

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 $0.9 \pm 0.1 \mu_B$ 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 reported^{4,5} that the ferromagnetic behavior was not observed unless the sample was well annealed above room temperature. While the ground state below T_c 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 $1 \times 0.5 \times 0.5$ 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 $K\alpha$ 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 $K\alpha$ 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-

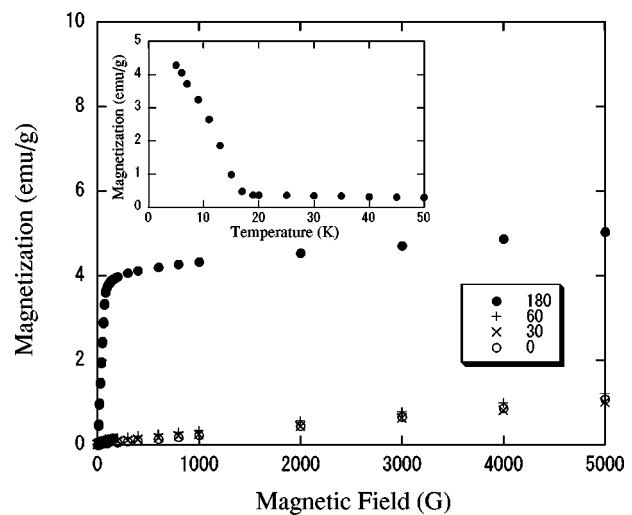


FIG. 1. Magnetization process of single-crystal TDAE-C₆₀ at 5 K. The open and closed circles denote the results for the as-grown and the well-annealed crystals, respectively. The inset shows the temperature dependence of magnetization for the well-annealed crystal.

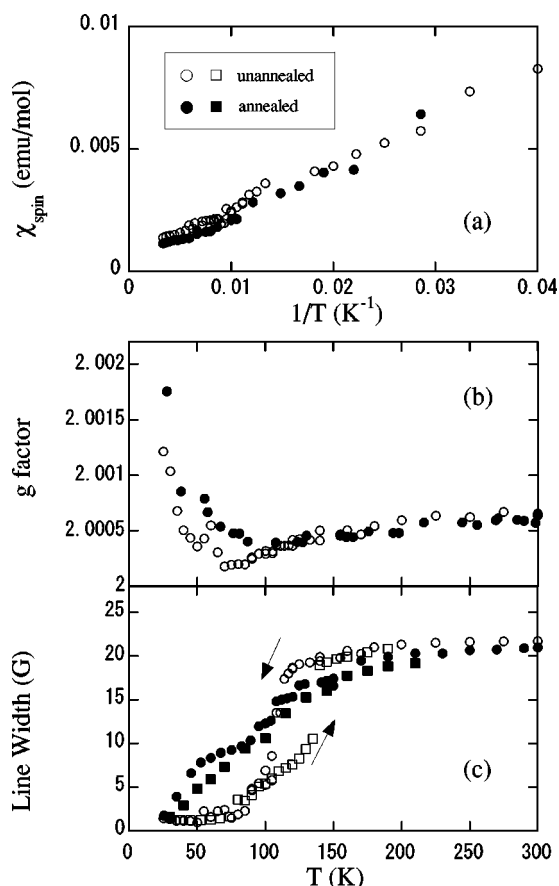


FIG. 2. Temperature variations of ESR parameters [(a) χ_{spin} , (b) g factor, and (c) ΔH_{pp}] of single-crystal TDAE- C_{60} . The open and closed circles denote the results for the as-grown and the well-annealed crystals, respectively. The magnetic field is applied parallel to the b axis.

rating the 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 $0.9 \pm 0.1 \mu_B$ from the magnitude of saturated magnetization. Note that this saturated magnetization in the single crystal is significantly higher than those of $0.3 \mu_B$ 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, χ_{spin} , at room temperature remains at almost the same value even if the crystal is annealed. The χ_{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 $A_g(2)$ mode among C_{60} intermolecular vibrational modes located at 1463 cm^{-1} for both cases. Using the linear relation between

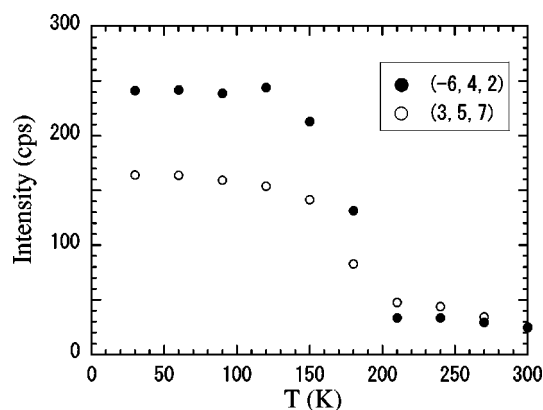


FIG. 3. Temperature variations of $(-6, 4, 2)$ and $(3, 5, 7)$ Bragg reflection intensities for the as-grown single-crystal TDAE- C_{60} .

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 (ΔH_{pp}) [see Fig. 2(b) and (c)]. In the case of as-grown crystals, ΔH_{pp} and g factors remain constant above 150 K for all directions. For $T < 150$ K, ΔH_{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, ΔH_{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 : $h+k=2n+1$, $hk0$: $h+k=2n+1$, $h0l$: $h=2n+1$ 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} deforms 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-

TABLE I. Change of lattice parameters at room temperature.

	a	b	c	β
as-grown	15.90(2)	13.07(2)	20.14(4)	93.10
well-annealed	15.82(5)	13.00(2)	19.93(5)	93.86

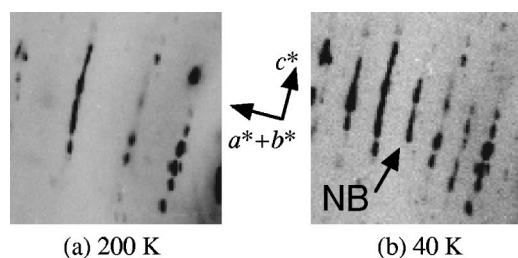


FIG. 4. X-ray photographs for the well-annealed single-crystal TDAE- C_{60} . The photos (a) and (b) are taken at 200 and 40 K, respectively.

nitude of the thermal motion of atoms and molecules. The abrupt increases in the Bragg intensities in Fig. 3 suggest the restriction of C_{60} motion below 150 K. Since C_{60} is not a perfect sphere, it is natural that the orientational ordering of C_{60} leads to a symmetry change as seen in the pure C_{60} crystal.⁹ No symmetry change in the as-grown crystals indicates that C_{60} freezes without the perfect orientational order. The ESR line shape transforms to Lorentzian with the narrowing of linewidth below the freezing temperature. It results from the fact that the magnetic exchange interaction works efficiently between the orientationally frozen C_{60} molecules, as Blinc *et al.* proposed.² The restriction of the C_{60} motion in the as-grown crystals is also reflected in the sharp decrease of the ESR linewidth below 150 K.

Next, we check the change of lattice parameters at room temperature with annealing.⁶ Table I shows an example of the change of lattice parameters. It is found that the lengths of all the crystal axes shrink after annealing. Especially remarkable is the shrinkage of the c axis, along which the C_{60} molecules are closely packed (about 1%), compared with the length before annealing. No change in the space group with annealing has been obtained. Next, we investigate the low-temperature symmetry of the well-annealed crystals. X-ray patterns for the well-annealed crystal at (a) 200 K and (b) 40 K are displayed in Fig. 4, where the reflections in the reciprocal $[a^*+b^*]c^*$ plane are shown. The intense Bragg points along the longitudinal series have even $h+k$ indices in Fig. 4(a). At 40 K, note the presence of new Bragg (NB) reflections between these series. Since these NB reflections have odd $h+k$ indices, the appearance of the NB reflection shows the structural phase transition from a C -centered lattice to a primitive lattice. An average NB reflection intensity is 0.1 times the average Bragg intensity. Figure 5 shows the typical temperature variations of the NB reflections. The smooth evolution of the NB reflection intensities with cooling indicates this phase transition is of second order. The temperature of the phase transition is around 180 K. The motion of the C_{60} molecules are continuously frozen below the same temperature range, because the ESR linewidth of the well-annealed crystals gradually decreases. Thus, the structural transition observed is probably associated with the orientational order of the C_{60} molecules. The relatively strong intensity of the NB reflections supports this idea. Since the phase transition is of second order, the space-group symmetry below 180 K will be a subgroup of $C2/c$. There are four subgroups of $P2_1/c$, $P2_1/n$, $P2_1/c$, and $P2_1/n$ with the primitive lattice. The $P2_1/n$ space-group symmetry allows that the orientations of the C_{60} molecules are alternately

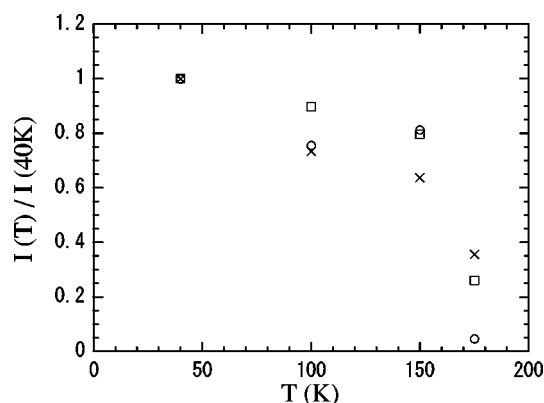


FIG. 5. Temperature variations of the normalized intensity of several new Bragg reflections for the well-annealed single-crystal TDAE- C_{60} .

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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- ¹K. Tanaka, T. Sato, K. Yoshizawa, K. Okahara, T. Yamabe, and M. Tokumoto, *Chem. Phys. Lett.* **237**, 271 (1995).
- ²R. Blinc, K. Pokhodnia, P. Cevc, D. Arčon, A. Omerzu, D. Mihailović, P. Venturini, L. Golič, Z. Trontelj, J. Lužnik, Z. Jegličič, and J. Pirnat, *Phys. Rev. Lett.* **76**, 523 (1996).
- ³D. Arčon, P. Cevc, A. Omerzu, and R. Blinc, *Phys. Rev. Lett.* **80**, 1529 (1998).
- ⁴Z. Jagličič, Z. Trontelj, J. Lužnik, J. Pirnat, and R. Blinc, *Solid State Commun.* **101**, 591 (1997).
- ⁵A. Mrzel, P. Cevc, A. Omerzu, and D. Mihailović, *Phys. Rev. B* **53**, R2922 (1996).
- ⁶T. Kambe, H. Negawa, Y. Nogami, and K. Oshima, *Synth. Met.* **103**, 2424 (1999).
- ⁷L. Barbedette, S. Lefrant, T. Yildirim, and J. E. Fischer, in *Physics and Chemistry of Fullerenes and Derivatives*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (World Scientific, London, 1995), p. 460.
- ⁸N. Koga and K. Morokuma, *Chem. Phys. Lett.* **196**, 191 (1992).
- ⁹T. Matsuo, H. Suga, W. I. F. David, R. M. Ibberson, P. Bernier, A. Zahab, C. Fabre, A. Rassat, and A. Dworkin, *Solid State Commun.* **83**, 711 (1992).
- ¹⁰T. Kawamoto, *Solid State Commun.* **101**, 231 (1996).
- ¹¹D. Mihailović, D. Arčon, P. Venturini, R. Blinc, A. Omerzu, and P. Cevc, *Science* **268**, 400 (1995).