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Three Components Organic Superconductors: Intercalation of KH into C_{60}

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IT IS OUR GREAT HONOUR TO DEDICATE THIS PAPER TO PROF. PETER DAY FOR HIS EXTENSIVE EFFORTS AND CONTRIBUTION IN PIONEERING AND DEVELOPING THE FIELD OF SOLID STATE CHEMISTRY AND MATERIAL SCIENCES

We have prepared $(KH)_3C_{60}$ as an initial composition by direct reaction of potassium hydride (KH) to C_{60}. $(KH)_3C_{60}$ had higher T_c (19.5 K) and larger lattice constant (14.351 Å) compared with K_3C_{60} prepared by doping of potassium metal. The expanded lattice constant is suggestive of the intercalation of hydrogen. The evidence of the inclusion of hydrogen was given by mass-analyzed thermal desorption experiment. We have also prepared $(NaH)_{4-x}(KH)_xC_{60}$ to study the substitutional effect of KH to $(NaH)_4C_{60}$. It was found that the superconducting phase is stabilized by substitution of only a few percent KH as seen in $(NaH)_{3.9}(KH)_{0.1}C_{60}$.

INTRODUCTION

Fifty years ago, several kinds of single component organic solids, such as polycyclic aromatic compounds, phthalocyanines, and also cyanine dyes, were major objects of study, and their quantitative investigation of electrical conductivity was started (1, 2). In 1954, we reported two component organic complex, perylene–bromine complex, having only a resistivity value of 8 Ωcm (3). To expand the research field of molecular conductors, we always considered introducing a new category. Several years ago, with the introduction of gaseous components such as hydrogen and nitrogen to the charge–transfer complexes, we found a third category to produce a new type of molecular conductors: three component organic conductors. In this article, we present three component organic superconductors of Na-X-C_{60} ($X = \mathrm{N, H}$) types (4–6).

Na-H-C_{60} is crystallized in a single face-centered-cubic (fcc) phase in contrast to Na-N-C_{60}, which is composed of two fcc phases. The crystal structure of the Na-H-C_{60} superconductor was solved by Rietveld analysis, in which Na^+ ions in the octahedral (O) and tetrahedral (T) sites are off-centered, suggesting the intercalation of hydrogen (7). The thermal desorption and theoretical calculation showed that hydrogen exists as a hydride ion with a fractional charge (5, 8). As another feature in the Na-H-C_{60} system, a nonsuperconductor (α-phase) as well as a superconductor (β-phase) was obtained as the main product (9). The multiplicity of phases originates in the instability that the small intercalants of sodium and hydride ions occupy the O-site with a large vacant space, which will take various configurations of $\mathrm{Na \cdots H}$ clusters.

In order to raise the phase-stability, we tried to intercalate potassium hydride (KH) with a larger ionic radius. As for a preparation by the use of KH, Lee *et al.* reported a difference of the magnetic relaxation between K_3C_{60} prepared by KH and K_3C_{60} prepared by metal-vapor doping (10). However, they did not make mention of the structural difference between them. In this article, we present the sample preparation of KH-doped C_{60} and the characterization by ESR, a low magnetic field microwave absorption signal (LFS), SQUID, powder X-ray diffraction (PXD), and mass-analyzed thermal desorption. The possibility of the intercalation of hydrogen in the KH-C_{60} system is discussed. Furthermore, we examined the substitutional effect of KH to the multiphasic Na-H-C_{60} system by changing the KH content from $x = 0.1$ to 3 in $(NaH)_{4-x}(KH)_xC_{60}$.

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EXPERIMENTAL

High pure C_{60} (>99.9%) was purchased from Hoechst Industry. Oil-dispersed KH powders received from Aldrich Chemical were washed by a dehydrated *n*-hexane and vacuum dried using an argon gas filled glove box with a gas circulation and purification system. Stoichometric amounts of C_{60} and dry KH were mixed in an agate mortar and transferred into a 5-mm diameter quartz tube in the glove box. The sample in the tube sealed under $\sim 10^{-4}$ Pa was heated in a muffle furnace.

ESR spectra were measured by a Bruker ESP300E X-band spectrometer with an Oxford ESR900 helium flow cryostat. The dc magnetization was measured by a Quantum Design $MPMS_2$ SQUID magnetometer. PXD data at room temperature for the samples in a 0.5-mm diameter quartz capillary sealed with Torr Seal were taken by a Rigaku R-AXIS IV imaging plate X-ray diffractometer with a 5 kW Mo$K\alpha$ ($\lambda = 0.71069$ Å) radiation. Mass-analyzed thermal desorption spectra were measured by Baratron 122AA-01000BB and 127A-00001B pressure/vacuum gauges and ULVAC MSQ150A and Balzers QMG064 quadrupole mass analyzers.

RESULTS AND DISCUSSION

I. $(KH)_3C_{60}$

We prepared $(KH)_3C_{60}$ as an initial composition to compare with K_3C_{60} which has been well characterized. In order to find the optimum reaction temperature, the sample was heated step-by-step. An evolution process of reaction was traced by ESR at room temperature and LFS at 5 K. A 150°C heat-treatment gave weak and asymmetric ESR. The LFS was weak at this step. At a step of 200°C heat-treatment, the ESR signal became intense and symmetric with a linewidth (ΔH) of ~ 10 G. After a 240°C heat-treatment, ΔH broadened to ~ 15 G and the LFS became quite strong with a large hysteresis.

Lots of $(KH)_3C_{60}$ samples were prepared by heating at 240°C for 5 h. Figure 1 shows the temperature dependence of the zero-field cooled (ZFC) and field-cooled (FC) magnetic susceptibility under a magnetic field of 2 G for a 17.2 mg sample with the biggest SQUID response. The ZFC susceptibility of -2.34×10^{-2} emu g^{-1} G^{-1} at 4.5 K gives $V_{SC} = 55\%$, where V_{SC} stands for a superconducting (SC) volume fraction. The onset T_c of superconductivity was found to be 19.5 K. This critical temperature seems to be a little higher than 18 K of K_3C_{60} thin film (11) and 19.3 K of K_3C_{60} powders (12). As for the ESR properties of the sample with $V_{SC} = 55\%$, it shows a Lorentzian line-shape spectrum of $\Delta H = 15.0$ G and $g = 2.0007$ at room temperature. These values are not in agreement with $\Delta H \sim 10$ G and $g = 2.0000$ for K_3C_{60} (13, 14), suggesting some difference in the crystal structure.

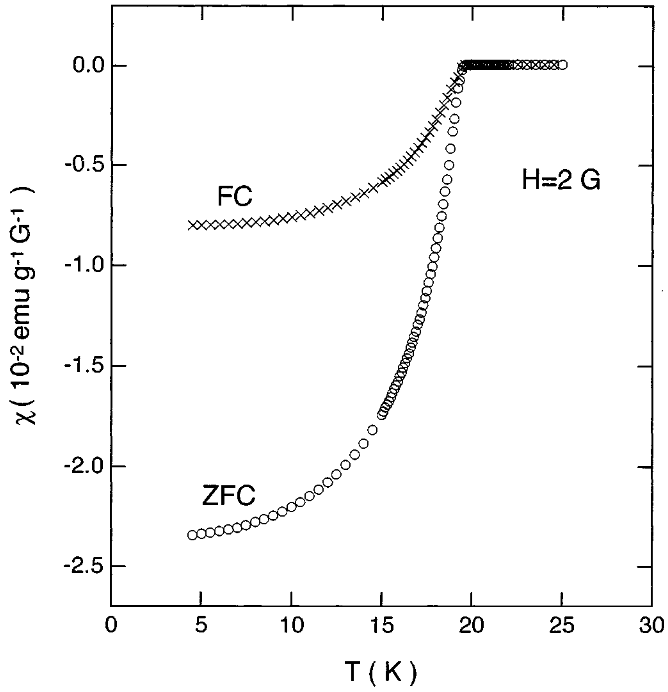

FIG. 1. Temperature dependence of the zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibilities of the nominal $(KH)_3C_{60}$ sample.

Figure 2 shows the PXD pattern of the sample with $V_{SC} = 55\%$. The whole profile corresponds to an fcc lattice with a lattice constant $a = 14.351(4)$ Å. This value is meaningfully larger than $a = 14.253(3)$ Å for K_3C_{60} (15). The expanded lattice constant of $(KH)_3C_{60}$ is suggestive of the intercalation of hydrogen; that is, K^+ ions in the O-site may be off-centered. According to the linear $T_c(a)$ relationship for

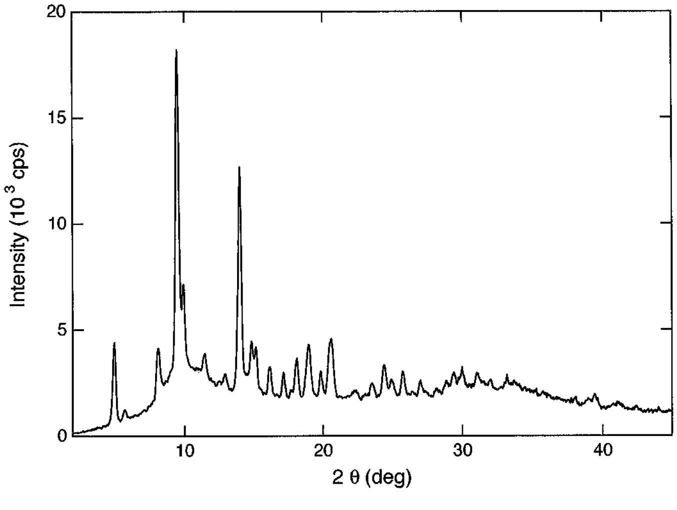

FIG. 2. Powder X-ray diffraction pattern of the nominal $(KH)_3C_{60}$ sample.

TABLE 1
Comparison of Physical Data between $(KH)_3C_{60}$ and K_3C_{60}

Compound	g	ΔH (G)	T_c (K)	a (Å)
$(KH)_3C_{60}$	2.0007	15	19.5	14.351
K_3C_{60}	2.0000	10	19.3	14.253

a family of alkali-metal doped M_3C_{60} superconductors (16), $a = 14.35$ of $(KH)_3C_{60}$ leads to $T_c \sim 25$ K. However, the observed 19.5 K is ~ 5 K lower. The suppression of T_c will be understood as the common feature in C_{60} based superconductors including the off-centered alkali-metal ions, like Na-X-C_{60} (X = N, H) and $(NH_3)_xNaM_2C_{60}$ (M = K, Rb) (17).

The overall comparison of ESR, SC, and X-ray properties between $(KH)_3C_{60}$ and K_3C_{60} is given in Table 1. It is natural to consider that $(KH)_3C_{60}$ is not the same as K_3C_{60}. The KH method has the crucial difference against the metal–vapor doping that potassium metal and hydrogen are coexisting at the thermal decomposition of KH. Hydrogen will be intercalated into the lattice at the same time that potassium is doped to C_{60}.

Hydrogen in the sample was experimentally detected by mass-analyzed thermal desorption. Part of the sample used in ESR, LFS, SQUID, and PXD experiments was analyzed under a constant heating rate of 5 K min^{-1}. Figure 3 shows the thermal desorption spectrum of H_2 molecules with $m/e = 2$. Three desorption bands were observed at 373, 725, and 1024 K as the peak temperature. This three-bands picture resembles those of H_xKC_8 (402, 447, and 512 K) (18) and $H_xK_3C_{60}$ (360, 700, and 920 K) (19), which were prepared by sorption of hydrogen to KC_8 and K_3C_{60}. The 373 K band in $(KH)_3C_{60}$ can be assigned to the adsorbed H_2 molecules on the surface, since it is located at the similar temperature to the 402 K band of H_xKC_8. The 725 and 1024 K bands due to the dissociated hydrogen (hydride ions) are shifted to the high temperature side by ~ 80 and ~ 150 K, respectively, compared with 644 and ~ 875 K for β-$(NaH)_4C_{60}$ (5). This means that hydride ions in $(KH)_3C_{60}$ are more strongly bounded in the C_{60} lattice than those in β-$(NaH)_4C_{60}$. In other words, a hydride ion in $(KH)_3C_{60}$ might have a negative charge larger than that in β-$(NaH)_4C_{60}$ which is calculated to be 0.2–0.3 for Na_3HC_{60} and Na_4HC_{60} model structures (8).

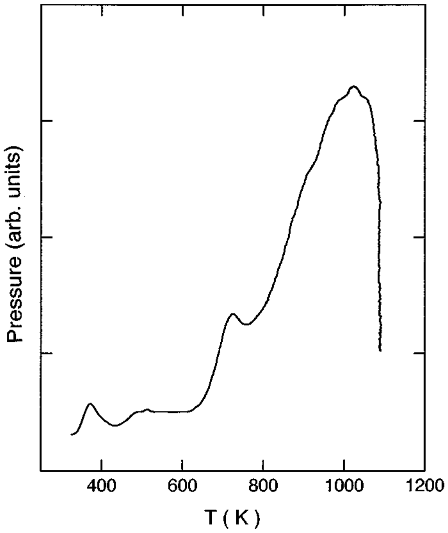

FIG. 3. Mass-analyzed thermal desorption spectrum of hydrogen of the nominal $(KH)_3C_{60}$ sample.

The mass-analyzed thermal desorption gives the quantitative amount of hydrogen by integrating the desorption spectrum shown in Fig. 3. The hydrogen content per C_{60} is given as $H/C_{60} = 1.1$, which is comparable to $H/C_{60} = 1.0$ in β-$(NaH)_4C_{60}$ (9). The final composition of $(KH)_3C_{60}$ may be K_3HC_{60}.

II. $(NaH)_{4-x}(KH)_xC_{60}$

In a preparation of NaH-C_{60}, we met with the problem that in one case high-quality SC samples are obtained and in another case weak or non-SC samples are obtained even if the preparation is done by the same way. On the contrary, the KH-preparation always afforded the samples with large V_{SC}. It is considered that the difference of phase-stability between Na-H-C_{60} and K-H-C_{60} is related to the size of alkali-metal ions. We thought that it would be interesting to investigate an effect on the phase-stability by replacing part of NaH in $(NaH)_4C_{60}$ with KH. The preparation of samples and evolution of ESR and LFS for $(NaH)_{4-x}(KH)_xC_{60}$ were carried out in the same way as $(KH)_3C_{60}$. The optimum reaction condition to get symmetric and broad ESR and strong and hysteretic LFS was found to be a 280°C heat-treatment. We prepared five compounds with the initial composition of $(NaH)_{4-x}(KH)_xC_{60}$ (x = 0.1, 0.5, 1, 2, 3) by heating at 280°C for 5 h.

Table 2 summarizes ESR properties (g-value and ΔH at room temperature) and SC properties (T_c and V_{SC}) for the compounds with x = 0.1, 0.5, 1, 2, and 3 of $(NaH)_{4-x}(KH)_xC_{60}$ including the reported data of β-$(NaH)_4C_{60}$ as $x = 0$ (20). The ESR and SC properties of several samples prepared for each compound were quite reproducible. All the compounds are bulk superconductors with V_{SC} of several tens of percent. ΔH and T_c increase with increasing the KH content x, whereas the g-value decreases with increasing x. However, if we take a g-shift ($\delta g = |g - g_0|$; g_0 being 2.0023 for free electron spin), δg also increases with increasing x.

Figure 4 shows the x dependence of δg, ΔH, and T_c. Three quantities change in a similar manner, showing a monotonic

TABLE 2
ESR and Superconducting Properties of $(NaH)_{4-x}(KH)_xC_{60}$

x	Compound	g	ΔH (G)	T_c (K)	V_{SC} (%)
0	$(NaH)_4C_{60}$	2.0014	10.4	15.2	77
0.1	$(NaH)_{3.9}(KH)_{0.1}C_{60}$	2.0013	11.1	17.6	40
0.5	$(NaH)_{3.5}(KH)_{0.5}C_{60}$	2.0011	13.2	18.4	50
1	$(NaH)_3(KH)C_{60}$	2.0010	13.9	19.0	30
2	$(NaH)_2(KH)_2C_{60}$	2.0008	15.1	19.2	40
3	$(NaH)(KH)_3C_{60}$	2.0006	15.8	19.6	35

positive increase. This systematic change suggests that $(NaH)_{4-x}(KH)_xC_{60}$ will be regarded as the substitutional solid solution in which Na^+ ions in the O- and T-sites are partially substituted with K^+ ions.

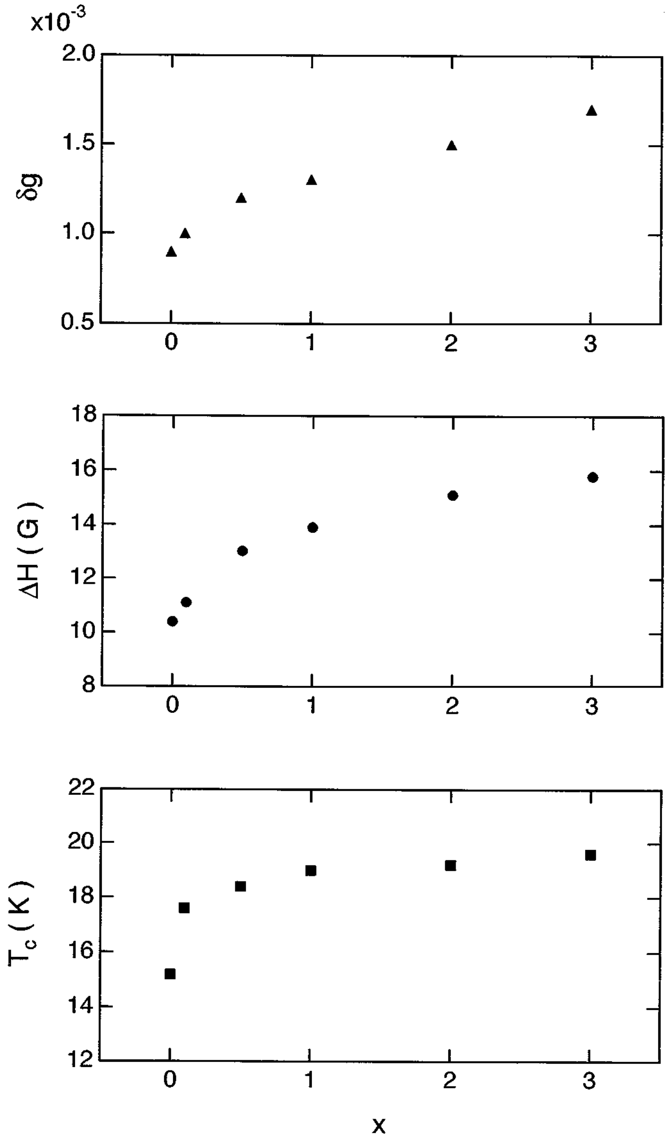

FIG. 4. g-shift (δg), linewidth (ΔH), and superconducting transition temperature (T_c) against x in $(NaH)_{4-x}(KH)_xC_{60}$.

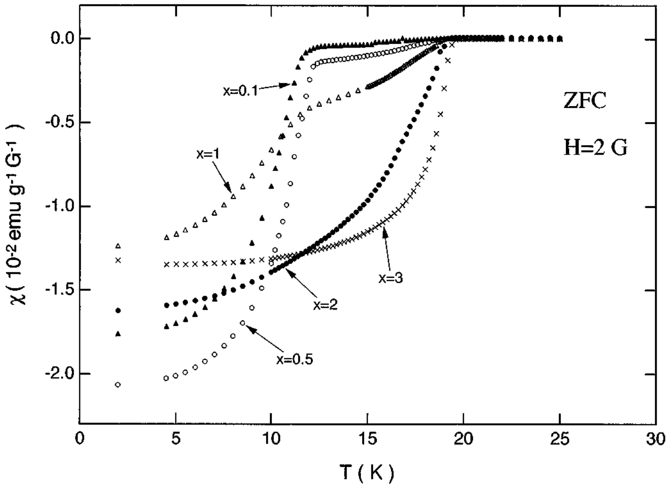

FIG. 5. Temperature dependence of the zero-field cooled magnetic susceptibility for the compounds with $x = 0.1$, 0.5, 1, 2, and 3 of $(NaH)_{4-x}(KH)_xC_{60}$.

The ZFC magnetic susceptibility under $H = 2$ G by SQUID for the compounds with $x = 0.1$, 0.5, 1, 2, and 3 is shown in Fig. 5. The temperature dependence of the compounds with $x = 0.1$, 0.5, and 1 (group A) is different from that of the compounds with $x = 2$ and 3 (group B). The group A compounds have a kink around 12 K. This behavior may be explained by weak links between superconducting grains, prohibiting the flow of shielding current (21). In contrast to group A compounds, group B compounds show a sharp drop below T_c. Especially, the temperature-dependent behavior of $(NaH)(KH)_3C_{60}$ closely resembles that of $(KH)_3C_{60}$ in Fig. 1.

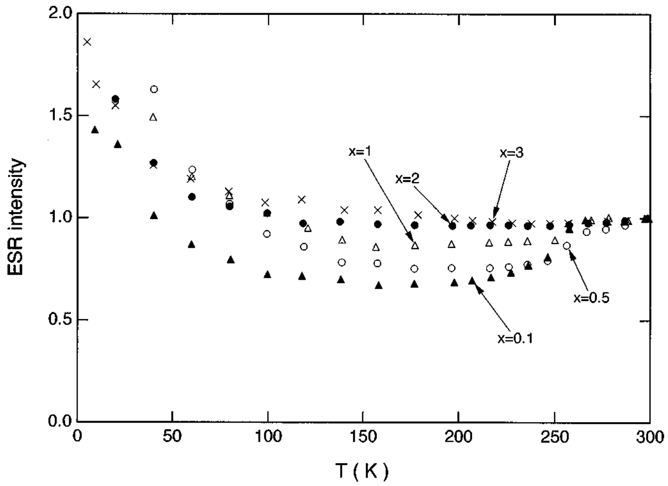

FIG. 6. Temperature dependence of the normalized ESR intensity to its room temperature value for the compounds with $x = 0.1$, 0.5, 1, 2, and 3 of $(NaH)_{4-x}(KH)_xC_{60}$.

The difference of physical properties between group A and group B compounds is also observed in the ESR intensity (Fig. 6) and PXD pattern (Fig. 7). We reported that β-$(NaH)_4C_{60}$ undergoes an fcc to simple cubic phase transition below 260 K with a sharp decrease of ESR intensity (6). As shown in Fig. 6, group A compounds have the phase transition around 260 K. The drop of ESR intensity becomes smaller with increasing x, which means the gradual suppression of the phase transition. In the group B compounds, the phase transition is entirely suppressed.

Figure 7 shows the variation of PXD patterns of the compounds with $x = 0.1$, 0.5, 1, 2, and 3 including the pattern of β-$(NaH)_4C_{60}$ as the standard for $x = 0$. The whole profiles of group A compounds almost retain the fcc profile of β-$(NaH)_4C_{60}$. At $x = 2$ for $(NaH)_2(KH)_2C_{60}$, the whole profile drastically changes in which the reflection at $2\theta = 14.0°$ becomes intense and the peak structure in the region of $2\theta > 16°$ obviously changes.

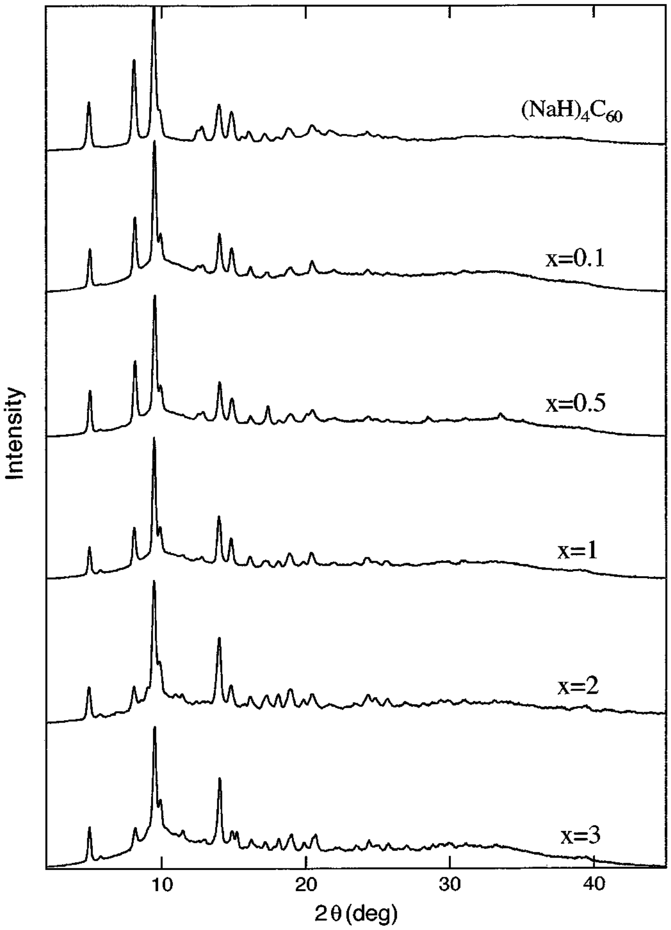

FIG. 7. Powder X-ray diffraction pattern for the compounds with $x = 0.1, 0.5, 1, 2$, and 3 of $(NaH)_{4-x}(KH)_xC_{60}$. Top panel shows the pattern of β-$(NaH)_4C_{60}$ (4).

Let us discuss the structural change depending on x in $(NaH)_{4-x}(KH)_xC_{60}$, supposing the solid solution model. The fcc structure possesses one O-site and two T-sites per C_{60} molecule. Here we introduce K^+ ions into this lattice. For the compounds with $x \leq 1$, K^+ ions entered not into the T-site but into the O-site, since the phase transition observed in group A compounds is characteristic in the compounds like Na_2MC_{60} (M = K, Rb, Cs) (22) in which the T-sites are filled with Na^+ ions. For the compound with $x \geq 2$, the second and more K^+ ions entered into the T-site, since two K^+ ions will be unable to be accepted in an O-site because of its larger radius. In short, the difference of physical properties between group A and group B compounds originates in the structural difference that the T-sites in group A compounds are filled with Na^+ ions, whereas the T-sites in group B compounds are filled with K^+ ions.

Another important result obtained from the study of $(NaH)_{4-x}(KH)_xC_{60}$ is that the SC β-phase can be stabilized by substitution of a small quantity of KH. As seen in $(NaH)_{3.9}(KH)_{0.1}C_{60}$, only 2.5% substitution is effective on the stabilization. The possible origin of the phase-stability by KH substitution is given as follows: The cubic phase is only known in K_3C_{60}, in contrast to cubic and orthorhombic phases in $(NaH)_4C_{60}$ (9). This means that K-doped C_{60} is easy to crystallize in the cubic phase. The nearest neighbouring distance between K^+ ions is about 14 Å which corresponds to the lattice parameter. Since the Coulomb interaction works as long-range force, the SC cubic phase will be formed even by substitution of a small amount of KH in $(NaH)_4C_{60}$.

SUMMARY

The intercalation of KH into C_{60} has been tried and the prepared sample has been characterized whether a potassium-hydrogen-C_{60} ternary compound is formed or not. The ESR, SC, and X-ray properties of $(KH)_3C_{60}$ as the initial composition are a bit different from those of the known K_3C_{60}. The expanded a and the suppression of T_c for $(KH)_3C_{60}$ is suggestive of the presence of off-centered K^+ ions due to the intercalation of hydrogen. The detection of hydrogen by mass-analyzed thermal desorption experiment convinces us of the formation of potassium-hydrogen-C_{60} ternary compound. The quantitative analysis of desorbed hydrogen gas gives K_3HC_{60} as the final composition.

The compounds with $x = 0.1$, 0.5, 1, 2, and 3 of $(NaH)_{4-x}(KH)_xC_{60}$ were prepared to study the substitutional effect of KH to the multiphasic $(NaH)_4C_{60}$. The g-value, ΔH, and T_c of these compounds systematically change depending on x. This behavior indicates that the picture of the substitutional solid solution will be suitable for $(NaH)_{4-x}(KH)_xC_{60}$. The temperature dependence of SQUID response and ESR intensity and PXD pattern are

quite different between the compounds with $x \leq 1$ and the compounds with $x \geq 2$. This difference originates in the manner of the T-site filling by Na^+ ions for $x \leq 1$ and K^+ ions for $x \geq 2$. It is also interesting that the KH substitution is effective on the stabilization of the SC phase.

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