Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B
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X-Ray Study of Phase Transition and Structure Analysis of Low Temperature Phase at 13K in C_{60} Single Crystal

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X-ray diffraction measurements in the temperature range from 300K to 14K and structure analysis at 13K were carried out using C_{60} single crystal in order to investigate the structure of low temperature phase. It was, firstly, observed that a new Bragg reflection of the (9 10 0) appeared continuously below about 160K and an anomalous behavior of the integrated intensity of this reflection was observed near 85K. Moreover, a diffuse scattering around the (2.5 2.5 2.5) reciprocal lattice point indicating the existence of a short range order $2a_0$-structure was observed below about 100K. A correlation length of this short range order $2a_0$-structure was about 130Å along the [1 1 1] direction at 16K. The structure analysis was not converged because of the existence of the twin structure and the occurrence of the anti-phase domain structure in low temperature phase.

1. INTRODUCTION

There are much interesting to the fullerenes, since the discovery of a C_{60} molecule[1] and a synthesizing method for solid C_{60}[2]. Various kinds of fullerene, e.g. C_{70}, C_{84}, carbon nanotubes, *etc.*, were found. The discovery of a superconducting state in alkali-metal-doped C_{60} compounds[3] had attracted much attention. Several studies are made to clarify the properties of these fullerenes. Solid C_{60} is a prototype of various fullerenes and many studies have been carried out both theoretically and experimentally. Regarding to the crystal structure, solid C_{60} has a face-centered-cubic (fcc) Bravais lattice at room temperature with a high degree of rotational disorder of C_{60} molecules. With decreasing temperature, solid C_{60} transformed from fcc to simple cubic (sc) Bravais lattice at about 260K. This structure phase transition was, firstly, reported by Heiney et al.[4] from the high-resolution synchrotron X-ray powder diffraction and differential scanning calorimetry. Other several studies confirmed the existence of this phase transition, but the temperature of the phase transition differed slightly for different samples, indicating the dependence of the quality of C_{60} samples. The structure of the low-temperature ordered phase was investigated by means of the profile fitting method of the X-ray[4-6] and neutron[7] powder diffraction studies. It was concluded that the space group of the low temperature ordered state was Pa3 and discussed the ordering of four independent C_{60} molecules. However, other space group of $P2_13$ at 100K was suggested from the convergent-beam electron diffraction study[8].

Further, two anomalies were observed at lower temperature regions. One anomaly was observed at about 160K from the sound velocity[9] and the dielectric measurements[10]. Another anomaly was observed at about 90K from the NMR[11], thermal expansion[12] and lattice parameter[13]. From the X-ray diffraction measurements[14], the existences of these two anomalies were, also, reported from the temperature dependence of the integrated intensity of Bragg reflection which appeared in sc structure. It was thought that these two anomalies were related to the ordering or freezing of C_{60} molecular reorientation in the solid state. Moreover, several interested informations for low temperature region were reported as follows. From the electron

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diffraction measurements[15], an occurrence of a new orientationally ordered-low temperature superstructure of $2a_0$-fcc was reported. The diffuse scattering of the streak line related to the above $2a_0$-fcc superstructure was observed by means of the X-ray diffuse scattering photograph[16]. Recently, the existence of the $2a_0$-fcc superstructure was searched by Fischer et al.[17], but not observed. They concluded that the intrinsic ground state in solid C_{60} was the simple cubic structure {space group Pa3, a(14K)=14.06Å} and that other structures might be stabilized by the defects or impurities. It is seen that the crystal structure of the low temperature order phase and the structural changes corresponding to the two anomalies at about 160K and 90K are not clear, yet. In this work, we carried out the X-ray diffraction experiments and structure analysis in order to clarify the crystal structure in the low temperature region using several C_{60} single crystals.

2. EXPERIMENTS

C_{60} single crystals were prepared by two different methods. One was prepared from carbon soot by extraction with toluene at room temperature. The C_{60} cluster purified by column chromatography[18] was dissolved in toluene. The solution of C_{60} (1-2 ml) was evaporated at about 40°C. Very small C_{60} crystals were obtained after evaporation of the solvents for 20-30 hours. Another was prepared by the sublimation method[19]. C_{60} crystals having the several size were grown, but they were not single crystal. These as-grown crystals were almost the polycrystal or had the twin structure related by the [1 1 1] twin axis.

X-ray diffraction measurements in the temperature range from 300K to 14K and structure analysis at 13K were carried out. A large χ-cradle automatic four-circle diffractometer, Rigaku AFC off-center type, was used for measuring X-ray scattering data with PG(002) monochromator and Mo-Kα X-rays obtained from 50kVx240mA source. A scintillation counter was used as a detector. The specimen temperature was controlled with ±0.05K through the use of a closed-cycle He-gas refrigerator.

3. RESULTS and DISCUSSION

3.1.X-ray diffraction study

Firstly, the lattice parameter and several reflections, which were forbidden in fcc structure, were measured as a function of temperature from 300K to 14K every 5K. The sample size was approximately 0.2x0.09x0.02 mm^3. This very small sample was not twin structure. The results were previously published in ref.20. A small jump in the lattice parameter was observed at 260K as shown Fig.3 in ref.20. Several Bragg reflections, which were forbidden in fcc structure, were appeared below 260K as shown Fig.2 in ref.20. We could not observe the hysteresis of the transition temperature because of the measurements every 5K. We carried out the re-examination of the lattice parameter and the several reflections, which were forbidden in fcc structure, every 0.5K near transition temperature used another small C_{60} sample. The hysteresis of the transition temperature was clearly observed in both the lattice parameter and the integrated intensity as shown in Fig.1. The value of the hysteresis was about 1K. This value consisted with the results of Moret et al.[14], but was slightly smaller than that by Fischer et al.[17]. The transition temperature was slightly different with the previous

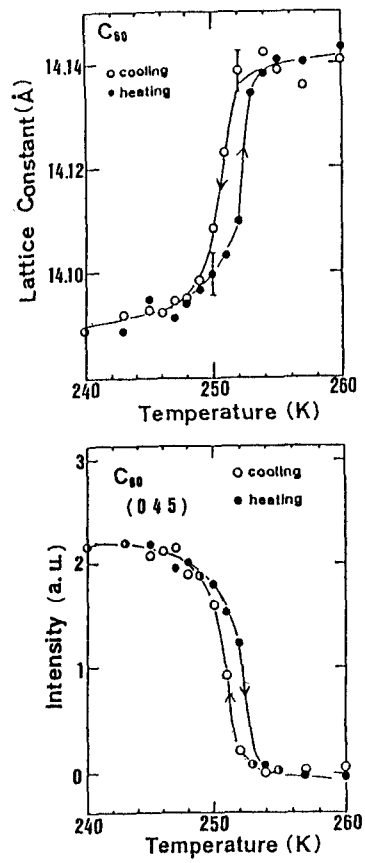

Fig. 1 Temperature dependences of the lattice constant and the integrated intensity of the (0 4 5) reflection near the transition temperature. The hysteresis of the transition temperature is about 1K.

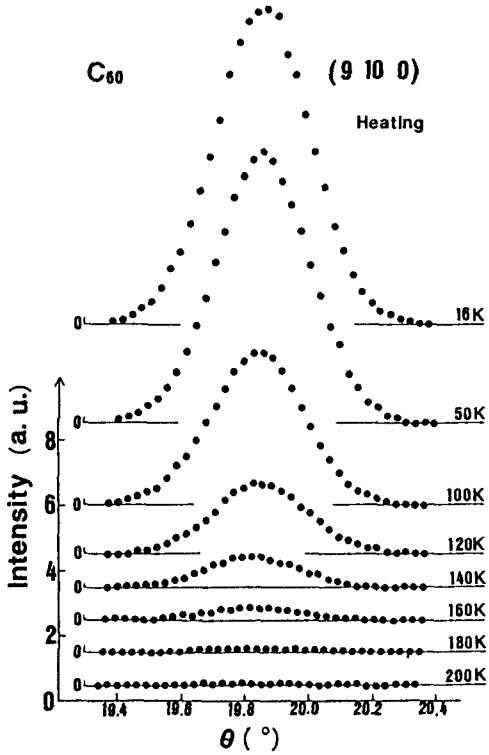

Fig. 2 Temperature dependence of the rocking curve of new Bragg reflection of the (9 10 0) on heating.

results in ref.20 and other studies. It was thought that this differences was due to the quality of C_{60} samples. We confirmed that the solid C_{60} transformed from fcc structure to sc structure at about 260K and this transition was 1st order transition with the hysteresis of about 1K. In these smaller samples, we could not observe the two anomalies at about 160K and 90K. Presumably, because the samples size were very small and the signal was very week.

Next, we searched the new Bragg reflections which corresponded to the two anomalies at about 160K and 90K. A large C_{60} sample, which was prepared by the sublimation method, was used. The sample size was approximately 1.0x1.0x0.4 mm^3. This large sample had the twin structure related by the [1 1 1] twin axis. The ratio of the volume of the twin was about 1 : 0.16, which was estimated from the intensity of the (1 1 1) reflection. We had been careful for the existence of this twin structure. Bragg reflection which appeared below 90K was not observed, but we found the new Bragg reflection

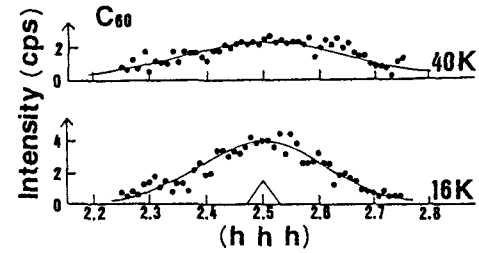

Fig. 3 The intensity distribution of X-ray diffuse scattering around the (2.5 2.5 2.5) reciprocal lattice point along the [1 1 1] direction at 16K and 40K. The small triangle gives the size of the resolution function in the [1 1 1] direction determined from the (2 2 20 Bragg reflection. Solid lines are the Lorentz function assuming that the correlation length along the [1 1 1] direction of 130Å at 16K and 100Å at 40K.

which appeared below about 160K. Figure 2 shows the temperature dependence of the rocking curves of the (9 10 0) Bragg reflection on heating. With increasing temperature, the (9 10 0) reflection decreased and completely disappeared above 200K. The shift in peak position corresponds to the change in the lattice parameter because this method of measurement involves symmetrical setting using the four-circle diffractometer. The full width at half-maximum (FWHA) was about 0.30° at 16K and did not changed below about 160K.

At 16K, we observed the diffuse scattering around the (2.5 2.5 2.5) reciprocal lattice point. Figure 3 shows the intensity distribution excluding the background of the X-ray diffuse scattering along the [1 1 1] direction around the (2.5 2.5 2.5) reciprocal lattice point at 16K and 40K. With increasing temperature, this diffuse scattering decreased and disappeared near 100K. We considered that at the lowest temperature region solid C_{60} was a $2a_0$-structure as the short range order state. A correlation length of this short range order 2a0-structure was estimated by the assumption of the Lorentz function. The solid lines in Fig.3 were the results assuming that the correlation length along [1 1 1] direction were about 130Å at 16K and about 100Å at 40K. These values of the correlation length at 16K and 40K correspond to the about 5 unit cells and about 4 unit cells of the sc a_0-structure, respectively. It is thought that at lowest temperature region, the long range order structure (or average structure) of the solid C60 is the simple cubic structure and the short

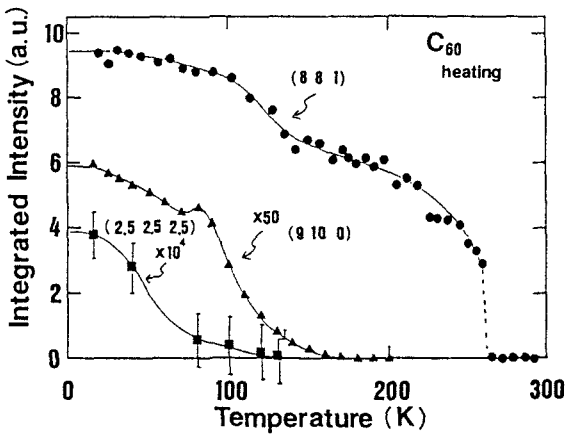

Fig. 4 Temperature dependences of the integrated intensity of the (8 8 1) and the (9 10 0) Bragg reflection and the diffuse scattering around the (2.5 2.5 2.5) reciprocal lattice point along the [1 1 1] direction.

range order structure is the $2a_0$-structure with correlation length of about 5 unit cells.

The temperature dependences of the integrated intensities of the (8 8 1) and the (9 10 0) Bragg reflections and the diffuse scattering around the (2.5 2.5 2.5) reciprocal lattice point are shown in Fig.4. The integrated intensity of the (8 8 1) reflection, which was forbidden in fcc structure, showed the two anomalies near 160K and 100K. These anomalous behaviors consisted to the results by Moret et al.[14]. The integrated intensities of the new Bragg reflection of the (9 10 0) continuously appeared near 160K with decreasing temperature. This implies that solid C_{60} has the structural change near 160K as the long range order structure, but it is not clear whystructural change occur in this temperature. Two ideas are analogized as follows. One is that a new structure phase transition occurs at this temperature. In this case, from the results of the convergent-beam electron diffraction study by Terauchi et al.[8], it is analogized that the solid C_{60} transforms to the space group of $P2_13$ from the Pa3 at about 160K as a second order transition. Another idea is that the appearance of the new Bragg reflection of the (9 10 0) is due to the results of the coupling of the several interactions related to the behavior of the ordering or freezing of the C60 molecules. In bcc Fe-Mn alloys[21], temperature dependence of the magnetic moment of Mn-atom is seen to the similar temperature dependence. In this case, the space group of low temperature region is Pa3. However, the detail of the reason of the appearance of the (9 10 0) reflection at about 160K is not clear at the moment. At about 85K, further, the integrated intensity of the (9 10 0) reflection showed the anomalous behavior. The structural change corresponding to this anomalous behavior is not clear, too. The diffuse scattering around the (2.5 2.5 2.5) reciprocal lattice point continuously appeared near 100K. With decreasing temperature, the integrated intensity of this diffuse scattering increased and had a point of inflection at near 50K, where the integrated intensity of this diffuse scattering rapidly increased. It is possible that the solid C_{60} is the glassy state as the average structure below about 100K. It is considered that this glassy phase transition is second order transition.

3.2. Structure Analysis at 13K

As mentioned above, there are several possibilities of the interesting structure in the low temperature region in solid C_{60}. However, it is considered that the long range order structure (or average structure) is the simple cubic structure, where C_{60} molecules in crystal are orientational order state. As mentioned in the section of the introduction, structure analysis of solid C_{60} on the lowest temperature was performed by means of the profile fitting of X-ray and neutron powder diffraction as the space group of Pa3. Another space group of $P2_13$ was suggested. We think that it is difficult whether the space group is Pa3 or $P2_13$. Because, the difference of the space group of $P2_13$ and Pa3 is only that the inversion symmetry exist or not exist.

The data collection for the structure analysis was carried out at 13K using C_{60} single crystal prepared by the sublimation method. The sample size was approximately 0.60x0.30x0.15 mm^3. The number of the observed reflection was about 13000 collected from the all area in the reciprocal lattice space with $2\theta_{max}=70.0°$. We checked the extinction rule of the space group of P213 and Pa3. The extinction rule of $P2_13$ is (*h*00) with *h*=even, where *h*, *k*, *l* is cyclically permutable. That of Pa3 is (*h*00) with *h*=even and (0*kl*) with *k*=even, where *h*, *k*, *l* is the cyclically permutable, too. In this stage, extinction rule of the observed reflection is likely to belong the $P2_13$. Be careful for the determination of the space group at 13K, because of the existence of the anti-phase domain structure. The structure analysis was carried out using the reflections of an asymmetric unit of Laue group of m3. The number of the used reflection was 1878. Correction for Lorentz-

polarization was applied, but the correction for the absorption was not applied. The full matrix least square method was made as used the initial parameter of the atomic position of David et al.[7]. The discrepancy factor $R=\Sigma||Fo|-|Fc||/\Sigma|Fo|$ is 0.32 in the case of the space group of Pa3 and 0.28 in the case of the space group of $P2_13$. These values were large and it was not determined whether the space group was $P2_13$ or Pa3. It is thought that the main reason of the large discrepancy factor is due to the existence of the twin structure and the occurrence of the anti-phase domain structure in lowest temperature region. The twin structure is occurred only during the crystal growth. The check of the existence and the volume ratio of this twin structure can be made by X-ray diffraction measurement in the case of single crystal. However, it is difficult to check of the anti-phase domain structure, which occur after the transformation from the fcc structure to the sc structure because the increase of the Z-number without the change of crystal symmetry (this case is cubic to cubic). It is considered that these anti-phase domains, at least, are four kinds. Because of the existence of these anti-phase domains, it is possible that the extinction rule of the observed reflection seems to correspond the space group of $P2_13$ when the space group is Pa3. However, the each carbon atoms in C_{60} molecules were clearly recognized in the results from the Fourier synthesize. It is considered that at 13K solid C_{60} is order state as a long range order structure (or average structure), but not the random glassy state.

4. CONCLUSIONS

X-ray diffraction measurements in the temperature range from 300K to 14K and structure analysis at 13K were carried out using C_{60} single crystals. Solid C_{60} transformed from fcc Bravais lattice to sc Bravais lattice at about 260K with the hysteresis of the transition temperature about 1K. This transition temperature depended to the quality of samples. New Bragg reflection of the (9 10 0) which appeared below about 160K was, firstly, observed. An anomalous behavior of the integrated intensity of this reflection was observed at near 85K. The diffuse scattering around the (2.5 2.5 2.5) reciprocal lattice point along the [1 1 1] direction was found below about 100K, which indicated the existence of the short range order 2a0-structure. The correlation length of this short range order 2a0-structure was about 130Å along the [1 1 1] direction at 16K. The structure analysis at 13K was attempted using C_{60} single crystal, but the space group and the precise atomic parameter were not determined at moment. We are undertaking to measure the line scan along the [1 1 0] and the [1 0 0] direction and the map scan in the first Brillouin zone of the sc a_0-structure to clarify the our observed short range order state. Moreover, it is necessary to study the other C_{60} samples that the our observed new Bragg reflection and the diffuse scattering are the intrinsic state or the effects of the defect or impurities, because of the conclusions by Fischer et al.[17].

ACKNOWLEDGMENT

We wish to thank Professors H.Shinohara, Y.Saito, K.Kikuchi, Y.Achiba and I.Ikemoto for providing us with purified C_{60}.

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