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Preparation and characterization of Na_xC_{60} using sodium azide

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Sodium-doped C_{60}, Na_xC_{60} (x=1~12), has been prepared by a thermal decomposition of sodium azide (NaN_3). Superconductivity around 12 K was observed in the samples of Na_xC_{60} (x=3~4). It is worthy of note that elemental analysis detected nitrogen which is produced at the thermal decomposition of NaN_3. This new sodium-doped C_{60} superconductor will be $Na_xN_yC_{60}$ where x is between 3 and 4, and y is unknown.

1. INTRODUCTION

Na_3C_{60} is a hopeful candidate of superconductors following K_3C_{60} and Rb_3C_{60}, but it does not become superconducting (SC) due to the disproportionation to Na_2C_{60} and Na_6C_{60} below 250 K [1]. The suppression of this phase separation would be important to search a new superconductor in sodium-doped C_{60}. Superconductivity in Na_2MC_{60} (M=K, Rb and Cs) seems to result from the suppression of the phase separation by replacing sodium with alkali-metal having a large ionic radius [2]. Recently, Zhou *et al.* found superconductivity of 29.6 K in $(NH_3)_4Na_2CsC_{60}$, where $(NH_3)_4Na^+$ ions are intercalated on the octahedral site [3]. Since Na-doped C_{60} system has a possibility to accommodate various Na compounds in the interstitial site, the appearance of the new SC phase would be expected.

After the earlier work by Bensebaa *et al.* [4], we prepared sodium-doped C_{60} utilizing the thermal decomposition of sodium azide. As the sodium atom, nitrogen atom and nitrogen molecule are generated at the initial stage of decomposition, a new phase of sodium-doped C_{60} might be created.

We have found superconductivity in sodium-doped C_{60} using the sodium azide [5]. This new SC phase seems to include nitrogen as some Na-N compound in the C_{60} lattice. In this paper, we report the details of sample preparation of Na_xC_{60} (x=1~12) and characterization of each sample by SQUID magnetization, powder X-ray diffraction and elemental analysis.

2. EXPERIMENTAL

The pure C_{60} was separated by a standard toluene extraction and HPLC from the soots produced through resistive heating of graphite. The purification to remove the solvent in C_{60} was done by the following two ways: (i) heat-treatment at 160 °C under $2x10^{-3}$ Pa and

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(ii) sublimation at 500 °C under $8x10^{-4}$ Pa. The purified C_{60} is hereafter named preheated-C_{60} and sublimated-C_{60}, respectively. NaN_3 was used as received from Wako (90 %) and Fluka (>99.5 %). Any metal impurity in Wako NaN_3 was not detected by an ICP atomic emission spectroscopy. Wako NaN_3 was dried at 120 °C in vacuum to remove water and methanol which are added as a stabilizer. The mixture of stoichiometric amounts of C_{60} and NaN_3 was placed in a 5 mm diameter ESR quartz tube. We connected a glass tube with a capillary which protects against an overflow of the sample along with the flow of nitrogen gas generated at the thermal decomposition of NaN_3. This reaction tube was set in a vertical furnace and evacuated to $4x10^{-4}$ Pa. We heated the sample at 370-390 °C for ~20 min to decompose NaN_3 under the dynamic vacuum. The azide decomposition was monitored by a pressure increase of a vacuum gauge. After the temperature was elevated up to 410 °C to complete the decomposition, the tube was quickly cooled to room temperature and sealed off. We also prepared the samples which were reacted along the same temperature scheme in the sealed ESR tube before the decomposition.

An SHE SQUID magnetometer was used to measure the d.c. magnetization. Powder X-ray diffraction was taken at room temperature using a Mac Science MXP^3 diffractometer with a 2 kW Cu Kα (λ= 1.54050 Å) radiation.

3. RESULTS AND DISCUSSION

We prepared Na_xC_{60} (x=1-12) samples using preheated-C_{60} and Wako NaN_3, which were reacted under the dynamic vacuum and annealed for 90 h at 200 °C. There was the unreacted sodium metal in the samples with x≥10. This means that the maximum composition of Na_xC_{60} will be Na_9C_{60}. Among these samples, Na_3C_{60} and Na_4C_{60} showed a strong low-field microwave absorption signal (LFS) with a clear hysteresis, indicating the SC character [5]. Figure 1 shows the temperature dependence of the zero-field cooled magnetic susceptibility for Na_4C_{60}. The sample was zero-field cooled down to 2 K, then the magnetization was measured up to 20 K under a magnetic field of 10 Oe. On warming the sample, the diamagnetic susceptibility was observed up to 12 K. On field cooling, a magnetic flux expulsion (Meissner effect) was clearly observed below 12 K, indicating the bulk nature of superconductivity in this sample. The magnitude of the susceptibility at 3 K corresponds to ~3 % as a volume fraction of the shielding diamagnetism.

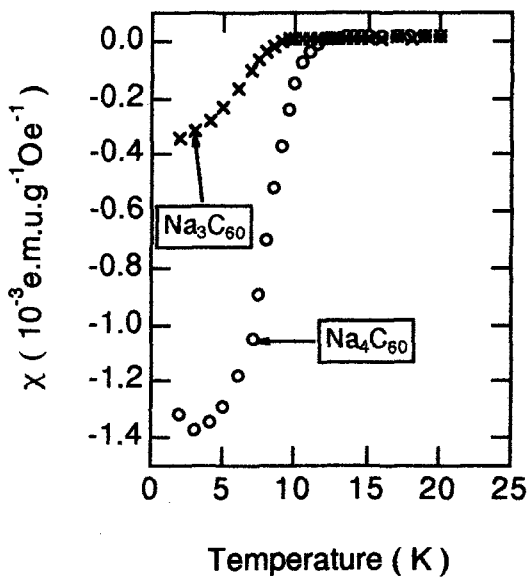

Figure 1. Zero-field cooled magnetic susceptibilities (H=10 Oe) of Na_4C_{60} prepared with Wako NaN_3 and preheated-C_{60}, and Na_3C_{60} prepared with Fluka NaN_3 and sublimated-C_{60}.

In an attempt to improve the quality of the sample, we prepared Na_3C_{60} using Fluka NaN_3 and sublimated-C_{60}, and annealed for 12 h at 200 °C. The maximum LFS intensity of this sample was rather stronger than that of Na_4C_{60} in Fig. 1. This result confirms that superconductivity is not extrinsic due to the impurity, but intrinsic because this sample is prepared with highly pure NaN_3 and C_{60}. The zero-field cooled magnetic susceptibility of Na_3C_{60} is also shown in Fig.1. The SC transition temperature (T_c) in this sample is around 10 K, which seems to be slightly lower than Na_4C_{60}. In the LFS study of Na_4C_{60} prepared with Wako NaN_3 and preheated-C_{60}, we have found the existence of two SC phases. The details of the experimental results are presented in the separate paper [6].

The LFS intensity of the sample prepared with Wako NaN_3 was preserved for long annealing at 200 °C, whereas the sample prepared with Fluka NaN_3 was quite sensitive to the annealing time and temperature. For example, we met several samples in which strong LFS almost disappeared after 1 h annealing at 400 °C or 50 h annealing at 200 °C. The elemental analysis for dried Wako NaN_3 detected hydrogen which may come from the residual water. We treated Fluka NaN_3 with water, where Fluka NaN_3 was dissolved in water and dried in vacuum at room temperature. Then we prepared Na_4C_{60} using wet Fluka NaN_3. In this sample, we could observe a strong LFS with a stability for long annealing at 200 °C. We think that water taken in the lattice plays an important role to stabilize the SC phase.

Figure 2 shows the diffraction pattern of Na_3C_{60} prepared with Wako NaN_3 and preheated-C_{60}, which were decomposed under the dynamic vacuum and annealed for 90 h at 200 °C. The powders were placed on a glass sample holder in a glove box filled with argon gas, following which the sample was covered with a Be disk and sealed with epoxy resin adhesives. Most reflections can be indexed on a face-centered-cubic (f.c.c.) lattice with a lattice parameter a=14.204(7) Å (phaseA). Another series of reflections are superimposed, which is assigned to an f.c.c. lattice

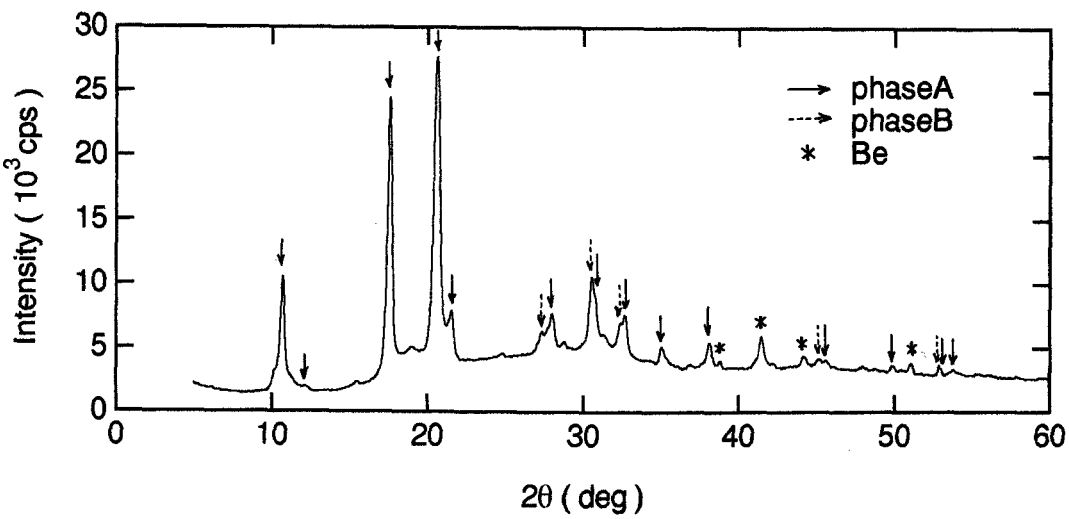

Figure 2. Powder X-ray diffraction pattern of Na_3C_{60} prepared with Wako NaN_3 and preheated-C_{60}.

of a=14.333(6) Å (phaseB). It is not clear which phase is responsible to the SC phase. According to the relationship between T_c and the lattice constant [2], phaseA will be the SC phase. The superimposed powder pattern represents that this sample is not homogeneous and the SC phase is likely to coexist with the non-SC phase.

Noteworthy is the detection of nitrogen by the elemental analysis for the sample which shows a strong LFS. The quantitative measurement of nitrogen content is very difficult, because the sample weight gradually changes due to an instability in the air. At the moment, therefore, it is not clear on the chemical formula of this new SC phase. Judging from the fact that the samples with x=3 or 4 show good LFS and SQUID signal, this SC phase will be expressed by $Na_xN_yC_{60}$ where x is between 3 and 4, and y is unknown. We also do not know what kind of sodium-nitrogen compounds such as NaN, Na_2N, Na_3N, NaN_2 *etc.* are intercalated on the octahedral site in the C_{60} lattice. We suppose that N_2Na^+ ion will be intercalated taking into account the following considerations: (1) In the sample prepared with pure Fluka NaN_3, the disappearance of strong LFS after high-temperature annealing may be caused by a dissociation as $Na^+ + N_2\uparrow$. (2) The stability of the sample prepared with Wako NaN_3 including water may result from an effect that water molecules surrounding Na^+ ion protect from the dissociation of nitrogen molecule.

All of samples decomposed in the sealed ESR tube did not show any LFS, which means that it is important to decompose under the dynamic vacuum to get the SC $Na_xN_yC_{60}$. The moderate amount of nitrogen will contribute to create the SC phase.

Furthermore we have a preliminary result that Na_9C_{60} shows fairly strong LFS, which suggests a presence of another SC phase with a different structure. The detailed characterization is in progress.

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