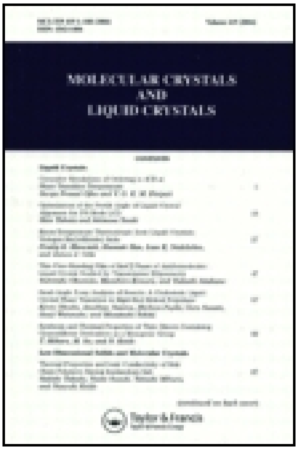

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Structural Phase Transition in $(NH_3)K_3C_{60}$

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Crystal structure of the ammoniated alkali fulleride, $(NH_3)K_3C_{60}$, was studied by high resolution x-ray diffraction experiments. We found a structural phase transition at low temperature. A superstructure appears below the transition temperature, $T_s \simeq 150$ K, and it originates from the orientational ordering of K-NH_3 pairs in the octahedral site. Below T_s, K-NH_3 pairs align in an antiferroelectric fashion, which is understood by electrostatic interaction between them. We also measured a deuteration effect to the transition. Similar transition was observed in $(ND_3)K_3C_{60}$ and difference in T_s was very little.

Keywords: C_{60}; ammoniated alkali fulleride; structural phase transition; synchrotron x-ray diffraction

INTRODUCTION

Many kinds of atoms and molecules are known to be intercalated into C_{60} crystal. One interesting structural aspect in fullerene intercalation compounds is that an additional degree of freedom is produced by intercalation, that is, an intercalant can have more than two stable orientations in a large interstitial site of fullerene crystal. The intercalant rotates or jumps to other orientation at high temperature, while an ordered state accompanied with a structural phase transition is expected at low temperature. In C_{60}-*n*-pentane clathrate, Faigel *et al.*[1] found such a transition from an orthorhombic to a monoclinic structure by x-ray diffraction measurements, and they predicted a freezing of *n*-pentane by molecular dynamics calculation. This type of transition is also expected in ammoniated alkali fullerides because most of them has a positional disorder of intercalants at room temperature. In $(NH_3)K_3C_{60}$, the room-temperature crystal structure has been determined as a face-centered-orthorhombic structure slightly distorted from *fcc*[2]. K and NH_3 in the octahedral site are oppositely displaced in the ⟨110⟩ direction from the site center, and this K-NH_3 pair directs randomly in one of four equivalent directions. This is plausibly dynamic disorder at high temperatures where ammoniation is carried out (from room temperature to 100 °C), and we expect an ordered state caused by freezing of intercalant motion at low temperature. This situation reminds us of potassium-ammonia intercalated graphite, in which the K-NH_3 layer constitutes a two-dimensional liquid at room temperature[3] and the translational diffusion of intercalants freezes at low temperature[4].

In this paper, we report on the high resolution x-ray diffraction study in $(NH_3)K_3C_{60}$. Structural phase transition was observed at $T_s \simeq 150$ K, and the orientational ordered state of K-NH_3 pairs in the octahedral site was confirmed. We also present the result of a deuterated sample, $(ND_3)K_3C_{60}$.

EXPERIMENTAL

The polycrystalline samples of $(NH_3)K_3C_{60}$ and $(ND_3)K_3C_{60}$ were synthesized by the direct reaction of K_3C_{60} and NH_3 gas. The detail was presented in the previous report[5]. The obtained samples were sealed in a thin glass capillary for x-ray diffraction experiments. Powder x-ray diffraction measurements were carried out by using synchrotron radiation x-rays at Photon Factory (BL-6C_1 and 18C) , KEK, Tsukuba. The incident x-ray was monochromatized at wavelength 1.100 Å with a Si double crystal. An imaging plate was used for detection of the diffraction rings, which was converted in the conventional spectrum by integrating the intensity along the Debye ring.

RESULTS AND DISCUSSION

Figure 1(a) shows the powder x-ray diffraction spectra of $(NH_3)K_3C_{60}$ at 300 K and 15 K. The spectrum at 300 K can be understood by an face-centered-orthorhombic structure, which is consistent with the previous report[2]. At 15 K, however, we observed a number of extra peaks and found a structural phase transition. These peaks correspond to the index of half an integer or the forbidden reflections in the face-centered lattice at 300 K; for example, a peak at $2\theta = 7.1°$ is indexed to $(\frac{3}{2}\frac{1}{2}\frac{1}{2})$ and $(\frac{1}{2}\frac{3}{2}\frac{1}{2})$, while that at 6.0° corresponds to (110). The unit lattice vectors at the low-temperature phase should have a double size of the fundamental ones. From the reflection conditions $h+k, k+l, l+h = integer$ (here, hkl is the index in the fundamental unit cell) and the absence (100), (010), and (001) peaks, we can determine the space group as *Fddd*.

As for the origin of the superstructure, we can consider some possibilities, such as the C_{60} dimer or polymer formation, the orientational ordering of C_{60} molecules, or the positional ordering of K and NH_3 at the octahedral site. The possibility of dimerization or polymerzation is very low because

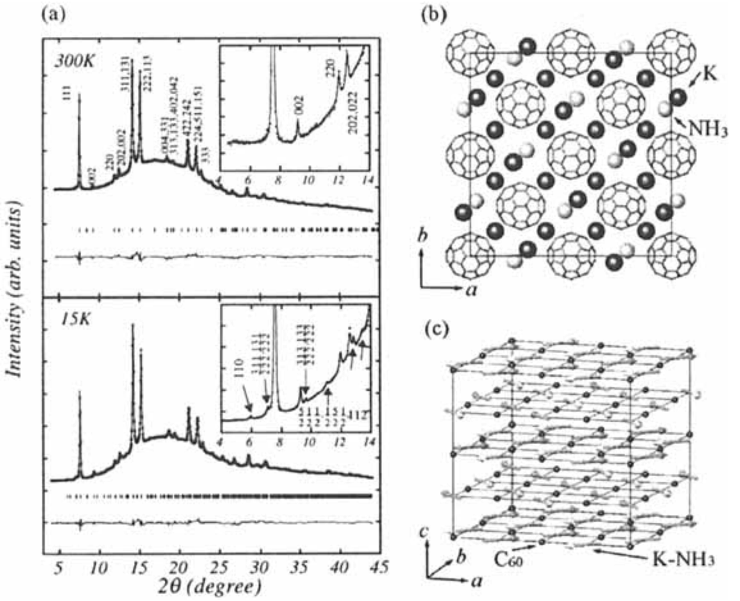

FIGURE 1 (a) : Powder x-ray diffraction spectra of $(NH_3)K_3C_{60}$ at 300 K (upper panel) and 15 K (lower panel). The insets are magnifications of the low-angle region. The cross marks represent observed intensity, and solid lines are the results of Rietveld refinement. The arrows indicate the superlattice reflections. (b) : Crystal structure of the low-temperature phase near $z=0$. (c) : Schematic view of the unit cell. The arrows represent K-NH_3 pairs. Potassium atoms in the tetrahedral site are not shown for simplicity.

the intermolecular distance of C_{60}, 10.1 Å in the present case, is too large to form a covalent bond. The orientational ordering of C_{60} cannot explain the observed strong intensity of superlattice reflections in the low-angle region. Therefore we proceed the structural analysis on the basis of the positional ordering of K-NH_3 pairs.

In order to satisfy the space group *Fddd*, we should put the off-centered potassium atom on the $32h$ (origin choice 2) position $(\frac{1}{4}+\delta_x,\delta_y,0)$, where $(\frac{1}{4},0,0)$ is the center of the octahedral site and $(\delta_x,\delta_y,0)$ is a displacement vector. The NH_3 molecule is placed at an off-centered position in the opposite direction to potassium. All C_{60} molecules are aligned in the same direction according to the previous report about the room-temperature structure. Based on this model, diffraction intensities were analyzed using the RIETAN Rietveld refinement program[6]. A good fit was obtained with R_{wp}=2.63% and R_I=2.45%. All positions of atoms and molecules were reported elsewhere[7]. As shown in Figs. 1(b) and (c), the ordered structure of the K-NH_3 pair is analogous to an antiferroelectric order. The two-dimensional (2D) structure of pairs in the *ab*-plane can be well understood by the electrostatic interaction between potassium ions. When considering the 3D configuration, we can consider two configurations of K-NH_3 pairs, that is, one is the parallel type where the pairs in the next nearest planes direct parallel or antiparallel to those pairs on the considered plane, and the other is the perpendicular type where the pairs direct perpendicular to those pairs considered. In the parallel type the (110) reflection should be forbidden, but it is observed in our case. Therefore we can conclude that the perpendicular type is realized in $(NH_3)K_3C_{60}$. However the Madelung energy calculation, where C_{60} is approximated as a point charge of $-3e$, gives a little smaller energy (58 K) for the parallel type. This inconsistency is not explained yet; we have to consider any higher order interactions.

Figure 2(a) shows the temperature dependence of intensity of the superlattice reflection. The reflection appears below $T_s \simeq 150$ K, the structural transition temperature. The intensity changes continuously below T_s and no appreciable thermal hysteresis was observed. These facts indicate that the phase transition is the second order.

The temperature dependences of the lattice constants are shown in Figs. 2(c) and (d). The difference between a_0 and b_0 is too small to distinguish, so that the average value is given in the figure. A most remarkable feature is an anomalous temperature dependence in the lattice constant a_0, that is, a negative expansion between 100 K and 150K, whereas we observe no anomaly in c_0. This temperature region just corresponds to that of the evolution of the superlattice reflections, which suggests that the negative expansion is closely related to the orientational ordering of the K-NH_3 pair in the *ab*-plane. In this connection we estimated the K-NH_3 distance from diffraction intensity. The distance below 75 K (where the superlattice reflection is saturated enough) is 2.57 ± 0.03 Å, but at 155 K (above T_s) it decreases to 2.47 ± 0.05 Å, namely a contraction of 0.1 Å. The contraction of the lattice constant, which is estimated as about 0.03 Å, is plausibly attributed to the contraction of the K-NH_3 distance. We do not have a clear explanation for this phenomenon. A posible interpretation is the steric effect and/or hydrogen bond between NH_3 and C_{60} molecules.

As for $(ND_3)K_3C_{60}$, we observed a similar structural phase transition. The spectra of $(ND_3)K_3C_{60}$ can be understood well by the same crystal structure as $(NH_3)K_3C_{60}$. Figures 2(a) and (b) show the temperature dependence of superlattice reflection intensity in $(NH_3)K_3C_{60}$ and $(ND_3)K_3C_{60}$,

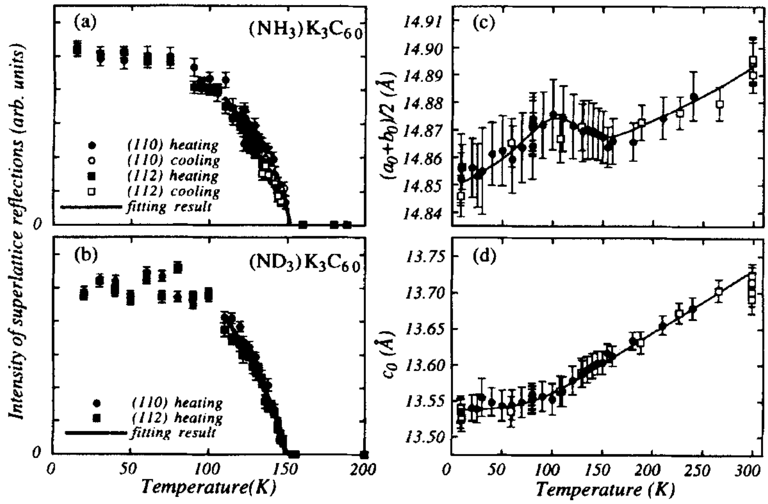

FIGURE 2 (a), (b) : Temperature dependence of superlattice reflection intensity of $(NH_3)K_3C_{60}$ and $(ND_3)K_3C_{60}$, respectively. Solid lines are fitting result described in the text. (c), (d) : Temperature dependence of the lattice constants in $(NH_3)K_3C_{60}$. Open makes and filled marks represent the data in cooing and heating run, respectively. Solid lines are guide to eyes.

respectively. Assuming the temperature dependence of superlattice reflection intensity as $I = I_0(T - T_s)^{2\beta}$ with a common critical exponent β for $(NH_3)K_3C_{60}$ and $(ND_3)K_3C_{60}$, and using data above 110 K, we obtained $T_s = 151.7 \pm 1.1$ K for $(NH_3)K_3C_{60}$, $T_s = 148.8 \pm 0.7$ K for $(ND_3)K_3C_{60}$, and $\beta = 0.34 \pm 0.02$. The estimated errors in T_s are too large to determine whether the difference between NH_3 and ND_3 is significant or not, but little influence of deuteration to T_s seems to support that the transition occurs mainly by the electrostatic interaction of K^+ ions.

CONCLUSION

We have studied the crystal structure of $(NH_3)K_3C_{60}$ and $(ND_3)K_3C_{60}$ by high resolution x-ray diffraction experiments and found a structural phase transition at $T_s \simeq 150$ K. The low-temperature phase has the doubled unit vectors along three axes with respect to the high-temperature phase. The transition is characterized by the orientational ordering of the K-NH_3 pair at the octahedral site of C_{60} lattice in an antiferroelectric fashion, whereas above T_s the pair orients randomly to one of four equivalent directions. The alignment of K-NH_3 pairs can be understood by electrostatic interaction of potassium ions and little change of T_s by deuteration supports this scheme. The superlattice intensity increases continuously below T_s, which means that the transition is second order. At 100 K< $T < T_s$, a negative thermal expansion is observed along the *a*- and *b*-axes. This is closely related to the observed K-NH_3 distance, which shows a contraction around T_s with increasing temperature.

Acknowledgments

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