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Structural phase transition in the ammoniated alkali C_{60} compound $(NH_3)K_3C_{60}$

Kenji Ishii, Tetsu Watanuki, Akihiko Fujiwara, and Hiroyoshi Suematsu
Department of Physics, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Yoshihiro Iwasa, Hideo Shimoda, and Tadaoki Mitani
Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

Hironori Nakao and Yasuhiko Fujii
Neutron Scattering Laboratory, Institute for Solid State Physics, The University of Tokyo, 106-1 Shirakata, Tokai,
Ibaraki 319-1106, Japan

Youichi Murakami and Hajime Kawada*
Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization,
1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

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X-ray diffraction measurements of $(NH_3)K_3C_{60}$ have revealed a structural phase transition at $T_s = 150$ K, which is attributed to the orientational order-disorder transition of the K-NH_3 pair at the octahedral site of the C_{60} lattice. The low-temperature phase has a face-centered-orthorhombic structure derived by doubling the unit lattice vectors of the high-temperature phase along three axes. 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 contraction of K-N interatomic distance. We also discuss the relation between the superconductivity and the local symmetry of C_{60} in the crystal. [S0163-1829(99)01306-5]

I. INTRODUCTION

Fullerenes are known to make compounds with various atoms and molecules, and especially alkali fullerides are intensively studied[1] because of the variation of the compounds and superconductivity[2]. Some of them make ternary compounds with ammonia molecules.[3–7] The most remarkable effect of ammoniation is the significant expansion of the lattice constant without changing the valence of C_{60}.[5] In these years many ammonia alkali fullerides have been investigated in order to obtain a higher superconducting transition temperature (T_c). This is because T_c in A_3C_{60}(A is an alkali atom) is known to increase crucially with the cubic lattice constant (a_0) or the intermolecular distance of C_{60}.[8–10] In the case of $(NH_3)_4Na_2CsC_{60}$ Zhou *et al.*[3] demonstrated that the cubic lattice constant increases from 14.132 Å to 14.473 Å on ammoniation, and T_c increases from 10.5 K to 29.6 K. However, in the case of $(NH_3)K_3C_{60}$ the superconductivity of the pristine K_3C_{60} disappears by ammoniation[4,5] and becomes a magnetic insulator below 40 K.[11,12] The room-temperature crystal structure of the compound has been determined by Rosseinsky *et al.*[4] as an orthorhombic structure slightly distorted from fcc. They pointed out that in the octahedral site of the C_{60} lattice K and NH_3 are oppositely displaced from the site center in the $\langle 110 \rangle$ direction, and the pair of K and NH_3 orient randomly to one of the $\langle 110 \rangle$ directions. We can speculate that the structural distortion from cubic symmetry or the orientational disorder of the K-NH_3 pair might be responsible for the disappearance of superconductivity.

In the present work we have studied the crystal structure of $(NH_3)K_3C_{60}$ at low temperatures, and have observed a phase transition at 150 K, which is attributed to the orientational order-disorder transition of the K-NH_3 pair. We will discuss briefly the relationship between the superconductivity and the local symmetry of C_{60} in ammoniated alkali fullerides.

II. EXPERIMENTAL PROCEDURES

The polycrystalline powder of $(NH_3)K_3C_{60}$ was prepared by ammoniation of K_3C_{60}. The pristine powder sample of K_3C_{60} was synthesized by the direct reaction of potassium vapor and C_{60} powder and annealed at 400°C for a month. After that, K_3C_{60} was exposed in dry ammonia of 0.5 atm at room temperature for 20 min. The ammoniated sample was annealed at 100°C for a month in a glass ampoule with 0.5 atm NH_3. The sample was sealed in a thin glass capillary for an x-ray diffraction experiment. We used two samples; sample A was used for the diffraction intensity measurement and the structural analysis, and sample B for the temperature dependence measurement of the lattice constant. In the x-ray diffraction study sample B was found to contain a trace of K_3C_{60}, so that the mean composition of NH_3 might be slightly smaller than 1.

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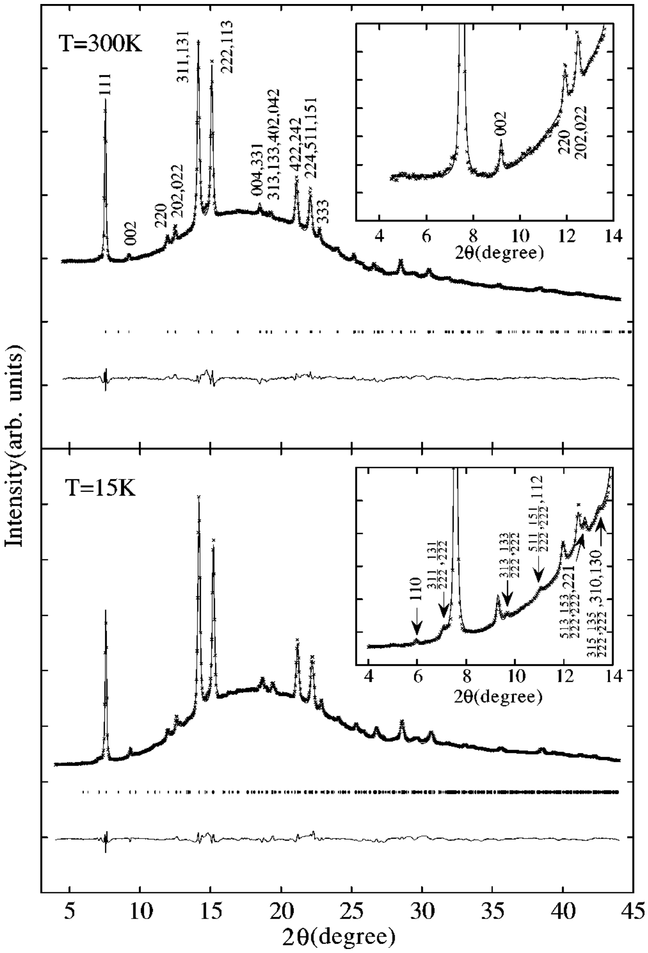

FIG. 1. Powder x-ray diffraction spectra of $(NH_3)K_3C_{60}$ at 300 K (upper panel) and 15 K (lower panel). The insets are magnification of the low-angle region. The cross marks represent observed intensity, and solid lines are the result of Rietveld refinements in the space group *Fmmm* for 300 K and *Fddd* for 15 K, respectively. The arrows in the lower inset indicate the superlattice reflections observed below T_s.

X-ray diffraction measurements were carried out by using synchrotron radiation x rays at Photon Factory ($BL6C_1$ and BL18C), KEK, Tsukuba. The incident x ray was monochromatized at wavelength 1.100 Å with a Si double crystal and collimated to 0.2–0.5 mm in diameter. 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.

III. EXPERIMENTAL RESULTS

Figures 1(a) and 1(b) show the diffraction spectra of $(NH_3)K_3C_{60}$ at 300 K and 15 K, respectively. For the 300 K spectrum we can assign all the peaks to the face-centered-orthorhombic cell with the lattice constants of $a_0 = 14.917 \pm 0.010$ Å, $b_0 = 14.971 \pm 0.010$ Å, and $c_0 = 13.692 \pm 0.004$ Å. The present values are consistent with the result of Rosseinsky *et al.*[4] However, at 15 K we have observed a number of extra peaks as shown in Fig. 1(b). These extra peaks correspond to the index of half an integer or the forbidden reflections in the face-centered lattice; 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 appearance of these superlattice and forbidden peaks indicates that the unit lattice vectors of the low-temperature phase should have a double size of the fundamental ones.

The observed peak indices can be presented by the conditions $h+k, k+l, l+h = integer$ (here, hkl is the index in the fundamental unit cell), and the reflections (100) and (010) ($2\theta = 4.2°$, if it exists) and (001) ($2\theta = 4.6°$) are not observed under the experimental condition. From these conditions we can uniquely identify this phase as the space group *Fddd*. As the origin of the structural phase transition 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-NH_3 pairs at the octahedral site. The possibility of dimerization or polymerzation is very low because the intermolecular distance of C_{60};10.1 Å in the present case is much larger than those of the C_{60} dimer or polymer, namely, 9.34 Å in the case of KC_{60} dimer[13] and 9.11 Å in KC_{60} polymer.[14] The orientational ordering of C_{60} cannot explain the observed strong intensity of superlattice reflections especially in the low-angle region. Therefore we proceed the structural analysis on 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 $32h$ position $(1/4 + \delta_x, \delta_y, 0)$, where (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. Based on this model we carried out the Rietveld refinement with use of the RIETAN program[15] on some assumptions. Namely, C_{60} molecules are considered to align in the specific direction according to the structural analysis of the room-temperature phase;[4] that is, three orthogonal twofold axes of the C_{60} molecule are put parallel to the unit lattice vectors. The bond length of C_{60} is fixed to 1.40 Å for the bond between two hexagons and 1.45 Å for that between hexagon and pentagon. The NH_3 molecule is approximated by a nitrogen atom and three hydrogen atoms at the same position; this approximation was taken because of the low scattering power of hydrogen atoms, so that we cannot determine the orientation of the ammonia molecule around its threefold axis. The occupancy of all atoms are fixed to unity.

After the refinement we obtain the best-fit spectra for 300 K and 15 K data as shown in Figs. 1(a) and 1(b), respectively. The calculation for 300 K on the space group *Fmmm* reproduces well the experimental spectrum; the weighted pattern R factor (R_{wp}) is 2.18%. For the low-temperature phase we also obtain a good fit with $R_{wp} = 2.63\%$. The lattice constants at 15 K are obtained as $a_0 = 29.792 \pm 0.010$ Å, $b_0 = 29.873 \pm 0.010$ Å, and $c_0 = 27.112 \pm 0.004$ Å and the molecular and atomic positions are given in Table I. As shown in Figs. 2(a) and 2(b), the crystal structure of the ordered phase is characterized by the alignment of the K-NH_3 pair; the K-NH_3 pair on the ab plane ($z = 0$, for example) aligns in the [110] direction with the same polarization, and the direction of the pair is antiparallel at the next chain on the same ab plane. The pairs on the upper ab plane ($z = 1/4$) direct to $[\bar{1}10]$ or $[1\bar{1}0]$, perpendicular to those on

TABLE I. The best-fit result of Rietveld refinement of the low-temperature phase (15 K) of $(NH_3)K_3C_{60}$ in the space group *Fddd* (origin choice 2). There are 60 crystallographically inequivalent carbon atoms, but only the center of the C_{60} molecule is represented for simplicity. The lattice constants are $a_0=29.791\pm0.010$ Å, $b_0=29.873\pm0.010$ Å, and $c_0=27.112\pm0.004$ Å. R factors for fit are $R_{wp}=2.63\%$ and $R_I=2.45\%$. B is the isotropic thermal parameter in the Debye-Waller factor, $\exp[-B(\sin\theta/\lambda)^2]$.

	Site	x	y	z	B(Å ^{2})
C_{60}	16*c*	0	0	0	3.9(3)
C_{60}	16*d*	0.5	0.5	0.5	3.9(3)
K^+	8*a*	0.125	0.125	0.125	3.7(3)
K^+	8*b*	0.125	0.125	0.625	3.7(3)
K^+	16*e*	0.375	0.125	0.125	3.7(3)
K^+	16*f*	0.125	0.375	0.125	3.7(3)
K^+	16*g*	0.125	0.125	0.375	3.7(3)
K^+	32*h*	0.285(5)	0.032(4)	0	7.2(6)
NH_3	32*h*	0.220(9)	−0.025(9)	0	7.2(6)

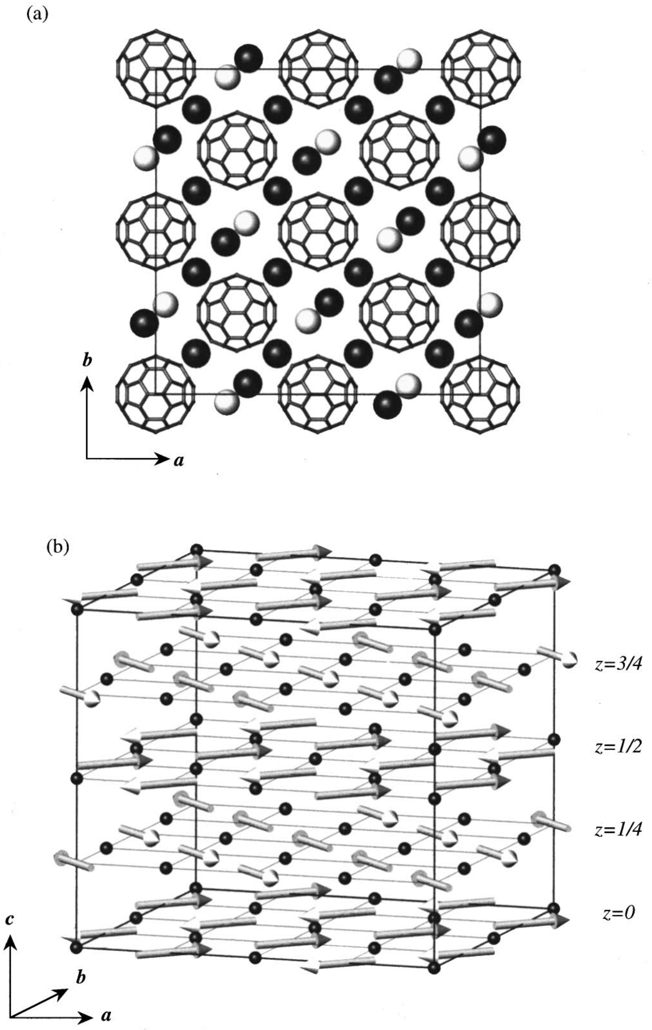

FIG. 2. (a) The $z=0$ section of the low-temperature phase of $(NH_3)K_3C_{60}$. Black and white balls represent K and NH_3, respectively. The crystal consists of the stack of the layers along *c* axis with the diamond glide. Antiferroelectric ordering of K-NH_3 pairs is clearly seen. (b) Schematic view of the unit cell. The black spheres represent the center of C_{60} molecules. The arrows represent antiferroelectrically aligned K-NH_3 pairs. Potassium atoms in the tetrahedral site are not shown for simplicity.

the considered plane $(z=0)$. Namely, the direction of the K-NH_3 pair is obtained by stacking the ab plane along the c axis with the glide vectors of $1/2(\pm\mathbf{a}\pm\mathbf{c})$ and $1/2(\pm\mathbf{b}\pm\mathbf{c})$, where **a,b,c** are the unit lattice vectors in the fundamental cell. This configuration is very similar to an antiferroelectric order.

Figure 3(a) shows the temperature dependence of intensity of the (110) reflection that is forbidden for the high-temperature phase. The reflection appears below $T_s=150$ 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 in sample B are shown in Figs. 3(b) and 3(c). The difference between a_0 and b_0 is too small to distinguish, so that the average value is given in the figure. The lattice constant a_0 (and b_0) of sample B is a little smaller than the result of the Rietveld analysis for sample A; the difference may come from a small deficiency of NH_3 in sample B. A most remarkable feature is an anomalous temperature dependence in the lattice constant a_0, that is, a negative expansion between 100 K and 150 K, 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 at some temperatures by the Rietveld refinement, as shown in Fig. 3(d). 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 have tried to detect any structural anomaly at 40 K, where the metal-insulator transition is reported in the susceptibility measurements.[11] However, we observed no appreciable extra peaks within the noise level, about 1/3 of the (110) reflection. Moreover, the spectrum at 75 K is satisfactorily explained by the same structural model as 15 K except for the thermal expansion of the lattice.

IV. DISCUSSION

In the present study we have revealed that the structural phase transition in $(NH_3)K_3C_{60}$ originates from the orientational order-disorder transition of the K-NH_3 pair at the octahedral site. At the low-temperature phase the pair orients to the ⟨110⟩ direction in a fashion of an antiferroelectric material, while at the high-temperature phase it takes random orientations and changes the direction dynamically. The dynamical motion of ammonia molecules was also observed in other experiments. Recent neutron inelastic scattering study reveals a sharp peak in the low-energy phonon density of states below 150 K and it increases in intensity with decreas-

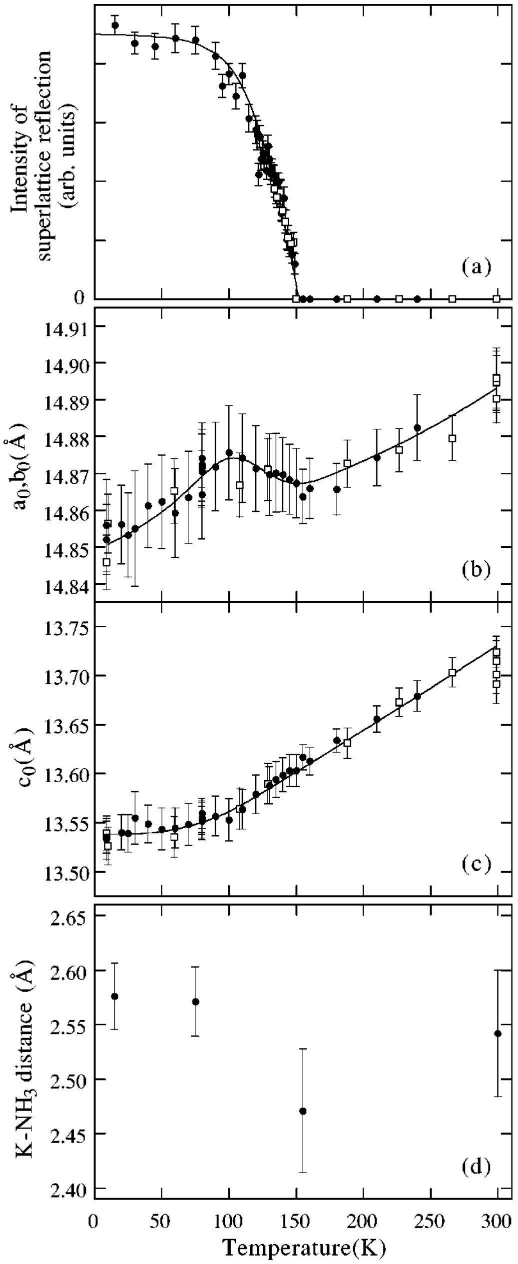

FIG. 3. (a) The temperature dependence of intensity of the (110) reflection, which is forbidden above T_s. (b) and (c) Temperature dependence of the lattice constants. The difference between a_0 and b_0 is so small that the averaged value is shown here. Open squares and filled circles are the data in cooling and heating runs, respectively. The solid lines are the guides to eyes. (d) The distances between K and NH$_3$ estimated from Rietveld refinements.

ing the temperature.[12] They suggested this peak is closely related to the libration of ammonia molecule. The appearance of the librational mode indicates the freezing of ammonia rotation. Moreover, Maniwa and Sugiura[16] observed the change in ^{1}H NMR spectra associated with the rotational motion of the threefold axis of the ammonia molecule above 100 K.

The ordered structure of the K-NH$_3$ pair in the present study (Fig. 2), 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. In this section we use the terms ''antiferroelectric'' order and ''dipole'' for the K-NH$_3$ pair, because K and NH$_3$ rotate in a pair just like a dipole around the octahedral center. The electric dipoles in a 2D array are energetically favorable for alignment parallel to each other in the direction of the dipole moment and antiparallel in the direction perpendicular to the moment, and this structure is realized in our case. When considering the 3D configuration, however, the situation becomes a little complicated. We have two configurations of dipoles, that is, one is the parallel type where the nearest-neighbor (NN) pairs in the next planes are parallel or antiparallel to those pairs on the considered plane, and the other is the perpendicular type where NN pairs are perpendicular to those pairs considered. 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. However, the perpendicular type is realized actually in (NH$_3$)K$_3$C$_{60}$; in the parallel type the (110) reflection should be forbidden, but it is observed in our case. This inconsistency is not explained yet; we have to consider any higher-order interactions.

As for the negative thermal expansion observed around T_s, we do not have a clear explanation. A possible argument is the steric effect between NH$_3$ and C$_{60}$ molecules. Namely, below T_s ammonia molecules orient with nitrogen pointing to a potassium atom and hydrogen atoms facing to C$_{60}$ molecules, and those hydrogens may act as a steric hindrance through the hydrogen bonding to C$_{60}$ molecules. Above T_s, ammonia molecules begin to rotate, which leads to a smaller effective radius of the molecule.

Next we discuss the relation between the crystal structure and the superconducting properties in ammoniated fullerides. T_c of superconducting alkali fullerides, A_3C$_{60}$, is well known to have an increasing function against the lattice constant a_0; this behavior is understood in terms of the increase of the electron density of state of the t_{1u} conduction band. In the case of ammoniated alkali fullerides the lattice constant increases from those of the pristine compounds, and a higher T_c can be expected according to the above relation. In this sense (NH$_3$)$_4$Na$_2$CsC$_{60}$ is a successful case, where T_c actually increases. However, the (NH$_3$)K$_3$C$_{60}$ is not the case, where the superconductivity disappears. This fact can be possibly understood by the structural difference, especially the local symmetry of the C$_{60}$ molecule in relation with the surrounding alkali cations and NH$_3$ molecules. In the case of the (NH$_3$)$_4$Na$_2$CsC$_{60}$, four NH$_3$ molecules form a tetrahedron whose center is occupied by an Na ion. Therefore, the local symmetry of the C$_{60}$ is T_h, which is the same as the fcc A_3C$_{60}$. This symmetry keeps the triple degeneracy of the t_{1u} molecular orbital, the density of state is increased by ammoniation, and T_c increases. On the other hand, in the case of (NH$_3$)K$_3$C$_{60}$, the local symmetry of the C$_{60}$ in the low-temperature phase is C_i, a lower symmetry than in the pristine K$_3$C$_{60}$. The symmetry reduction to C_i lifts completely the triple degeneracy of the t_{1u} molecular orbital and this may have a serious effect on superconductivity in this compound.[17]

V. CONCLUSION

In x-ray diffraction measurements of (NH$_3$)K$_3$C$_{60}$ we have found a structural phase transition at $T_s = 150$ K. The low-temperature phase has the doubled unit lattice vectors along three axes with respect to the high-temperature phase. The transition is characterized by the antiferroelectric ordering of the K-NH_3 pair at the octahedral site of C_{60} lattice, whereas above T_s the pair orients randomly to one of four equivalent directions. The superlattice intensity increases continuously below T_s, which means that the transition is second order. At $100\ \mathrm{K} < T < T_s$, a negative thermal expansion is observed along the *a* and *b* axes. This is closely related to the observed K-N interatomic distance, which shows a contraction around T_s with increasing temperature. We also discuss the disappearance of superconductivity in relation to the re-duction of the local symmetry of C_{60} molecule, which lifts the triple degeneracy of the t_{1u} orbital.

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*Present address: Kawada Research Corporation, 122-3 Yagihashi, Tsukuba, Ibaraki 305-0842, Japan.

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[17] Cs_3C_{60} is known to become a superconductor under hydrostatic pressure (Ref. 18) and the crystal structure is body-centered tetragonal in which the t_{1u} orbital lifts. However, the crystal has a disorder in the occupation of the Cs atom and it should be taken into account because the disorder of the alkali atom is considered to affect significantly to the superconductivity (Ref. 6). On the other hand, there is no disorder in $(NH_3)K_3C_{60}$ at low temperature and this enables us to extract the effect of the local symmetry on the superconductivity in alkali fullerides.

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