NMR evidence for Mott-Hubbard localization in (NH₃)K₃C₆₀

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¹³C, ¹H, and ³⁹K-NMR measurements of (NH₃)K₃C₆₀ unambiguously demonstrated that its magnetic properties are described as S = 1/2 localized spin system over the entire temperature range (300 K–4.2 K). A possible antiferromagnetic structure that appeared below 45 K is compatible with the orientational order of K-NH₃ pairs on the octahedral (O) site. The present NMR study strongly suggests that the Mott-Hubbard localization occurs due to the removal of the C₆₀ t₁₂-orbital degeneracy.

In alkali (A) fullerides A₃C₆₀ having face-centered-cubic (fcc) structure, the triply degenerated C₆₀ t₁₂ band (e.g., φ₁, φ₂, and φ₃) with half-filling is responsible for the observed metallic and superconducting properties.¹⁻³ Theoretically, however, a simple argument based on the Mott parameter, U/w ≫ 1, where U and w are the intramolecular Coulomb interaction and the bandwidth, respectively, leads to a Mott-Hubbard localization.¹,² This paradox was proposed to be solvable by taking into account orbital degeneracy, which increases the critical value for U/w to 2.5 (Refs. 1 and 4) and/or competition between spin fluctuations and phonon dynamics.⁵ In this perspective, the electronic state of trivalent C₆₀ compounds having distorted structure is interesting, because such distortions may remove the t₁₂-orbital degeneracy.

Rosseinsky et al. succeeded in preparing (NH₃)K₃C₆₀ having a noncubic structure, and found that the material does not show superconductivity.⁶ Further experiments revealed that (NH₃)K₃C₆₀ exhibits a metal-insulator transition at 40 K,⁷ at which the low-temperature (T) state was believed to be an antiferromagnetic (AF) or a spin-density wave state.⁸,⁹,¹⁰ Recently, we reported that the ground state is an AF state of 1μB/C₆₀. However, the question as to whether the system is insulating had not been resolved.⁹ In this paper, we report the NMR results that the magnetic properties of (NH₃)K₃C₆₀ are described as a localized spin system over the entire T range (300 K–4.2 K).

Sample preparation⁷,¹¹ and NMR techniques³,¹² have been reported elsewhere. The crystal structure is a face-centered-orthorhombic (fco) structure, in which K₆-NH₃ pairs in the O-site (K₁ refers to the O-site potassium) are ordered in an antiferroelectric (AFE) fashion at Tₐ ~ 150 K.¹¹ NMR spectra at 4.2 K were taken point by point as the frequency was varied. We used a sample having a NH₃ content of 0.98NH₃ per C₆₀, which is the same batch as sample A in the x-ray diffraction (XRD) studies.¹¹ dc-SQUID (superconducting quantum interference device) susceptibility shows anomalies at Tₐ ~ 150 K and Tₙ ~ 45 K associated with the AFE and the AF orderings, respectively. We also performed ¹³C-NMR for other samples having 1.14NH₃ and 1.05NH₃. Microscopic examinations revealed that the magnetic character strongly depends on the sample-quality, i.e., NH₃ content. Improvement of the quality and accumulation of experimental data enabled us to extract intrinsic behaviors. For example, a Curie tail observed at low T’s in the susceptibility data corresponds to 0.5% spins per C₆₀ in a well-controlled sample, (NH₃)₀.98K₃C₆₀, which is smaller than 2.6% spins for the previous sample having 1.14NH₃.⁷

Figures 1 and 2 show the T dependence of ¹³C-NMR spectra and ¹³C nuclear spin-lattice relaxation rate, 1/T₁, respectively. Above Tₐ, the ¹³C line is narrowed by rapid rotation of the C₆₀ molecules. In this T region, the susceptibility follows the Curie-Weiss law and yields the effective moment, μₑff ~ 1.746μB/C₆₀, and the Weiss temperature, Θ ~ –160 K, indicating the total spin ‘‘S = 1/2.’’ Correspondingly, 1/T₁ remains constant upon cooling, regardless of the applied magnetic field strength, as expected for a lo-

FIG. 1. T dependence of ¹³C-NMR spectra at H = 9.4 T (a) above Tₐ and (b) at 4.2 K. (I)80 K and (II)80 K show the spectra obtained at different times (t = 5 sec and 20 msec, respectively) after saturation of the nuclear magnetization. The dashed line is the calculation for μ₀ = 1μB/C₆₀, and the solid line is that for a 20%-impurity phase.
calized spin system. In this case, \( 1/T_1 \) is expressed as:
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1/T_1 = \sqrt{2}\pi (g\gamma_N)^2 (A_{iso}^2 + A_{dip}^2 / 2S(S+1)/(3\omega_{ex}^2)),
\]
where \( \omega_{ex}^2 = 8z^2S(S+1)/(3h^2) \) and \( T_N = |J|zS(S+1)/(3k_B) \), \( g \), \( \gamma_N \), \( A_{iso} \), \( A_{dip} \), \( z \), and \( J \) are the \( g \) factor, the nuclear gyromagnetic ratio, the isotropic hyperfine coupling constant, the number of nearest-neighbor moments, and the exchange constant, respectively. Using \( A_{iso} = 0.326 \) kOe/\( \mu_B/C_{60} \), \( A_{dip} = 1.58 \) kOe/\( \mu_B/C_{60} \), \( T_N = 45 \) K, and \( S = 1/2 \), \( 1/T_1 \) is estimated to be 13.04 sec^{-1} for the fco structure in which \( z = 8 \). This agrees well with the observed value, 13 sec^{-1}, implying that a localized model having \( S = 1/2 \) is applied to the present system.

Below \( T_s \), the \( ^{13}C \) NMR spectrum broadens over the range from -500 to +500 ppm which exceeds the range of -100\(-\)400 ppm for various fullerenes.\(^2,3,14\) The spectra ‘‘\( (I)80 \) K’’ and ‘‘\( (II)80 \) K’’ were taken at different times (\( t = 5 \) sec and 20 msec, respectively) after saturation of the nuclear magnetization. The spectrum ‘‘\( (II)80 \) K’’ for \( t = 20 \) msec splits into several lines (at least more than three) at around 500 ppm (line A), -300 ppm (line B), and 195 ppm (line C), suggesting a hybridization effect, as discussed later. In ‘‘\( (II)80 \) K’’ for \( t = 5 \) sec, we can see that only line C forms a peak. This indicates that \( T_1 \) for line C (\( T_{1C} \)) is longer than those for lines A and B (\( T_{1A} \) and \( T_{1B} \), respectively).

In order to avoid mixing of the \( 1/T_1 \) of line C, which has a large peak intensity, and those of lines A and B, we used a longer rf-pulse width, 40 \( \mu \)sec, for lines A and B than that, 6 \( \mu \)sec, for line C. \( 1/T_{1A} \) and \( 1/T_{1B} \) were obtained by fitting a stretched exponential function to magnetization recovery (MR) data using parameter \( \alpha \approx 0.8 \). Meanwhile, \( 1/T_{1C} \) was tentatively determined by fitting \( M_C(t) = M_0[1 - S_{AB}/S_C \exp(-t/T_{1A}) - S_{AB}/S_C \exp(-t/T_{1B})] \) to MR data. For \( T_s < T_N \), \( S_{AB}/S_C < 0.8/0.2 \) is obtained, suggesting the intensity of the line C is 20% for the entire range. For \( T_s > T_N \), \( S_{AB}/S_C < 0.2/0.8 \) because of a wipeout effect due to a magnetic ordering.

\( 1/T_{1C} \) shows a remarkable drop by an order just below \( T_s \) and is nearly proportional to \( T \) down to 4.2 K, without any anomaly at \( T_N \). In the sample having 1.14NH\(_3\), neither the spectral splitting related to lines A and B below \( T_s \) nor the

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Thus, lines A and B are inherent in the AF ordering, whereas line C originates in the impurity phase. This also implies that the electronic state is very sensitive to the NH\(_3\) content and that off-stoichiometric ammoniation leads to imperfect AFE and AF ordering.

In contrast, both \( 1/T_{1A} \) and \( 1/T_{1B} \) remain constant upon cooling through \( T_s \), suggesting that the local moment picture is maintained. This implies that the averaged effective exchange frequency due to nearest-neighbor \( C_{60} \) spins does not change through \( T_s \). The difference between \( 1/T_{1A} \) and \( 1/T_{1B} \) may instead be attributed to that of the hyperfine coupling constant.

Below \( T_N \approx 45 \) K, the \( ^{13}C \) NMR spectrum is unusually broadened around a narrow central line [see Fig. 1(b)]; the width is about 27000 ppm (~2.7 MHz) at 4.2 K, which indicates the AF order. Since the line broadening is mainly attributed to on-site dipolar hyperfine interactions with the local spin density at the carbon 2\( p_z \) orbital, we can deduce the dipolar field due to the spin density as \( H_{2p_z} = -0.6(1/\hbar^2)_{2p_z} \mu_{2p_z} \cos \alpha \sin \beta \cos \beta \), and \( \mu_{2p_z} = \mu_{B}/60 \). \( \mu_0 \) is defined as the magnitude of the magnetic moment per \( C_{60} \), and \( \alpha \) and \( \beta \) are the polar angles between the applied magnetic field \( H \) and the carbon 2\( p_z \) orbital. Here, we assume the spin-flop phase of the AF ordered state, \( \mu_{B} \parallel H \).\(^15,16\) The line width is estimated to be \( \Delta f \approx 2.4 \) MHz/\( \mu_B/C_{60} \) (~24000 ppm) using \( \langle 1/\hbar^2 \rangle_{2p_z} \approx 1.89/\hbar^2 \), where \( \hbar^2 \) is the Bohr radius.\(^12\) We found that the observed spectrum can be reproduced by the calculation using \( \mu_0 = \mu_B/C_{60} \) and the 20%-impurity phase, as shown in Fig. 1(b).

Figures 3 and 4 display NMR spectra for \(^1H\) and tetrahedral site potassium (\(^{39}K_7\))\(^17\), respectively. Below \( T_s \), the \(^{39}K_7\) NMR shows the isotropic positive shift of +200 ppm with spectral broadening to be different from that of K\(_3\)C\(_{60}\), whereas the \(^1H\) NMR does not show any ana-
lies. These findings suggest that the C_{60} hybridizes with the K_{O} orbital rather than the H orbital, as expected from the XRD studies.\textsuperscript{31}

Below $T_N$, $^{1}$H- and $^{39}$K_{T}-NMR spectra\textsuperscript{19} also show line broadening. The $^{1}$H- and $^{39}$K_{T}-NMR provide information on the AF ordering vector through the local field, $\vec{H}^{\text{loc}} = \sum_i [3(\mu_i \cdot \vec{r}) \vec{r}_i / r^5 - \mu_i \cdot \vec{r}_i]$, where $\vec{r}_i$ is the position of $i$th C_{60} molecule and the notation $\cdot$ represents the component of $\vec{H}^{\text{loc}}/\vec{H}$. For simplicity, any helical or noncollinear magnetic structure was disregarded and we confined ourselves to perform calculations only for the AF structures with ordering vectors, $\vec{Q} = (0 \ 0 \ 2), (1 \ 1 \ 1), (1 \ 2 \ 0), (2 \ 2 \ 1)$, and $(2 \ 2 \ 0)$ with respect to the low $T$ fcc unit cell. These structures are deduced from the mean-field theory and the former three $\vec{Q}$’s correspond to type I, II, and III fcc AF structures, respectively, whereas the latter two correspond to the body-centered-tetragonal AF structures with $\vec{Q} = (1/2 \ 1/2 \ 1/2)$ and $(1/2 \ 1/2 \ 0)$, respectively.\textsuperscript{20} The calculations were performed for the spin-flop phase with $\mu_0 = 1 \mu_B/C_{60}$, and the sum runs over neighbor C_{60}’s of $^{39}$K_{T} ($i$ = 1 to 4) and $^{1}$H ($i$ = 1 to 6). The position of hydrogen is averaged over the 1D NH_{3} molecular rotation.\textsuperscript{21} As shown in Figs. 3 and 4, good agreements with the observed spectra are obtained for a 3D-AF structure so as to satisfy the 3D-AFE order where 2D-AF sheets with planer ordering vectors of $q^{+}_{2D} = (1 \ 1)$ and $q^{-}_{2D} = (-1 \ 1)$ are stacked alternatingly along the c axis: other $\vec{Q}$’s yield 1.7–3.5 times as broad linewidth as the observed $^{1}$H-NMR width. Here, the 20%-impurity phase was taken into account. Figure 5 shows the obtained AF structure, in which black and white rugby balls correspond to opposite spins. Here we note that the AF structure is not the simple $\vec{Q}$, but rather the complicated $\vec{Q}$ that is well correlated with the AFE structure. This suggests that the K_{O}-NH_{3} arrangement within the $ab$ plane plays an important role in the AF ordering.

Next, we discuss the ground state of the system. The present result satisfies the Rhodes-Wohlfarth relation of $\mu_C/\mu_0 \approx 1$, where $\mu_C = (1 + \mu_C^{eff})^{0.5} - 1$, for the localized electron system.\textsuperscript{22} In itinerant electron magnets, however, the total spin usually shrinks in the ordered state, i.e., $\mu_C/\mu_0 > 1$.\textsuperscript{22} Thus, (NH_{3})K_{3}C_{60} is described as a localized electron system having a low-spin (LS) configuration of $S=1/2$ over the entire $T$ range, strongly suggesting that the stoichiometric (NH_{3})K_{3}C_{60} is a Mott-Hubbard insulator.

Why does the Mott-Hubbard localization take place? The lattice expansion and the distortion from a cubic structure seem insufficient to induce the localization, because both fcc A_{3}C_{60}’s having almost the same cell volume and C_{3}A_{3}C_{60} having a distortion are not insulators.\textsuperscript{2,3,11} A possible origin is the symmetry breaking at C_{60} sites due to an interaction with the K_{O}-NH_{3} pairs. This would remove the $t_{1u}$ degeneracy due to a Jahn-Teller effect\textsuperscript{23} assisted by an asymmetric crystal field and lead to the Mott-Hubbard localization.\textsuperscript{1,4} The $^{13}$C and $^{39}$K_{T} NMR spectra indicate that the interaction between C_{60} and K_{O} ions, which lowers the local symmetry at C_{60} site, is more substantial than that in fcc A_{3}C_{60}’s: the broader $^{13}$C spectra and the larger shift of $^{39}$K_{T} spectra at low $T$.

Furthermore, such a strong interaction between the $t_{1u}$ band and the pairs may cause the $t_{1u}$ orbitals at $T_s$. This is a kind of molecular orbital order of $\phi_5$ and $\phi_9$, as shown by the rugby balls in Fig. 5. Thus the close relationship between the AF and the AFE order is considered to be a natural consequence of the molecular orbital order; the black (white) rugby balls couple each other through the K_{O} atoms, whereas there is no K_{O} between the black and white rugby balls in the $ab$ plane.

Theoretical investigations have suggested that the degenerated $t_{1u}$ level is unstable for the trivalent C_{60} and may be split into three levels in the LS configuration\textsuperscript{23} due to a strong electron-phonon interaction, i.e., the Jahn-Teller effect.\textsuperscript{5} In the present case, the Jahn-Teller distortion and band splitting are realized by the aid of the interaction between K_{O} ion and the $t_{1u}$ orbital. Thus, the AFE order causes the molecular orbital ordering and the AF ordering. The coupling between the $t_{1u}$ band and the K_{O}-NH_{3} pairs must be responsible for the realization of the AF ground state. This is
consistent with the result that the imperfect AFE ordering prevents the AF order, as mentioned earlier.

In conclusion, 13 C, 1 H, and 39 K-NMR studies have provided evidence that (NH₃)K₃C₆₀ is the S = 1/2 localized spin system and strongly suggested that the ground state is a Mott-Hubbard AF insulator having $\mu_0 \sim \mu_B/C_{60}$. The previously observed metallic behaviors are probably due to the imperfect AFE and molecular orbital ordering. We propose that the magnetic structure is the 3D AF order correlated with the AFE arrangement and is accompanied by the molecular orbital order. The present study established that the electronic state of the fcc $A_3C_{60}$ is close to the Mott-Hubbard localization and is sensitive to the local symmetry at C₆₀ site.

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17. N. Muroga et al. (unpublished); The present 39 K-NMR spectrum is due to the K_T site, on the analogy of (NH₃)$_{0.55}$NaRb₂C₆₀, where any O site ²²Na-NMR signal cannot be observed because of the electric field gradient.
19. The quadrupole effect is negligible on the analogy of (NH₃)$_{0.55}$NaRb₂C₆₀ (Ref. 16) and Na₂CsC₆₀ [T. Saito et al., J. Phys. Soc. Jpn. 64, 4513 (1995)].