Physical properties of C$_{60}$ intercalated graphite films

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Abstract. Recently, Miura and Tsuda have synthesized C$_{60}$ intercalated graphite film (C$_{60}$/Gr) and reported that the C$_{60}$/Gr consists of alternating close-packed C$_{60}$ monolayers and graphite layers. They also found that its frictional force is minimal up to the loading force of 100 nN using AFM. [Miura K and Tsuda D 2005 e-J. Surf. Sci. Nanotech. 3 21]

Thus, we have started to study the physical properties of C$_{60}$/Gr and carried out NMR, Raman scattering and specific heat measurements. These results suggest that C$_{60}$ in C$_{60}$/Gr rotates at room temperature.

1. Introduction
Molecular bearing has been an attractive subject of nanotribology, and C$_{60}$ molecule is one of the candidates. Recently, Miura and Tsuda have synthesized C$_{60}$ intercalated graphite film (C$_{60}$/Gr) and found that C$_{60}$/Gr shows superlubricity. They reported that its frictional force is minimal up to the loading force of 100 nN using AFM. [1]

C$_{60}$ crystal has drawn interest as a novel molecular solid, because the molecular unit is so large and symmetric. It is known that C$_{60}$ crystal shows a structural phase transition at around 250 K, and above this temperature, C$_{60}$ molecule obtains the modes of rotation, in addition to six modes of movement (three translations and three librations). [2] It is important to examine the motional state of C$_{60}$ in C$_{60}$/Gr, in order to interpret the superlubricity of this material. Thus, we have started to study the physical properties of C$_{60}$/Gr and carried out NMR, Raman scattering and specific heat measurements.

2. Experimental
2.1. Sample preparation of C$_{60}$ intercalated graphite film
C$_{60}$/Gr were prepared according to the literature.[3-5] Small pieces of graphite (highly oriented pyrolytic graphite: HOPG) were first expanded by the reaction mixture of concentrated sulfuric acid and nitric acid. Then, C$_{60}$ and expanded graphite were enclosed in a vacuum-sealed quartz tube and were placed in a furnace at 600°C for 15 days. The weight ratio of C$_{60}$ in C$_{60}$/Gr is about 40%.
2.2. Experimental procedure

We have carried out NMR, Raman scattering and specific heat measurements for C\textsubscript{60}/Gr. The details of the experimental procedure are described below.

For magic angle spinning (MAS) NMR measurements, C\textsubscript{60}/Gr was mixed with Na\textsubscript{2}SO\textsubscript{4} in a weight ratio of 1:50 to avoid arcing in a NMR probe. The mixture was put into a rotor made of silicon nitride, and was set in the direction of MAS, 54.74° with respect to a static magnetic field. The MAS NMR experiments were performed at 75.431 MHz for \textsuperscript{13}C, by pulse inversion recovery method. The MAS NMR spectra were recorded on a homebuilt 7.1 T spectrometer with a Tecmag Apollo spectrometer and a Doty SuperSonic MAS 7 mm probehead. The MAS NMR experiments were performed at room temperature. To elucidate the effect of rotation of C\textsubscript{60}, these spectra were recorded at a sample spinning speed of 3.8 kHz and in the stationary state.

Raman spectra were measured using the micro Raman system with the CCD camera cooled by liquid N\textsubscript{2}. The resolution of the spectrometer was about 24 cm\textsuperscript{-1}. 5154 Å line of an Ar\textsuperscript{+} laser was used for excitation. The laser power was kept less than 10 mW. The incident laser was focused by the objective lens (x40).

The specific heat was measured using the Quantum Design physical property measurement system (PPMS). For the measurements, C\textsubscript{60}/Gr was mixed with Ag powder in a weight ratio of about 1:1 for a good thermal contact, and a pellet was prepared by pressing together and heating in hydrogen atmosphere at 200 °C for 2 h. The mass of the pellet was 15 mg. It was glued onto the platform of the calorimeter by Apiezon grease. The measurements were performed in the temperature range between 2 and 300 K, using a relaxation method within the accuracy of 1.2%. The heat capacity of the thermometers, heater, platform and Apiezon grease (known as the addenda) were measured before depositing the pellet. This addenda was then subtracted from the subsequently measured total heat capacity, which includes the pellet. The heat capacity of the pellet accounts for 35-75% of the total heat capacity.

3. Results and discussion

The NMR measurements was performed at the room temperature. Figure 1 shows the MAS NMR spectra, together with that of the specimen in the stationary state. In the MAS NMR spectra, a broad resonance line of 108 ppm corresponds to a background, and a sharp resonance line of 140 ppm corresponds to C\textsubscript{60} in C\textsubscript{60}/Gr. The resonance line width (7.5 ppm) of 140 ppm becomes four times wider in the stationary state than the width (1.8 ppm) under the sample spinning condition. This indicates that there exists the anisotropic rotational motion. However, even in the stationary state, the line width of the NMR spectra is rather sharp compared with that of the powder pattern of the C\textsubscript{60} at low temperature, where C\textsubscript{60} crystals order orientationally.[2] These results indicate that the rotational motion of C\textsubscript{60} intercalated into

![Figure 1. MAS NMR spectra of C\textsubscript{60}/Gr at the sample spinning speed of 3.8 kHz, together with those of the specimen in the stationary state.](image-url)
graphite, is obviously free at the room temperature.

At room temperature, we measured Raman spectra to examine the effect of the rotational motion of C$_{60}$ in C$_{60}$/Gr. The obtained Raman spectra are shown in Fig. 2. Two peaks of 1467 cm$^{-1}$ and 1595 cm$^{-1}$ are clearly observed, and they are assigned to A$_g$ and H$_g$ of C$_{60}$.[6] Full linewidths at half maximum of A$_g$ and H$_g$ modes are 24 cm$^{-1}$ and 48 cm$^{-1}$, respectively. For C$_{60}$ crystal at room temperature, the broadening of H$_g$ mode caused by the effect of the rotation has been reported.[6] The broad linewidth of H$_g$ mode in the present experiment can be attributed to the rotation.

![Raman spectra of C$_{60}$/Gr at room temperature.](image)

Figure 2. Raman spectra of C$_{60}$/Gr at room temperature.

Figure 3 shows the specific heat of C$_{60}$/Gr as a function of temperature. The data shown in the figure contains the heat capacity of graphite, which increases monotonously with increasing temperature.[7] The ratio of graphite heat capacity in C$_{60}$/Gr is estimated as about 80% of the total heat capacity at 300 K. It was found that the specific heat of C$_{60}$ in C$_{60}$/Gr increases with increasing temperature and its slope becomes a little slow as the temperature approaches about 100 K.

![Specific heat of C$_{60}$/Gr as a function of temperature.](image)

Figure 3. Specific heat of C$_{60}$/Gr as a function of temperature.

It was found that the specific heat at 100 K is much larger than that of 6(N/60)$k_B$, which comes from the Dulong-Petit law for C$_{60}$ molecules with six modes (three translational and three librational). Above around 100 K, the specific heat increases more rapidly than below this temperature, and a broad peak at around 250 K was observed. It is well known that the specific heat of C$_{60}$ crystal has a peak at about 260 K, which is understood as the anomaly associated with the orientational melting transition.[8] The peak of C$_{60}$ in C$_{60}$/Gr indicates the change in the rotational motion of C$_{60}$. The rotational motion of C$_{60}$ is supposed to be more free above the peak temperature than below. The results are consistent with those of NMR and Raman scattering, which supports the rotational motion of C$_{60}$ in C$_{60}$/Gr at room temperature.
4. References

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