

X-ray-diffraction study of the phase transition in a C₆₀ single crystal

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X-ray-diffraction experiments of single-crystal C₆₀ were carried out at temperatures from 300 to 14 K. A small jump in the lattice parameter was observed at the transition temperature $T_C = 260$ K, implying that this was a first-order transition. The integrated intensity of the Bragg reflections observed below T_C , which corresponded to the order parameter transformed from the orientational disorder state to the orientational order state, was proportional to the anomalous part of the lattice parameter.

The discovery of a C₆₀ molecule¹ and a synthesizing method for solid C₆₀ (Ref. 2) has inspired many studies in the physical and chemical properties of this new form of carbon. Recently, the discovery of a superconducting state in alkali-metal-doped C₆₀ compounds³ has attracted much attention.

At room temperature, single-crystal x-ray diffraction⁴ shows that pure C₆₀ crystal is a face-centered-cubic (fcc) Bravais lattice with a high degree of rotational disorder. The ¹³C nuclear magnetic resonance (NMR) measurements^{5,6} reveal that C₆₀ molecules in the solid state exist in the dynamical disorder state and reorient rapidly and isotropically at room temperature. With decreases in temperature, this rotation is slowed down. A phase transition of the pure C₆₀ crystal has been reported in several papers.⁷⁻⁹ High-resolution synchrotron x-ray powder diffraction experiments conducted by Heiney *et al.*⁷ showed that the C₆₀ crystal undergoes a weak first-order phase transition at $T_C = 249$ K, where the crystal is transformed from the fcc structure of the orientational disorder state of C₆₀ molecules to the simple cubic (sc) structure of the orientational order state. Very recent results of NMR experiments by Tycko *et al.*⁸ show that the phase transition reported by Heiney *et al.*⁷ occurs at $T_C = 260$ K, as determined by observation of the change in spin-lattice relaxation time T_1 ; i.e., just above T_C , C₆₀ molecules appear to execute continuous rotational diffusion, while below T_C , they appear to jump between symmetry-equivalent orientations. These authors' interpretation was consistent with the results of the x-ray diffraction experiments conducted by Heiney *et al.*⁷ Pressure experiments were carried out using several methods.¹⁰⁻¹³ At weak-pressure regions, the fcc-to-sc ordering transition temperature T_C increases with increasing pressure and another phase transition appears near T_C .¹² In the regions above about 10 GPa, C₆₀ crystal transforms from a sc structure phase to a low-symmetry insulator phase.^{11,13}

Regarding the structure of the low-temperature sc phase, Heiney *et al.*⁷ performed a profile fitting using their structure model, but several misfits were seen.

Sachidanandam and Harris¹⁴ commented to Heiney *et al.* that the $Pa\bar{3}$ space group gave a better representation of the orientational order phase than the $Pn\bar{3}$ space group, which is used in Ref. 7. Heiney *et al.* replied¹⁵ that the reflection data at 11 K in Ref. 7 were fitted by the $Pa\bar{3}$ space group, except for the underestimation of seven and the overestimation of two reflections due to the stacking faults.

In this study, an x-ray scattering experiment of C₆₀ single crystal was conducted in order to clarify the mechanism of the structure phase transition at T_C and understand the property of the low-temperature sc phase of C₆₀ crystal and examine the temperature dependence of the lattice parameter at temperatures ranging from 300 to 14 K. The temperature dependence of the lattice parameter yields information for the structure phase transition at T_C . For instance, the phase transition at T_C is of first or second order. To examine the extinction rule, it is possible to determine the space group of the low-temperature sc phase, which is $Pn\bar{3}$ or $Pa\bar{3}$. C₆₀ was prepared from carbon soot by extraction with toluene at room temperature. The C₆₀ cluster purified by column chromatography¹⁷ was dissolved in toluene. The solution of C₆₀ (1–2 ml) was evaporated at about 40°C. C₆₀ crystals were obtained after evaporation of the solvent for 20–30 h. As-grown crystal was used and the sample size was approximately $0.2 \times 0.09 \times 0.02$ mm³. A large χ -cradle automatic four-circle diffractometer, Rigaku AFC off-center type, was used for measuring x-ray scattering data with a PG(002) monochromator reflecting Mo $K\alpha$ x rays obtained from a 50-kV–240-mA source. A scintillation counter was used as a detector. The specimen temperature was controlled within ± 0.05 K through the use of a closed-cycle He-gas refrigerator.

At 14 K, we observe the $(0\ k\ l)$ reflection with $k = \text{even}$, $l = \text{integer}$. The space group of the low-temperature sc phase was $Pa\bar{3}$, in agreement with the results of x-ray and neutron powder diffractions.¹⁶ Figure 1 shows the temperature dependence of the rocking curve of $(0\ 4\ 5)$ reflection upon heating. The solid lines are guides for the eye. The $(0\ 4\ 5)$ reflection disappears above 260 K. The

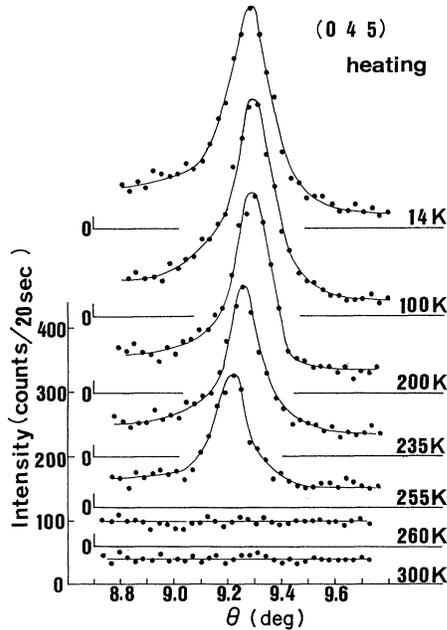


FIG. 1. Temperature dependence of the rocking curve of the (0 4 5) reflection in C_{60} single crystal on heating. The phase transition occurs at 260 K. The solid lines are guides for the eye.

shift in peak position corresponds to the change in the lattice parameters because this method of measurement involves symmetrical setting using the four-circle diffractometer. Figure 2 shows the temperature dependence of the integrated intensities of (0 4 5), (0 $\bar{4}$ $\bar{5}$), (6 2 1), and (4 3 4) reflections. These reflections disappear above 260 K, because of the extinction rule of the fcc lattice.

The observed lattice parameter a is plotted in Fig. 3 as a function of temperature. The value of the lattice parameter is determined by the least-square method using 25 reflections. A small jump is observed at $T_C = 260$ K. This behavior shows that the phase transition of C_{60} crystal from fcc to sc is a first-order transition. To estimate

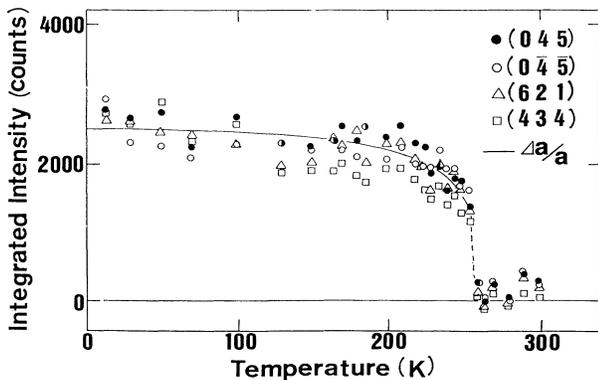


FIG. 2. Integrated intensities of (0 4 5), (0 $\bar{4}$ $\bar{5}$), (6 2 1), and (4 3 4) reflections in C_{60} as a function of temperature. These reflections do not occur in a fcc lattice, and (0 4 5) and (0 $\bar{4}$ $\bar{5}$) reflections do not occur in the space group of $Pn\bar{3}$.

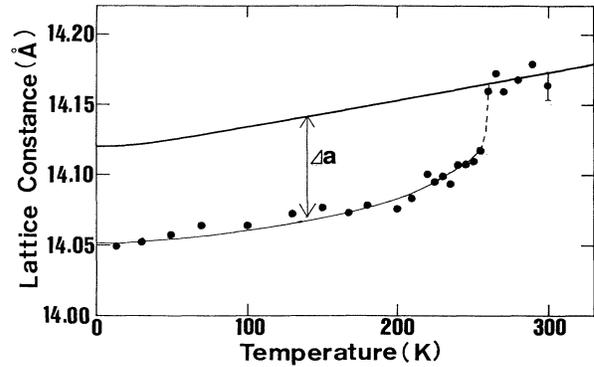


FIG. 3. Temperature dependence of lattice parameter in C_{60} crystal. These values are determined by the least-square method using 25 reflections. The thick line extrapolated to 0 K is the result calculated by the Debye approximation using the data of the fcc high-temperature phase and assuming a Debye temperature of 73 K. The thin line is a guide for the eye.

the anomalous parts of the lattice parameter, we calculated the lattice parameter based on the Debye approximation:

$$\Delta a = a - a_0 = A \epsilon(\Theta_D/T), \quad (1)$$

$$\frac{\epsilon(\Theta_D/T)}{9RT} = \left[\frac{T}{\Theta_D} \right]^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx. \quad (2)$$

Here $\epsilon(\Theta_D/T)$ is Debye energy with Debye temperature Θ_D , a_0 is the lattice parameter at 0 K, A is a proportional constant, and R is the gas constant. A and a_0 are fitting parameters. The calculation is carried out using the data above 260 K. The results extrapolated to 0 K are represented by the thick line. The Debye temperature Θ_D is assumed to be 73 K. The thin line is a guide for the eye. The temperature dependence of the anomalous part Δa is derived from the difference of the observed lattice parameter and the calculated one. The integrated intensities as shown in Fig. 2 are related to the anomalous parts.

The free energy F is represented in terms of the order parameter ϕ and the strain e :

$$F = F_0 + \frac{1}{2} A \phi^2 + \frac{1}{4} B \phi^4 + \frac{1}{6} C \phi^6 + D \phi^2 e + \frac{1}{2} E e^2. \quad (3)$$

Here, A is a function of temperature and F_0 , B , C , D , and E are constant values. We speculate that the order parameter ϕ indicates the rotation angle of the C_{60} molecule reported by Sachidanandam and Harris.¹⁴ In their report, in the low-temperature sc phase, the C_{60} molecules centered at (0,0,0), ($\frac{1}{2}, \frac{1}{2}, 0$), ($\frac{1}{2}, 0, \frac{1}{2}$), and ($0, \frac{1}{2}, \frac{1}{2}$) are rotated through an angle $\phi \neq 0$ in the (1,1,1), (1,-1,-1), (-1,-1,1), and (-1,1,-1) directions, respectively. From the equilibrium condition $\partial F / \partial e = 0$, it is found that e is proportional to ϕ^2 . The variable e corresponds to $\Delta a/a$, and ϕ^2 corresponds to the integrated intensity which appears in the low-symmetry phase. The solid line in Fig. 2 shows the results of the above equation. It is evident that the temperature dependence of the integrated intensities is accurately predicted by the theory. Pre-

cise structure analyses, above and below transition temperature, are necessary to understand these mechanisms in detail.

Very recently, a coherent quasielastic neutron-scattering study¹⁸ was performed in the high-temperature fcc phase. In that study, the broadening of the spectra was observed and the rotational diffusion constant was

given. It is expected that these similar results of critical diffuse scattering will be observed near T_C . Presently, measurements of critical diffuse scattering are being conducted in an attempt to examine the dynamical property.

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