PHASE TRANSITION AND ISOTOPE EFFECT IN $Na_xH_yC_{60}$ SUPERCONDUCTOR

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Introduction

We found a three components superconductor which consists of sodium, hydrogen and C_{60} [1]. The onset T_c was observed around 15 K and the composition was estimated at x=3.6 and y=1-2 in $Na_xH_yC_{60}$ from Rietveld refinement and thermal desorption spectroscopy (TDS) [2]. It is important that the composition x of Na is slightly larger than 3, unlike M_3C_{60} superconductors. And hydrogen exists as a hydride ion to cancel the excess positive charge over 3. As another feature, the $Na_xH_yC_{60}$ ternary compound contains the off-centered tetrahedral and octahedral Na cations [3], in contrast to the alkali metal-C_{60} binary compound containing the on-centered cations.

In this paper, we report the two phase transitions observed in $Na_xH_yC_{60}$ and the effect of isotopic substitution of deuterium for hydrogen.

Experimental

The sample preparation by direct intercalation of sodium hydride (NaH) into C_{60} was in detail described in the first paper [1]. For the Na-D-C_{60} compound, 98 % isotopic purity NaD was purchased from Strem Chemicals. Oil-dispersed NaD powders were washed several times by a dehydrated n-hexane and vacuum dried. The superconducting (SC) Na-D-C_{60} samples were obtained by heating at 300 °C for 1 h, compared with 280°C-1h heating for the Na-H-C_{60} compound.

Powder X-ray diffraction (PXD) was carried out with a Rigaku R-AXIS IV imaging plate X-ray diffractometer with a 5 kW Mo $K\alpha$ (λ=0.71069 Å) radiation. The dc magnetization was measured with a Quantum Design $MPMS_2$ SQUID magnetometer. ESR spectra were recorded on a Bruker ESP300E X-band spectrometer.

Results and Discussion

(1) Non-SC to SC phase transition

We prepared the samples of $(NaH)_nC_{60}$ (n=1-6), where n is an initial composition. The SC samples were obtained at n=3-4. High-quality samples with a large SC volume fraction (V_{SC}) are obtainable, but the number is a few and most of the samples are nonsuperconducting. However we found that a non-SC sample (α-phase) can

be converted into an SC sample (β-phase) by heating around 300 °C under the dynamic vacuum. It is also found that superconductivity can be enhanced by introducing hydrogen gas even if the converted sample has weak SC character. Very interestingly, β-phase turns back to α-phase by dynamically pumping on warming from liquid helium to room temperatures. From this α-phase it is again possible to get β-phase just like at the first time by vacuum heating. Figure 1 shows schematically how α- and β-phases can be transformed from one into another.
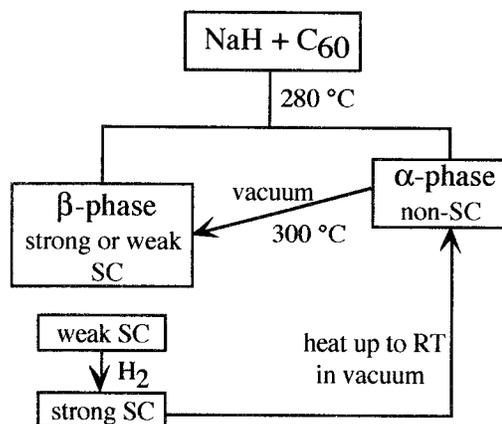

Figure 1. Flow diagram of the reversible phase change in the Na-H-C_{60} system.

According to the Rietveld analysis using the PXD data, α-phase has an orthorhombic structure (space group *Pmmm*), in contrast to a face centered cubic (fcc) structure (*Fm3m*) for β-phase. The broken symmetry in α-phase leads to the disappearance of superconductivity.

(2) Fcc to simple cubic phase transition

We already observed a phase transition around 260 K from ESR (see Fig. 4) and NMR measurements for the SC $Na_xH_yC_{60}$ [4]. In order to understand the nature of this transition, we performed the low-temperature PXD for the converted V_{SC}=26 % sample with a nominal $(NaH)_{3.9}C_{60}$ which was loaded in 0.7 mm diameter quartz capillary. The room-temperature profile is in agreement with the *Fm3m* one reported previously [3]. Below the transition temperature, it starts to be deformed from the *Fm3m* profile. At 100 K, the profile shown in
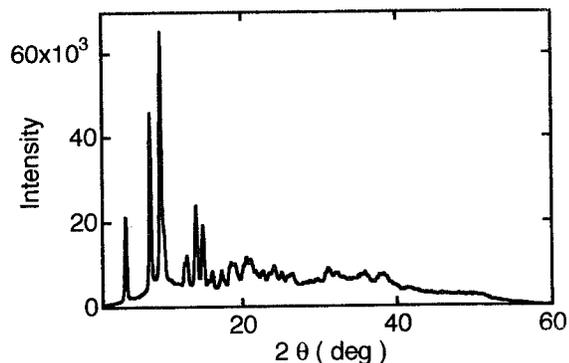
Figure 2. PXD profile at 100 K for the SC $Na_xH_yC_{60}$.

Fig. 2 can not be assigned to the fcc structure. The preliminary Rietveld refinement presents that the low-temperature phase is assigned to simple cubic ($Pa\bar{3}$) with a lattice constant $a=14.196(5)$ Å, in which C_{60} molecules are ordered in contrast to the disordered C_{60} in the room-temperature phase.

(3) Isotope effect

We prepared lots of $(NaD)_nC_{60}$ (n=3.9-4.0) samples. So far we obtained the good samples with V_{SC}=7, 9, 12, 23 and 28 %. For all the samples, the onset T_c was observed around 12 K. Figure 3 shows the temperature dependence of the zero-field-cooled (ZFC) magnetization under H=2 G for the D compound with the highest V_{SC}=28 % and the H compound with the highest V_{SC}=77 %. We find a big isotopic shift to be ΔT_c~3 K, compared with a small shift (ΔT_c=0.65 K) for isotopic substitution of ^{13}C for ^{12}C in Rb_3C_{60} [5].
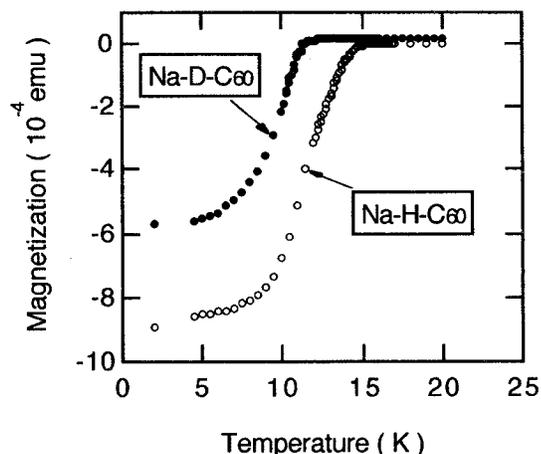

Figure 3. Plots of ZFC magnetization *vs.* temperature for the $Na-D-C_{60}$ and $Na-H-C_{60}$ compounds.

The phonon-mediated pairing BCS theory predicts that

$T_c \propto M^{-\alpha}$ (α=0.5) for simple metals, where M is the ionic mass. The experimental value, ($T_c(H)/T_c(D)$)= 15/12=1.25, is nearly equal to the calculated value, ($M(D)/M(H)$)$^{0.5}$=1.41, suggesting that the phonon of H^- ions is related to superconductivity in the present system. For discussion on the isotope effect, we must carefully look at the identity of the structure between both compounds and the degree of hydrogen or deuterium doping. We are now in progress to analyze the crystal structure by PXD and the deuterium content by TDS for the D compound. We are also planning to study inelastic neutron scattering for the H and D compounds to get information about phonons.

We measured ESR of the D compound with V_{SC}=28 %. As shown in Fig. 4, the D compound also underwent the phase transition around 250 K against 260 K for the H compound.

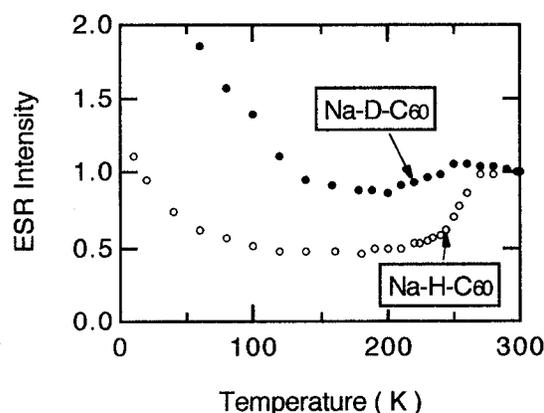**Figure 4.** Plots of ESR intensity *vs.* temperature for the $Na-D-C_{60}$ and $Na-H-C_{60}$ compounds.

A 10 K lower transition temperature for the D compound may be due to the difference of the motion between hydride and deuteride ions.

References

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