NMR evidence for Mott-Hubbard localization in $(NH_3)K_3C_{60}$

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^{13}C, ^{1}H, and ^{39}K-NMR measurements of $(NH_3)K_3C_{60}$ unambiguously demonstrated that its magnetic properties are described as a $S=1/2$ 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-NH_3 pairs on the octahedral (O) site. The present NMR study strongly suggests that the Mott-Hubbard localization occurs due to the removal of the C_{60} t_{1u}-orbital degeneracy.

In alkali (A) fullerides A_3C_{60} having face-centered-cubic (fcc) structure, the triply degenerated C_{60} t_{1u} band (e.g., ϕ_x, ϕ_y, and ϕ_z) 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 C_{60} compounds having distorted structure is interesting, because such distortions may remove the t_{1u}-orbital degeneracy.

Rosseinsky *et al.* succeeded in preparing $(NH_3)K_3C_{60}$ having a noncubic structure, and found that the material does not show superconductivity.[6] Further experiments revealed that $(NH_3)K_3C_{60}$ 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 $1\mu_B/C_{60}$. 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 $(NH_3)K_3C_{60}$ are described as a localized spin system over the entire T range (300 K–4.2 K).

Sample preparation[7,11] and NMR techniques[3,12] have been reported elsewhere. The crystal structure is a face-centered-orthorhombic (fco) structure, in which K_O-NH_3 pairs in the O-site (K_O refers to the O-site potassium) are ordered in an *antiferroelectric* (AFE) fashion at $T_s\sim150$ K.[11] NMR spectra at 4.2 K were taken point by point as the frequency was varied. We used a sample having a NH_3 content of $0.98NH_3$ per C_{60}, 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 $T_s\sim150$ K and $T_N\sim45$ K associated with the AFE and the AF orderings, respectively. We also performed ^{13}C-NMR for other samples having $1.14NH_3$ and $1.05NH_3$. Microscopic examinations revealed that the magnetic character strongly depends on the sample-quality, i.e., NH_3 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 C_{60} in a well-controlled sample, $(NH_3)_{0.98}K_3C_{60}$, which is smaller than 2.6% spins for the previous sample having $1.14NH_3$.[7]

Figures 1 and 2 show the T dependence of ^{13}C-NMR spectra and ^{13}C nuclear spin-lattice relaxation rate, $1/T_1$, respectively. Above T_s, the ^{13}C line is narrowed by rapid rotation of the C_{60} molecules. In this T region, the susceptibility follows the Curie-Weiss law and yields the effective moment, $\mu_{eff}\sim1.746\mu_B/C_{60}$, and the Weiss temperature, $\Theta\sim-160$ K, indicating the total spin ''$S=1/2$.'' Correspondingly, $1/T_1$ remains constant upon cooling, regardless of the applied magnetic field strength, as expected for a lo-

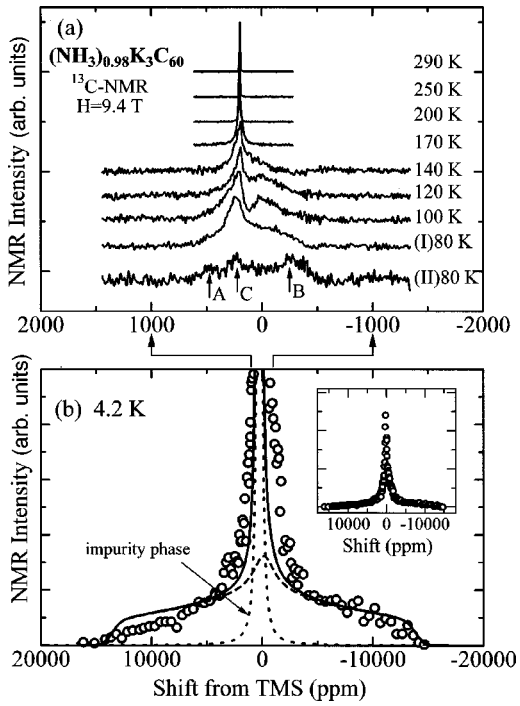

FIG. 1. T dependence of ^{13}C-NMR spectra at $H=9.4$ T (a) above T_N and (b) at 4.2 K. (I)80 K and (II)80 K show the spectra obtained at different times ($t=5$ sec and 20 msec, respectively) after saturation of the nuclear magnetization. The dashed line is the calculation for $\mu_0=1\mu_B/C_{60}$, and the solid line is that for a 20%-impurity phase.

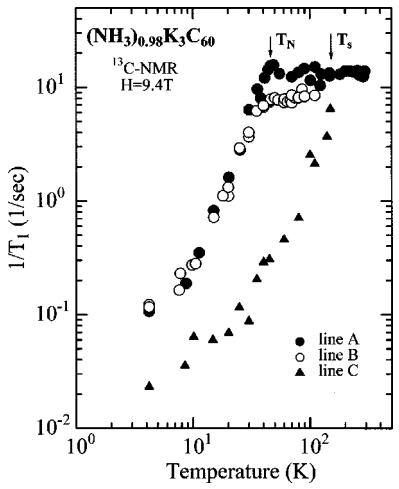

FIG. 2. T dependence of ^{13}C $1/T_1$. Magnetization recovery (MR) above T_s is fitted by a single exponential function. Below T_s, the $1/T_1$'s are measured for lines A, B, and C.

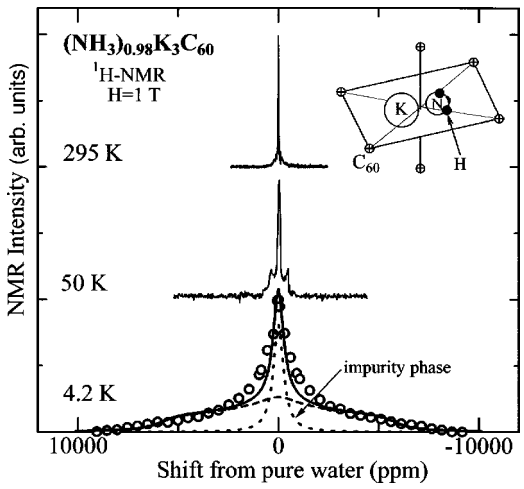

FIG. 3. T dependence of ^{1}H-NMR spectra. The dashed line is the calculation for $\mu_0=1\mu_B/C_{60}$, and the solid line is that for 20%-impurity phase. Here, the calculated line was convoluted by a computed spectrum using the Lorentzian fit to the 50 K spectrum. The inset shows the local symmetry of the octahedral site below T_s.

calized spin system. In this case, $1/T_1$ is expressed as[13] $1/T_1=\sqrt{2\pi}(g\gamma_N)^2(A_{iso}^2+A_{dip}^2/2)S(S+1)/(3\omega_{ex})$, where $\omega_{ex}^2=8zJ^2S(S+1)/(3\hbar^2)$ and $T_N=|J|zS(S+1)/(3k_B)$; g, γ_N, A_{iso}, A_{dip}, z, and J are the g factor, the nuclear gyromagnetic ratio, the isotropic hyperfine coupling constant, the dipolar coupling constant, the number of nearest-neighbor moments, and the exchange constant, respectively. Using $A_{iso}=0.326$ kOe/(μ_B/C_{60}),[12] $A_{dip}=1.58$ kOe/(μ_B/C_{60}).[12] $T_N=45$ 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 $-100\sim+400$ ppm for various fullerides.[2,3,12,14] 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 ''(I)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 μsec, for lines A and B than that, 6 μsec, 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 $\alpha\sim0.8$. Meanwhile, $1/T_{1C}$ was tentatively determined by fitting $M_C(t)=M_0[1-S_{AB}\exp(-t/T_{1A})-S_C\exp(-t/T_{1C})]$ to MR data. For $T_s>T>T_N$, $S_{AB}/S_C\sim0.8/0.2$ is obtained, suggesting the intensity of the line C is 20% for the entire range. For $T<T_N$, $S_{AB}/S_C\sim0.2/0.8$ 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 magnetic spectral broadening below T_N were observed.[7] 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-neighboring 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 $T_N\sim45$ K, the ^{13}C NMR spectrum is unusually broadened around a narrow center line [see Fig. 1(b)]; the width is about 27 000 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 $2p_z$ orbital, we can deduce the dipolar field due to the spin density as $H_{2p_z}=-0.6\langle 1/r^3\rangle_{2p_z}\mu_{2p_z}\cos\alpha\sin\beta\cos\beta$, and $\mu_{2p_z}=\mu_0/60$. μ_0 is defined as the magnitude of the magnetic moment per C_{60}, and α and β are the polar angles between the applied magnetic field $\vec{H}$ and the carbon $2p_z$ orbital. Here, we assume the spin-flop phase of the AF ordered state, $\vec{\mu}_0\perp\vec{H}$.[15,16] The line width is estimated to be $\Delta f\sim2.4$ MHz/(μ_B/C_{60}) ($\sim24\,000$ ppm) using $\langle 1/r^3\rangle_{2p_z}\sim1.89/a_B^3$, where a_B is the Bohr radius.[12] We found that the observed spectrum can be reproduced by the calculation using $\mu_0=1\mu_B/C_{60}$ and the 20%-impurity phase, as shown in Fig. 1(b).

Figures 3 and 4 display NMR spectra for ^{1}H and tetrahedral site potassium ($^{39}K_T$),[17] respectively. Below T_s, the $^{39}K_T$ NMR shows the isotropic positive shift of $+200$ ppm with spectral broadening to be different from that of K_3C_{60},[18] whereas the ^{1}H NMR does not show any anoma-

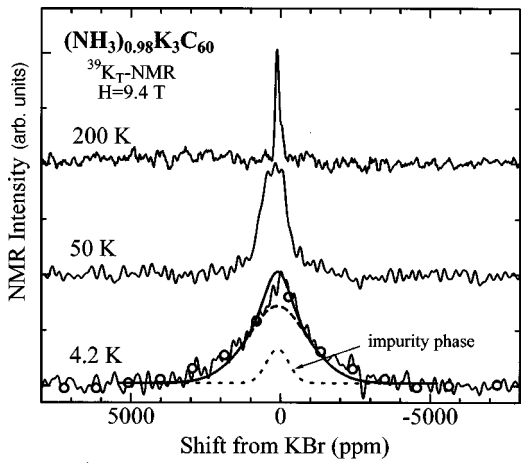

FIG. 4. T dependence of ^{39}K-NMR spectra. The dashed line is the calculation for $\mu_0 = 1\mu_B/C_{60}$, and the solid line is that for the 20%-impurity phase. Here, the calculated line was convoluted by a computed spectrum using the Gaussian fit to the 50 K spectrum.

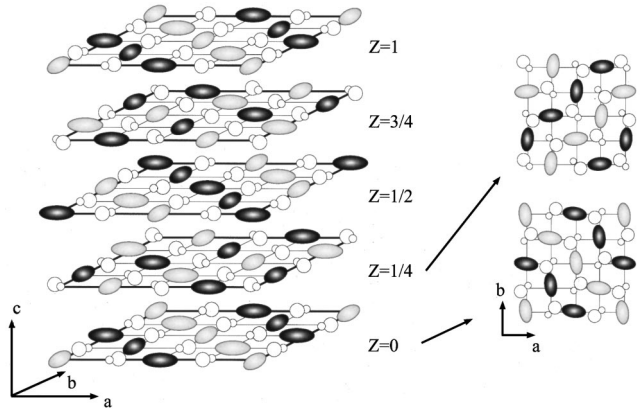

FIG. 5. Proposed AF structure and *molecular orbital order*. Rugby balls and open large and small balls represent ϕ_x or ϕ_y of the C_{60} t_{1u} orbitals, K and NH_3, respectively. Black and white rugby balls correspond to opposite spins. For simplicity, K_T atoms are not shown.

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.[11]

Below T_N, ^{1}H- and $^{39}K_T$-NMR spectra[19] also show line broadening. The ^{1}H- and $^{39}K_T$-NMR provide information on the AF ordering vector through the local field, $\vec{H}_{\parallel}^{loc} = \Sigma_i[3(\vec{\mu}_{0i}\cdot\vec{r}_i)\vec{r}_i/r_i^5 - \vec{\mu}_{0i}/r_i^3]_{\parallel}$, where $\vec{r}_i$ is the position of ith C_{60} molecule and the notation ''$\parallel$'' represents the component of $\vec{H}^{loc}\|\vec{H}$. 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 fco 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.[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.[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 $\vec{q}_{2D}^{+}=(1\ 1)$ and $\vec{q}_{2D}^{-}=(-1\ 1)$ 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 $\mu_C/\mu_0 \sim 1$, where $\mu_C = (1+\mu_{eff}^2)^{0.5} - 1$, for the localized electron system.[22] In itinerant electron magnets, however, the total spin usually shrinks in the ordered state, i.e., $\mu_C/\mu_0 > 1$.[22] Thus, $(NH_3)K_3C_{60}$ 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 $(NH_3)K_3C_{60}$ 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_3C_{60}'s having almost the same cell volume and Cs_3C_{60} having a distortion are not insulators.[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[23] assisted by an asymmetric crystal field and lead to the Mott-Hubbard localization.[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_3C_{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 order at T_s. This is a kind of *molecular orbital order* of ϕ_x and ϕ_y, 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[23] due to a strong electron-phonon interaction, i.e., the Jahn-Teller effect.[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 $(NH_3)K_3C_{60}$ is the $S=1/2$ localized spin system and strongly suggested that the ground state is a Mott-Hubbard AF insulator having $\mu_0 \sim 1\mu_B/C_{60}$. 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 C_{60} site.

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