Molecular dynamics and structural phase transition in C\textsubscript{60} nanowhiskers

Hideaki Kitazawa, Kenjiro Hashi, Tuexun Wuernisha, Kayoko Hotta, Cherry L. Ringor, Takao Furubayashi, Atsushi Goto, Tadashi Shimizu, and Kun'ichi Miyazawa

National Institute for Materials Science, Tsukuba, Ibaraki, 305-0047, Japan

E-mail: KITAZAWA.Hideaki@nims.go.jp

Abstract. Nanowhiskers of C\textsubscript{60} (C\textsubscript{60} NWs) have been formed by a liquid-liquid interfacial precipitation method which uses an interface of the concentrated toluene solution of C\textsubscript{60}/2-propanol. In order to study the motion of C\textsubscript{60} molecules in nanowhiskers, we have performed measurements of low-temperature X-ray diffraction, magnetic susceptibility, specific heat and \textsuperscript{13}C-NMR for C\textsubscript{60} NWs. The temperature dependence of lattice constant for C\textsubscript{60} NWs is in good agreement with that for pristine C\textsubscript{60} powder, which demonstrates the large discontinuity at \(T_c \sim 265\) K caused by the structural phase transition. However, the temperature dependence of magnetic susceptibility for C\textsubscript{60} NWs exhibits a faint anomaly at \(T_c\). The temperature dependence of specific heat for C\textsubscript{60} NWs shows two small anomalies at 232 K and 254 K. High resolution \textsuperscript{13}C-NMR measurements of the C\textsubscript{60} NWs indicate that both of toluene and 2-propanol molecules interact with the C\textsubscript{60} NW molecules in the suspension and the precipitate states obtained from the LLIP method. The broader linewidth of \textsuperscript{13}C-NMR in the dried C\textsubscript{60} NWs compared with that in the pristine C\textsubscript{60} powder indicates that the slower molecular reorientation in the dried C\textsubscript{60} NWs compared with that in the pristine C\textsubscript{60} powder. Since a rapid rotation of C\textsubscript{60} molecules could be directly detected by \textsuperscript{13}C-NMR, polymer formation between C\textsubscript{60} molecules is unlikely in C\textsubscript{60} NWs at room temperature.

1. Introduction

Fullerene C\textsubscript{60} nanowhiskers (C\textsubscript{60} NWs) have been easily formed by a liquid-liquid interfacial precipitation (LLIP) method [1]. When 2-propanol (isopropyl alcohol) is gently added to a toluene solution saturated with C\textsubscript{60}, fibrous fullerene single crystals with diameters as small as submicrons were precipitated at the interface between solutions. The initial TEM experiments suggested the existence of polymerization between C\textsubscript{60} molecules along the growth axis [1]. However, subsequent X-ray diffraction (XRD) measurements revealed that the first precipitated crystals from the liquid phase have solvated structures with a hexagonal structure [2]. After the evaporation of solvent molecules in air, the structure rapidly changed into a face centered cubic (fcc) structure like a C\textsubscript{60} solid. Since the Raman spectroscopic study revealed the photochemical polymerization [3], the irradiation of electron beam may affect the change of interaction between C\textsubscript{60} molecules. Thus there is still uncertainty for the crystal structure of C\textsubscript{60} NWs under the various experimental conditions. It is well known that the solid C\textsubscript{60} undergoes an orientational ordering transition at \(T_c \sim 260\) K. The phase transition is from nearly free rotating state of the molecules forming the fcc structure (space group...
to a phase wherein the molecules undergo only a ratchet type of correlated rotation about <111> directions of simple cubic (sc) structure (space group Pa3) [4, 5]. If the polymerization between C₆₀ molecules occurs in C₆₀ NWs, some dynamics such as a rotation of C₆₀ molecules observed above $T_c$ and structural phase transition at $T_c$ should be affected in C₆₀ NWs. Since the ordering transition has been investigated with a wide range of techniques such as X-ray [4], neutron diffraction [6], NMR [5], and specific heat [7] etc., it is worthwhile understanding the dynamics of C₆₀ molecules in C₆₀ NWs by means of several kinds of techniques. We have performed measurements of low-temperature XRD, magnetic susceptibility, specific heat and $^{13}$C-NMR for C₆₀ NWs to obtain the information of C₆₀ dynamics in C₆₀ NWs.

2. Experimental procedures

The C₆₀ NWs (dried C₆₀ NWs in air) were prepared by the above mentioned LLIP method from pristine C₆₀ powder (99.5%, MTR Ltd.). In order to determine the temperature dependence of lattice constants the powder XRD experiments were performed by using a Rigaku diffractometer (CuKα radiation) with a low-temperature option. The powder samples were mixed with a standard Si material (NIST SRM 640b) to obtain the more precise lattice constants. All the peaks below $2\theta = 35^\circ$ were well indexed by the fcc crystal symmetry of the solid C₆₀ except for small unknown peaks which may come from the remaining phases with solvated structure or other foreign phases. Each lattice constant $a$ of C₆₀ NWs and pristine C₆₀ powder was estimated from the some assigned peaks below $2\theta = 35^\circ$. The DC magnetic susceptibility $\chi(T)$ was measured in a magnetic field of 0.1T and 3 T for temperatures from 1.9 to 300 K by using a SQUID magnetometer (Quantum Design Co., Ltd.). The specific heat measurements were performed between 4 K and room temperature for pressed C₆₀ NWs and pristine C₆₀ powder with the relaxation method by a PPMS instrument (Quantum Design Co., Ltd). In order to investigate the interaction between solvent and C₆₀ NW, NMR measurements were performed at 11.7 T (125.8 MHz for $^{13}$C) using a JEOL ECA500 spectrometer. A 4 mm sample tube was used for a magic-angle-spinning (MAS) NMR measurement. Fourier transformed (FT) NMR spectra were obtained from free-induction-decay (FID) signals following a $\pi/2$ pulse of 2.4 μs. All NMR experiments were performed at room temperature. We have prepared three C₆₀ NW samples for NMR experiments: suspension C₆₀ NWs obtained by the LLIP method [1]; precipitate C₆₀ NWs; and dried C₆₀ NWs. The suspension C₆₀ NW sample was packed in a glass tube with 4 mm diameter for NMR measurements. The precipitate C₆₀ NWs were obtained from the suspension C₆₀ NWs by centrifugation. Both of the suspension and the precipitate C₆₀ NWs contain toluene and 2-propanol as solvent, while the dried C₆₀ NWs contain no solvent.

3. Results and discussion

3.1. Low-temperature XRD

Figure 1 shows XRD patterns near the 220 peak of C₆₀ NWs as a function of temperature. The peak position for the 220 reflection shifts largely between 260 K and 270 K. Figure 2 shows the temperature dependence of lattice constants for C₆₀ NWs and pristine C₆₀ powder. Both curves demonstrate large discontinuities at ca. 265 K which correspond to the structural phase transition at $T_c \sim 260$ K from the sc structure at low temperatures to the fcc structure at high temperatures [4]. Both curves are almost the same within the present experimental error bar. Overall temperature evolutions of lattice constants for both samples are in good agreement with the result determined from neutron diffraction [6] except for the anomaly at $T_{sg} \sim 90$ K which corresponds to the frozen rotation motion.

3.2. Magnetic susceptibility

Figure 3 shows the temperature dependence of magnetic susceptibility $\chi(T)$ for C₆₀ NWs and pristine C₆₀ powder. A clear step-like transition at 260 K was observed in the pristine C₆₀ powder as shown in
Figure 1. 220 peak in the XRD pattern of C_{60} NWs as a function of temperature. Each pattern is vertically shifted by +200 cps without overlapping.

the inset of figure 3. This susceptibility discontinuity is attributed to the change in the intramolecular geometry at orientational order-disorder transition [8]. On the other hand, the discontinuity is very tiny but visible in the C_{60} NWs. This reduction of anomaly at 260 K suggests that the structural phase transition is incomplete or short-range in the C_{60} NWs below T_c. The overall field-cooled \( \chi(T) \) curves of the C_{60} NWs and pristine C_{60} powder can be well fitted by the Curie-Weiss law \( \chi(T) = C/(T - \theta_p) + \chi_0 \) by the solid curves in figure 3. The \( C, \theta_p \), and \( \chi_0 \) is the Curie constant, \( Np_{\text{eff}}^2/3k_B \), the paramagnetic Curie temperature, and temperature-independent term, respectively, where \( N, p_{\text{eff}}, \) and \( k_B \) is a number of magnetic moments, the effective moment, and the Boltzmann constant. If the spin amplitude of magnetic moment is assumed to be 1/2, the number of magnetic moments corresponds to 1.20 % and 0.693 % in a unit cell for C_{60} NWs and pristine C_{60} powder, respectively. The estimated magnetic moments may originate from any magnetic impurity. The obtained parameters are listed in Table 1. The \( \chi(T) \) curves of pristine C_{60} powder below ca. 100 K depends on between zero-field-cooled (ZFC) and field-cooled (FC) processes, but the \( \chi(T) \) curve of C_{60} NWs does not exhibit such a hysteresis. The hysteresis can be explained in terms of a transition into a frozen magnetic glass state below \( T_{sg} \sim 90 \) K [9].

Table 1. Magnetic parameters of C_{60} NWs and pristine C_{60} powder.

|        | m (mg) | \( \chi_0 \) (emu/mol) | C (emu/molK) | \( \theta_p \) (K) | \( N \) / mol | \( N \) (%) / unit cell |
|--------|--------|-------------------------|--------------|-------------------|--------------|-------------------------|
| C_{60} NWs | 27.3   | -1.521(6) \times 10^{-3} | 4.51(2) \times 10^{-3} | -1.61(2) | 7.24 \times 10^{21} | 1.20 |
| pristine C_{60} | 38.0   | -1.154(4) \times 10^{-3} | 2.60(2) \times 10^{-3} | -1.61(2) | 4.17 \times 10^{21} | 0.693 |
3.3. Specific heat
Figure 4 shows the temperature dependence of specific heat for pressed C\textsubscript{60} NWs and pristine C\textsubscript{60} powder. A large peak at 254 K in the pressed pristine C\textsubscript{60} powder must be caused by this structural phase transition [7]. The single anomaly observed in the pressed pristine C\textsubscript{60} splits into two small anomalies in the pressed C\textsubscript{60} NWs at 254 K and 232 K. The former anomaly at 254 K is smaller than that for pressed pristine C\textsubscript{60} powder. The latter anomaly at 232 K is not observed in the pressed pristine C\textsubscript{60} powder. This splitting of anomaly at 254 K in the pressed pristine C\textsubscript{60} powder is a strong evidence of suppression of the structural phase transition in C\textsubscript{60} NWs. The specific heat in pressed C\textsubscript{60} NWs starts to deviate from 6 K to higher temperature. This means that the entropy in pressed C\textsubscript{60} NWs is reduced up to room temperature as compared with that in pressed pristine C\textsubscript{60} powder.

3.4. NMR
Figure 5 shows the NMR spectra for the suspension of C\textsubscript{60} NWs with and without a proton decoupling. The proton decoupling was performed by the WALTZ pulse sequence. A peak at 143 ppm comes from the C\textsubscript{60}NWs and the remaining peaks come from toluene. The splits of the toluene peaks due to the J coupling with protons were eliminated by the proton decoupling. It is interesting that the peak of C\textsubscript{60}NWs is also affected by the proton decoupling. This indicates that the protons of the solvent exist near the C\textsubscript{60} NW and the C\textsubscript{60} NW interacts with the proton of the solvent. It seems that the linewidth of the C\textsubscript{60} NW peak without the proton decoupling, originates from dipole fields of the proton, because MAS-NMR spectrum of C\textsubscript{60} NW (not shown) has a narrow single peak. The narrowing of the linewidth of C\textsubscript{60} NW peak by the proton decoupling is caused by partial decoupling of the dipole field of the proton with the WALTZ pulse sequence.

To clarify the effect of the interaction between the C\textsubscript{60} NW and solvent on NMR spectra, NMR measurements were performed on the precipitate sample. Figure 6 shows the proton decoupled NMR spectra of the suspension and the precipitate C\textsubscript{60} NWs. All peaks of toluene and 2-propanol in the
precipitate sample were broadened compared with the corresponding peaks of the suspension sample. This means that both of toluene and 2-propanol molecules cannot reorient freely in the precipitate state. It seems that both of toluene and 2-propanol molecules are bound by C\textsubscript{60} NW in the precipitate sample.

Figure 5. NMR spectra of the suspension of C\textsubscript{60} NWs at 11.7 T with and without the proton decoupling. The proton decoupling was performed by the WALTZ pulse sequence.

Figure 6. Proton decoupled NMR spectra of the suspension and the precipitate C\textsubscript{60} NWs at 11.7 T. The proton decoupling was performed by the WALTZ pulse sequence.

Figure 7. Proton decoupled NMR spectra of the dried C\textsubscript{60} NWs and pristine C\textsubscript{60} powder at 11.7 T. No signal of solvent was observed for the dried C\textsubscript{60} NWs.

The peak of the C\textsubscript{60} NWs in the precipitate sample is also broader than that in the suspension sample. This indicates that the dipole field from the protons of the solvent in the precipitate sample is larger than that in the suspension sample. It seems that, however, there is another reason for the broadening. The NMR spectra of the dried C\textsubscript{60} NWs and pristine C\textsubscript{60} powder show a single peak at 143 ppm as shown in figure 7. The linewidth of the dried C\textsubscript{60} NWs is larger than that of pristine C\textsubscript{60} powder. Both of the linewidth of the dried C\textsubscript{60} NWs and the pristine C\textsubscript{60} powder are not affected by the proton decoupling, because there is no solvent in the samples. It seems that the difference of the linewidth between the dried C\textsubscript{60} NWs and the pristine C\textsubscript{60} powder comes from the difference in the molecular dynamics. Rapid and isotropical reorientation of the pristine C\textsubscript{60} molecules averages out the chemical shift anisotropy (CSA) at room temperature [5]. The CSA powder pattern is recovered gradually with decreasing temperature, because the molecular reorientation becomes slower with decreasing temperature. It seems that a slower molecular reorientation of the dried C\textsubscript{60} NWs is responsible for the broader linewidth of the dried C\textsubscript{60} NWs compared with the pristine C\textsubscript{60} powder. The difference of the molecular dynamics between the dried C\textsubscript{60} NWs and the pristine C\textsubscript{60} powder also...
affects the spin-lattice relaxation time $T_1$. The $T_1$ for the dried C$_{60}$ NWs is about 18 s, while that for the pristine C$_{60}$ powder is 38 s. Since a rapid rotation of C$_{60}$ molecules could be directly detected by $^{13}$C-NMR, polymer formation between C$_{60}$ molecules is unlikely at room temperature. Measurements of the temperature dependence of the relaxation time $T_1$ for the dried C$_{60}$ NWs is required for more detailed discussion of the molecular dynamics.

4. Conclusion
The present research can be summarized as follows. The low-temperature XRD of C$_{60}$ NWs measurements revealed the existence of the structural phase transition at $T_c \sim 255$ K from the sc structure at low temperatures to the fcc structure. However, the strong suppression of anomalies in the magnetic susceptibility and the specific heat of C$_{60}$ NWs at $T_c$ suggest the above-mentioned phase transition is incomplete or short-range. High resolution $^{13}$C-NMR measurements of the C$_{60}$ NWs indicate that both of toluene and 2-propanol molecules interact with the C$_{60}$ NW molecules in the suspension and the precipitate states obtained from the LLIP method. The broader linewidth of the dried C$_{60}$ NW compared with that of the pristine C$_{60}$ powder indicates that the slower molecular reorientation in the dried C$_{60}$ NW compared with that in the pristine C$_{60}$ powder. Thus, judging from the degree of peak width in C$_{60}$ NW, the formation of polymerization must be not realized in room temperature. The polymerization between C$_{60}$ molecules along the growth axis suggested by the TEM observation [1] may be the consequence of the electron beam irradiation.

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