Annealing effects on the magnetic and structural properties of single-crystal TDAE-C-60

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Annealing effects on the magnetic and structural properties of single-crystal TDAE-C₆₀

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Annealing effects on the magnetic and structural properties of single-crystal TDAE-C₆₀ are investigated. When a crystal is well-annealed at 350 K, ferromagnetic ordering takes place below 16 K, though no magnetic phase transition is shown in as-grown crystal. The saturated magnetization was obtained to be 0.9±0.1μB per C₆₀. It was first found that the well-annealed crystal shows a structural phase transition around 180 K, probably associated with the orientational ordering of C₆₀ molecules. On the other hand, the as-grown crystal undergoes no structural phase transition at least down to 30 K while the motion of C₆₀ molecules is restricted below around 150 K. The possible relation between the low-temperature structure and the magnetic ordering is discussed.

The origin of the magnetic phase transition in TDAE-C₆₀ has attracted significant attention. Although extensive studies have been carried out using powder samples,¹ the ground state of this salt has not been settled. Recently, Blinc et al. succeeded in synthesizing single crystals² and observed ferromagnetic resonance with an extremely small anisotropy field.³ They also reported⁴,⁵ that the ferromagnetic behavior was not observed unless the sample was well annealed above room temperature. While the ground state below Tc is settled to be ferromagnet, both the annealing effects on the magnetic property and the microscopic origin of the ferromagnetic interactions in TDAE-C₆₀ have remained as the subject of discussion. This ferromagnetic transition of 16 K is the highest among organic materials; therefore, the understanding of its mechanism is highly desirable. In this paper, we report effects of the annealing treatment on the magnetic and structural properties of single-crystal TDAE-C₆₀.

Single crystals were prepared by directly mixing C₆₀ solution in toluene with TDAE under a high-purity N₂ gas condition. The solution was held in an incubator, whose temperature was kept about 27 °C, for two weeks. The typical size of the obtained crystal was about 1×0.5×0.5 mm³. Since the present salts are unstable in air, the single crystals were put into a quartz capillary tube with He gas in order to prevent sample degradation.

At first, we selected the as-grown single crystals without twin boundary using x-ray imaging plate diffractometer Rigaku R-AXISIV. Then, we measured the magnetization of the as-grown crystal using the MPMS2 superconducting quantum interference device (SQUID) magnetometer. The crystal was annealed in this magnetometer at 350 K for 30 min and its magnetization was successively measured. We repeated this annealing procedure until its ferromagnetic magnetization below 16 K became independent of both temperature and magnetic field. After this annealing procedure, we checked the quality of the crystal at room temperature using x-ray. For low-temperature x-ray measurements of the as-grown crystals, the Huber four circle diffractometer 5042 with a monochromatized Mo Kα x-ray beam (54 kV, 200 mA) and the Air Product DE201 cryocooler were used. For low-temperature x-ray measurements of the well-annealed crystals, a homemade rotatable x-ray camera with a focused Mo Kα x-ray beam (55 kV, 35 mA) and the Iwatani gas 501 cryocooler were used. The single crystal was mounted on the sample holder so as to rotate around the c axis. Electron spin resonance (ESR) measurements were performed at X band using the Bruker ESP300e spectrometer equipped with the Oxford ESR910 continuous flow cryostat. We measured the temperature variations of ESR parameters (spin susceptibility, linewidth, and g factor) of as-grown and well-annealed single crystals.

Figure 1 shows the magnetization process of a single crystal at 5 K. The sample was cooled under zero-field conditions. For as-grown crystals, the susceptibility is Curie-like and no magnetic phase transition was detected below 5 K. When a crystal is first annealed, a ferromagnetic moment appears below around 16 K. In addition, the ferromagnetic component is enhanced with the passage of the annealing time and finally saturates. The time that is required for satu-

![FIG. 1. Magnetization process of single-crystal TDAE-C₆₀ at 5 K. The open and closed circles denote the results for the as-grown and the well-annealed crystals, respectively. The inset shows the temperature dependence of magnetization for the well-annealed crystal.](Image)
unpaired spins are on each C$_{60}$ molecule, the unpaired spin value even if the crystal is annealed. The x which is consistent with the previous result. 2 The temperature variation in the single crystal is significantly higher than those of saturated magnetization. Note that this saturated magnetization is about 180 min for the samples used. (However, this value is not so meaningful because it probably depends on the sample mass.) Assuming that all unpaired spins are on each C$_{60}$ molecule, the unpaired spin per C$_{60}$ is estimated to be 0.9±0.1µ$_B$ from the magnitude of saturated magnetization. Note that this saturated magnetization in the single crystal is significantly higher than those of 0.3µ$_B$ in the powder annealed samples in the previous report. 6 The temperature dependence of the magnetization for the well-annealed crystal is shown in the inset of Fig. 1. The ferromagnetic phase transition occurs around $T_c$ = 16 K, which is consistent with the previous result. 2

The temperature variations of the ESR parameters above $T_c$ are shown in Fig. 2. For both as-grown and well-annealed crystals, the ESR line shape at room temperature corresponds neither to a Lorentzian nor a Gaussian, but the shape transforms to a Lorentzian below 150–170 K. The spin susceptibility, $\chi_{\text{spin}}$, at room temperature remains at almost the same value even if the crystal is annealed. The $\chi_{\text{spin}}$ for both cases exhibit Curie-like behavior in the whole temperature range with the same Curie constant. Thus, the amount of spin density, i.e., the amount of charge transfer from C$_{60}$ to TDAE, is not affected by annealing. Our preliminary Raman-scattering measurements support this result. We observed $A_1g(2)$ mode among C$_{60}$ intermolecular vibrational modes located at 1463 cm$^{-1}$ for both cases. Using the linear relation between its frequency and the ionicity of C$_{60}$ molecules, 7 C$_{60}$ molecules are considered to be monovalent. This value corresponds well to the results by magnetization and ESR measurements. Remarkable annealing effects were observed both for g factors and for linewidths ($\Delta H_{pp}$) [see Fig. 2(b) and (c)]. In the case of as-grown crystals, $\Delta H_{pp}$ and g factors remain constant above 150 K for all directions. For $T < 150$ K, $\Delta H_{pp}$ exhibits a sharp jump around 150 K with a hysteresis behavior and then the g factors begin to decrease below this temperature. In contrast, for a well-annealed one, $\Delta H_{pp}$ decreases gradually from room temperature to 20 K with cooling and has no jump around 150 K. The g factor in this case is almost independent of temperature through 150 K. Below 50 K, the steep increases of g factors for both cases are probably due to the demagnetization originated in the shape of crystals.

Let us focus on the structural property of as-grown crystals. We investigated the space-group symmetry of as-grown crystals through the extinction rule of Bragg reflection. No substantial peak more than $10^{-4}$ times of the Bragg intensity were observed at the indices as follows: hkl: $h+k=2n+1$, h0l: $h+k=2n+1$, h0l: $h=2n+1$ or $l=2n+1$, 0kl: $k=2n+1$, h00: $h=2n+1$, 0k0: $k=2n+1$, 00l: $l=2n+1$, both at 30 K and 297 K. These results clearly show that the space group remains C2/c and no structural phase transition occurs. The tight-binding calculation indicates that C$_{60}$-1 deform from the I$_h$ state to the D$_{3d}$, D$_{5d}$, and D$_{2h}$ states due to the Jahn-Teller effect. 8 The thermal transition between these states is usually called a pseudorotation, because each state corresponds to one of different orientations of the C$_{60}$-1 molecule. NMR measurements in well-annealed crystals indicate that this pseudorotation begins to freeze out below 170 K$^2$. For as-grown crystals, the intensities of (−6,4,2) and (3,5,7) Bragg reflections show abrupt decreases above 150 K with heating (see Fig. 3). These Bragg reflections have large diffraction angles; therefore, their intensities are dependent on temperature factors, i.e., the mag-

FIG. 3. Temperature variations of (−6,4,2) and (3,5,7) Bragg reflection intensities for the as-grown single-crystal TDAE-C$_{60}$.

![FIG. 3. Temperature variations of (−6,4,2) and (3,5,7) Bragg reflection intensities for the as-grown single-crystal TDAE-C$_{60}$.

<table>
<thead>
<tr>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-grown</td>
<td>15.90(2)</td>
<td>13.07(2)</td>
<td>20.14(4)</td>
</tr>
<tr>
<td>well-annealed</td>
<td>15.82(5)</td>
<td>13.00(2)</td>
<td>19.93(5)</td>
</tr>
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</table>

TABLE I. Change of lattice parameters at room temperature.
The orientations of the C\(_60\) molecules are alternately ordered along the nearest (c axis) and next-nearest (a + b direction) neighbors. This orbital ordering structure is one of the models of the ferromagnetic interactions between C\(_60\) molecules.\(^{10}\)

Finally, we discuss the relation between the magnetic ordering and the orientational ordering of C\(_60\) molecules. This coupling was also suggested by the high magnetic-field measurement.\(^{11}\) In the as-grown crystal, there is no structural phase transition, and C\(_60\) freezes in glassy state without the orientational order. The large hysteresis observed in the ESR linewidth seems to correspond to this orientational glass transition. The orientational disorder leads to the distribution of exchange interactions between molecules, resulting in no magnetic phase transition or in spin-glass behavior. On the other hand, in the well-annealed crystal, the second-order structural phase transition exists. The orientational order gradually grows below this temperature, and it is reflected in the continuous decrease of the ESR linewidth. As a result, the exchange interactions will become uniform and then the long-range ferromagnetic ordering occurs at \(T_c\).

In summary, we found that the well-annealed TDAE-C\(_{60}\), which has \(T_c = 16\) K, shows the structural phase transition around 180 K, probably associated with the orientational ordering of the C\(_60\) molecules. On the other hand, the as-grown crystal undergoes no structural phase transition at least down to 30 K, and possibly has the orientational disorder of the C\(_60\) molecules below 150 K. It is necessary to consider the ferromagnetic interactions in accordance with the low-temperature structure. We plan to examine the low-temperature x-ray measurements in well-annealed crystals.

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