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Solid state ^{1}H NMR of $(KH)_3C_{60}$ was measured in the temperature range between −80 and 60 °C. A doublet spectrum composed of main peak at −7.0 ppm and shoulder peak at −0 ppm was observed at room temperature. The negative chemical shift of the main peak indicates that hydrogen in $(KH)_3C_{60}$ exists as a hydride-like ion. The 60 °C spectrum became singlet at −5.8 ppm due to motional narrowing.

Keywords: fullerene; superconductor; potassium doped C_{60}; intercalation compound; hydrogen; ^{1}H NMR

INTRODUCTION

We reported superconductivity at 15 K in the sodium-hydrogen-C_{60} ternary compound prepared by thermal decomposition of sodium hydride (NaH)[1]. However, we faced the problem that contrary to the superconducting (SC) β-phase, the non-SC α-phase was also obtained even by the same preparation[2]. The appearance of multiphase originates in the circumstance that the small intercalants of sodium and hydride ions fill the large octahedral space. In order to suppress the instability, we adopted potassium hydride (KH) with a larger ionic radius. In the previous paper, we presented that, as we expected, the KH-preparation affords the stable SC $(KH)_3C_{60}$ samples and $(KH)_3C_{60}$ has a lattice constant larger than K_3C_{60}[3]. The expanded lattice constant suggested the intercalation of hydrogen. The suppression of T_c in $(KH)_3C_{60}$ was

understood as the characteristic feature in C_{60} based superconductors including off-centered alkali-metal ions. Hydrogen in $(KH)_3C_{60}$ was detected by mass-analyzed thermal desorption experiment and the hydrogen content per C_{60} by integrating the desorption spectrum was estimated to be ~ 1 .

In this paper, we present the experimental results of solid state ^1H NMR which gives additional evidence of the intercalation of hydrogen.

EXPERIMENTAL

$(KH)_3C_{60}$ samples were synthesized as follows: A mixture of stoichiometric amounts of KH and C_{60} powders was sealed in a 5 mm quartz tube and the tube was heated at 240 °C for 5 h in a muffle furnace[3].

^1H NMR spectra were measured on a Varian UNITY plus-300 spectrometer at 299.88 MHz. The sample in a Pyrex tube of 5 mm (diameter) x 10 mm (length) was set in a 7 mm ZrO_2 rotor. The measurement was done with a CPMG (Carr-Purcell Meiboom-Gill) method[4]. The intensity data were accumulated by 800 scans. The temperature control was performed with an Oxford Instruments Model VTC4. All ^1H NMR spectra were referenced externally to tetramethylsilane at 0 ppm.

RESULTS AND DISCUSSION

Figure 1 displays the temperature dependence of ^1H NMR spectra of $(KH)_3C_{60}$. At -80 °C, a doublet spectrum was observed at -8.0 ppm (signal A) and 5.6 ppm (signal B). When the temperature was increased, the NMR intensity of two signals increased and they approached each other with downfield shifts of signal A and upfield shifts of signal B. At room temperature, the separation of two signals became unclear showing a shoulder-like peak of the signal B. Finally, at 60 °C, the NMR intensity extremely increased and a singlet spectrum was observed at -5.8 ppm. For easiness to see, the peak positions of two signals against temperature are plotted in Fig. 2. The spectral change between -80 and 60 °C was quite reversible.

Let us consider the origin of two signals. In the measurement of ^1H NMR of KH powders at room temperature, a singlet spectrum was observed at -6.3 ppm. This value is close to -7.0 ppm of the signal A as the main peak. The negative chemical shift indicates that most of hydrogen in $(KH)_3C_{60}$ exists as a

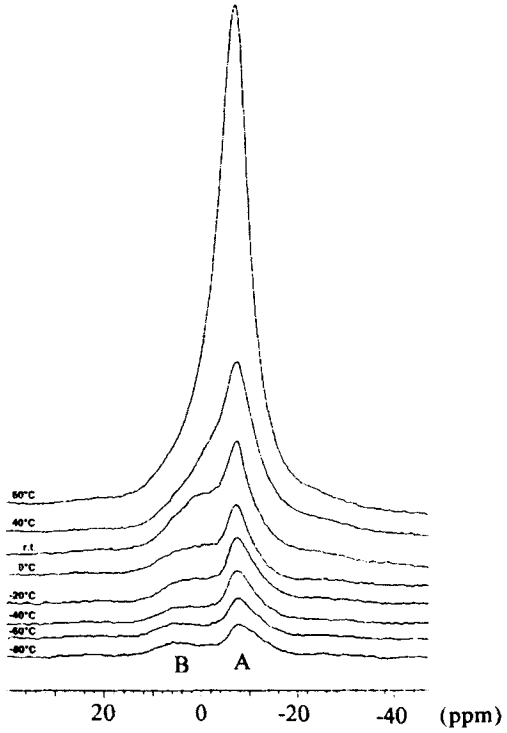

FIGURE 1 Temperature dependence of ^1H NMR spectra of $(KH)_3C_{60}$.

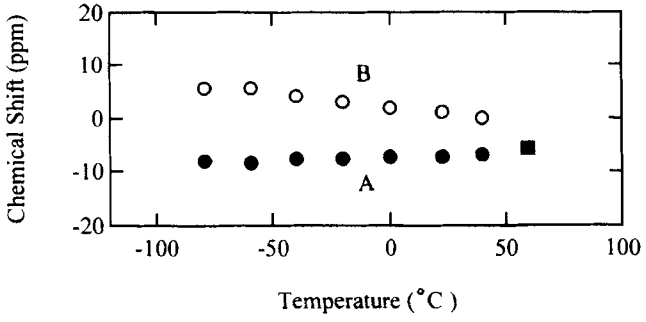

FIGURE 2 Temperature dependence of the peak positions of two signals in Fig. 1.

hydride-like ion. The origin of the signal B is unknown, but the plausible interpretation will be given as some hydride species with a covalent bond nature, judging from its positive chemical shift.

According to the result of the mass-analyzed thermal desorption study for $(KH)_3C_{60}$, H_2 molecules were desorbed with three bands at 100, 452 and 751 °C[3]. The 100 °C band is due to the adsorbed H_2 molecules on the surface. The higher two bands are assigned to H_2 molecules formed by the association of hydride ions upon heating. These two bands seem to correspond to two signals observed in the ^1H NMR measurement. From the comparison of the relative intensity between thermal desorption and ^1H NMR spectra, the 751 °C band corresponds to the signal A, whereas the 452 °C band corresponds to the signal B.

Now we discuss the spectral change of doublet-singlet from a viewpoint of site exchange[5]. Taking into account the similarity to β-$(NaH)_4C_{60}$ in crystal structure and hydrogen content[2,6,7], hydrogen in $(KH)_3C_{60}$ will be also intercalated in the octahedral (O) site. Each O-site possesses two sites for two hydride species observed in thermal desorption and ^1H NMR. Two hydride species may be closely positioned at the interstitial site. At low temperature, they are separately observed in ^1H NMR due to slow exchange rate between two sites. On the contrary, at high temperature, the exchange rate becomes so fast that a singlet ^1H NMR spectrum is observed at the in-between resonance field. The interpretation of the extreme enhancement of the NMR intensity at 60 °C is given as follows: The mobility of the proton heightens with the temperature rise, and the NMR intensity rises in order to slowly settle the magnetization vector.

References

[1] K. Imaeda, J. Kröber, H. Inokuchi, Y. Yonehara, and K. Ichimura, *Solid State Commun.*, **99,** 479 (1996).

[2] K. Imaeda, J. Kröber, C. Nakano, H. Inokuchi, and K. Ichimura, *J. Phys Chem. B,* **101,** 10136 (1997).

[3] K. Imaeda, F. Tian, H. Inokuchi, and K. Ichimura, *J. Solid State Chem.*, in press.

[4] S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, **29,** 688 (1958).

[5] A. Carrington and A. D. McLachlan, in *Introduction to Magnetic Resonance,* (Chapman and Hall, London, 1979), Chap. 12, p.204.

[6] C. Nakano, K. Imaeda, J. Kröber, and H. Inokuchi, *Chem. Lett.*, **1997,** 343.

[7] S. Suzuki, K. Nakao, K. Imaeda, C. Nakano, and H. Inokuchi, *J. Phys. Soc. Jpn.*, **67,** 2802, (1998).