in Fig. 1. It consists of a 1:2:1 triplet of 1:1:1 triplets. (The intensity and shape of the central line are
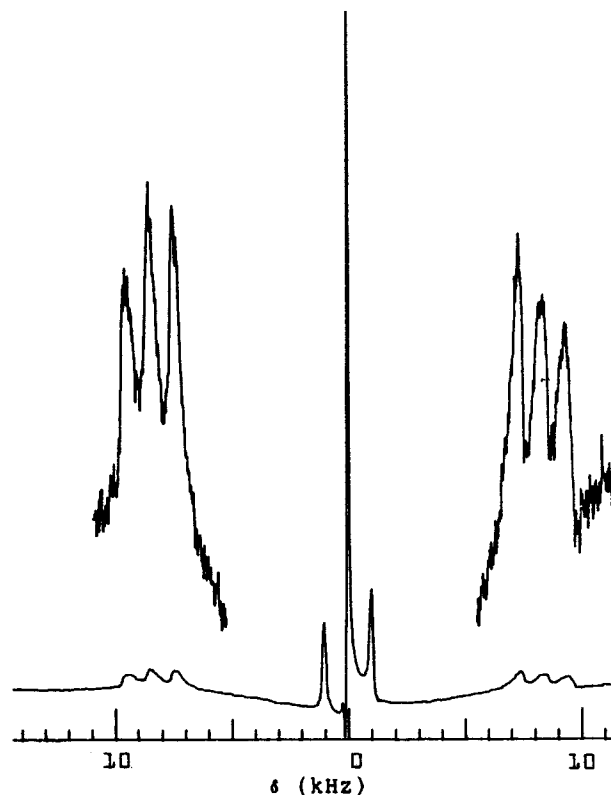

Fig.1 Proton NMR spectrum of NH_3 in $KC_{24}(NH_3)_{4.3}$ at 60 MHz. B_0 in the plane of the intercalated HOPG sheets.

warped by liquid NH_3 wetting the specimen). The same spectrum with doubled splittings was seen for B_0 parallel the c-axis. (These spectra were reproduced on a second specimen of the same composition). The interior triplet was clearly visible at all orientations of the c-axis with respect to B_0. Thus far, the outer triplets have been detectable only near values of 0 and 90 deg. of the angle β between the c-axis and the magnetic field direction. We ascribe the 1:2:1 triplet to nuclear dipolar coupling of the protons of NH_3 among themselves[3], and the 1:1:1 splittings to

nuclear dipolar coupling of the protons to ^{14}N (of spin 1). The 1:2:1 triplet implies: 1) rapid rotation ($\nu > 10^6 Hz$) of the NH_3 molecule about its C_3 axis; 2) preferred orientation of that C_3 axis with respect to the graphite c-axis, (ideally at a unique angle θ); 3) rapid precession of the C_3 axis, at the fixed angle θ, about the graphite c-axis. This last motional averaging effect may be due to reorientation accompanying translational diffusion or to rotation at a site or some combination of both. From the ^1H linewidth the diffusion coefficient of NH_3 is greater than 5×10^{-10} cm^2 s^{-1}. The preferred orientation of the C_3 axis emerges from the 1:2:1 splitting in terms of an order parameter S, defined through

$$\Delta\nu_{obs} = \Delta\nu_{max} \cdot S \cdot (3\cos^2\beta - 1)/2$$

$$\Delta\nu_{max} = (3\mu/r^3)\gamma/h = 180.16/r^3 \text{ kHz.}$$

Here μ is the proton moment, γ its gyromagnetic ratio, h is Planck's constant and r the proton-proton separation (in Å) in the equilateral triangle (which for NH_3 is 1.66Å). Thus, $\Delta\nu_{max} = 39.385$ kHz. From $\Delta\nu_{obs}$ (β=0) of 17.0 kHz, $S = \pm 0.43$ at room temperature. From the definition

$$S = \left\langle 3\cos^2\theta - 1 \right\rangle/2,$$

where the brackets indicate an average of the function over the allowed values of θ, we find "most probable" values of θ of 38(S+) or 78°(S-). It is most unlikely that the distribution in θ is anything near a δ function, given the soft potential implied by the rapid rotational and diffusional motions, and given the small moment of inertia of NH_3. We believe there to be considerable thermal averaging as well as zero point vibration about mean values of θ of either 0 or 90°. Variation of the order parameter with temperature may decide the sign of the order parameter[4]. The order parameter of ND_3 as revealed by ^2D NMR studies in this system would assess zero point effects.

The 1:1:1 splitting due to ^{14}N implies that S_z is a good quantum number for ^{14}N, at least for certain orientations of the GIC with respect to B_0, that the states of S_z are long lived, and that rapid proton exchange does not occur. The proton spectrum is indeed that of an ammonia molecule.

The ^{13}C spectra for both KC_{24} and the ternary are shown in Fig. 2. The doublets for KC_{24} show the two kinds of carbon associated with A-B stacking of the two graphite layers in contact - those above rings and those above carbon atoms in the adjacent layer, both types of carbon in equal abundance. For stage I, $KC_{24}(NH_3)_{4.3}$ there is only one kind of carbon atom, due to rapid diffusion of K+ and NH_3 in the gallery. As a tentative measure of the electron concentration we take the anisotropy of the ^{13}C spectra, defined as $A = (\delta_\perp - \delta_\parallel)$ where $\delta_\parallel$ ($\delta_\perp$) is the

mean shift of ^{13}C for β=0 (90) deg. For graphite, KC_{24}, and $KC_{24}(NH_3)_{4.3}$ the anisotropies are 180, 61, and 78 ppm respectively. Assume that the anisotropy is proportional to the conduction electron concentration[5]; then ca 14% of the electrons originally transferred to graphite in KC_{24} are lost to the potassium and/or NH_3 in $KC_{24}(NH_3)_{4.33}$. Actually, the presence of NH_3 with its strong proton signal makes the ternary a good candidate for determination of the density of states at the Fermi level by the Schumacher-Slichter technique.
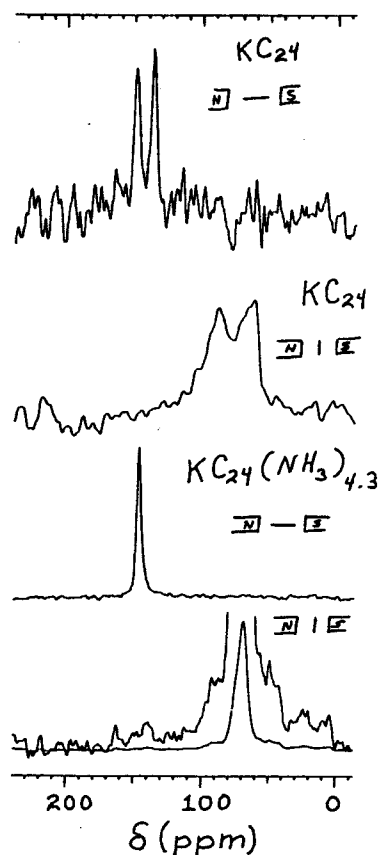

Fig.2. Carbon-13 NMR spectra of graphene carbon atoms in KC_{24} and in $KC_{24}(NH_3)_{4.3}$ at 15 MHz. The line between the schematic magnetic pole pieces indicates a graphene plane viewed edge on, and tells the orientation of those planes in the GIC with respect to the applied constant magnetic field B_0.

References

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