Structure and physical properties of Na4C60 under ambient and high pressures

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Structure and physical properties of Na$_4$C$_{60}$ under ambient and high pressures

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The structure and physical properties of two-dimensional polymeric Na$_4$C$_{60}$ (body-centered monoclinic, space group I$2/m$) are studied in a wide temperature region from 12 to 300 K at 1 bar, and in a pressure region up to 53 kbar at 300 K. The temperature dependence of lattice constants suggests a structural anomaly below 100 K where the variation of spin susceptibility is observed from electron spin resonance. The thermal expansion of the unit-cell volume $V$ is smaller than that of monomeric Rb$_2$C$_{60}$ and K$_2$C$_{60}$. The compressibility of $c$ is larger than that of $a$ and $b$, which can be well explained by the repulsion between Na ions. The compressibility of the center-to-center distance in the (101) plane is $\sim 7$ times smaller than that in the (101) plane, which can be well explained by the formation of the polymer chains. Further, a possibility of a three-dimensional polymerization is discussed on the basis of the pressure dependence of C$_{60}$...C$_{60}$ distances.

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I. INTRODUCTION

Recently, phases formed through a polymerization of C$_{60}$ were discovered in metal intercalated C$_{60}$.$^{1-17}$ First, AC$_{60}$ (A = K, Rb, and Cs) forms a one-dimensional (1D) polymer between C$_{60}$ molecules through [2 + 2] cycloaddition to lead a four-membered ring.$^{1-8}$ AC$_{60}$ shows interesting properties characteristic of 1D organic conductors. The polymer phases of RbC$_{60}$ and CsC$_{60}$ are metallic above 50 K, and transform to an insulating state below 50 K. The electron spin resonance (ESR) shows that the transition is based on the instability of the 1D metal through a spin-density-wave.$^{4-8}$

Second, a metastable phase of AC$_{60}$ forms a (C$_{60}$)$_2^-$ dimer with a single C-C bond.$^{4,7-12}$ This phase is realized by quenching fcc AC$_{60}$ from 500 K to temperatures below 270 K. ESR and optical studies suggested a diamagnetic insulating ground state for the metastable phase of AC$_{60}$.$^{9,10,13}$ Third, Na$_2$RbC$_{60}$ forms a 1D polymer of C$_{60}$ connected by a single C-C bond.$^{14,15}$ It is known that Na$_2$RbC$_{60}$ is a cubic fullerene superconductor with superconducting transition temperature ($T_c$) of 3.4 K at 1 bar, and loses cubic symmetry at a modest pressure below 3 kbar.$^{16}$ Recently, Bendele et al. found that Na$_2$RbC$_{60}$ loses its cubic symmetry and forms a 1D polymer with the single C-C bonds when cooling slowly to temperatures below 230 K.$^{14,15}$ This transition was confirmed by $^{13}$C and $^{23}$Na NMR experiments.$^{17}$ Fourth, Na$_4$C$_{60}$ forms a 2D polymeric phase with a body-centered-monoclinic (bcm) structure of space group $I2/m$. In this phase, the C$_{60}$ molecules are connected through single C-C bonds in the (101) plane.$^{18}$ This phase exhibits a metallic behavior, contrary to other insulating AC$_{60}$ phases,$^{19-22}$ and transforms to a nonmagnetic phase (body-centered-tetragonal (bct): $I4/mmm$) at 500 K,$^{23}$ whose structure is the same as those of K$_2$C$_{60}$ and Rb$_2$C$_{60}$.$^{24,25}$ ESR shows that this phase transition is a metal-metal transition.$^{26}$ The metallic behavior of Na$_4$C$_{60}$ can be reasonably explained by smaller lattice constants than those of the other AC$_{60}$, which are understood as the nonmagnetic molecular Jahn-Teller Mott insulator.$^{26,27}$ Further, the temperature dependence of spin susceptibility $\chi_{\text{spin}}$ of Na$_4$C$_{60}$ estimated from ESR shows a transformation from temperature-independent (Pauli-like) behavior to a rapidly increasing one below 100 K, and a further rapidly decreasing one below 20 K.$^{18}$

The first purpose of the present study is to search for a structural transition below 100 K from the temperature dependence of the x-ray diffraction of Na$_4$C$_{60}$ at 1 bar, in order to clarify the origin of the magnetic transition. The second purpose is to search for phases in Na$_4$C$_{60}$ under pressure and to study the structures and physical properties of 2D polymeric Na$_4$C$_{60}$ under pressure.

II. EXPERIMENT

The Na$_4$C$_{60}$ sample was prepared by annealing stoichiometric amounts of C$_{60}$ and Na metal for 100 h at 723 K under a vacuum of $10^{-5}$ Torr; a trace of benzene contained in C$_{60}$ powder was removed before annealing. The sample was introduced into a glass capillary for Raman and x-ray-diffraction measurements at 1 bar, into diamond-anvil cells for x-ray-diffraction measurements under pressure, and into a quartz tube for ESR measurement at 1 bar. ESR spectra were recorded from 290 to 16 K with a Bruker ESP300 ESR spectrometer. The temperature was regulated within $\pm 1$ K with an Oxford He flow Cryostat (ESR910). The spin susceptibility $\chi_{\text{spin}}$ was determined by comparing the integrated intensity of the ESR for the sample with that for CuSO$_4$5H$_2$O ($\chi_{\text{spin}} = 6.00 \times 10^{-6}$ emu/g at 290 K).$^{28}$ The raman spectrum was measured by using an ISA Confocal LABRAM system at an excitation of 632.8 nm with a He-Ne laser. The x-ray-diffraction pattern was measured with synchrotron radiation at the BL-1B in the Photon Factory of High Energy Accelerator Research Organization (KEK-PF). The wavelengths $\lambda$ used for the x-ray-diffraction measurements were 1.002(2) Å in a temperature region below 300 K at 1 bar, and 0.6904(1) Å in a pressure region from 1 bar to 53 kbar at 300 K.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show a Raman peak for a C$_{60}$ intramolecular Ag(2) mode, and an x-ray-diffraction pattern at
electron transfer to C$_{60}$ results in a redshift of 7 cm$^{-1}$ employed; the C$_{60}$ molecule is centered on the origin of the coordinates of 60 C atoms in a C$_{60}$ molecule were generated by the symmetry operations of the monoclinic lattice, where the a, b, c, and β reported in Ref. 18 were employed; the C$_{60}$ molecule is centered on the origin of the unit cell. Fourth, the coordinates of independent 30 C atoms were chosen in the I2/m lattice, where a disordered C$_{60}$ molecule related by a twofold rotation axis along b was automatically formed by the symmetry operations of the I2/m; the Eulerian angles are ψ = −124.7°, θ = 154.2°, and φ = −130.9°. As reported by Oszlanyi et al., it is difficult to distinguish the space groups of I2/m and P211/n based on the x-ray powder diffraction pattern. Consequently, we adopted the space group I2/m in the analysis of x-ray-diffraction pattern according to Oszlanyi et al. The Na ions were located at 4h and 4i. The Rietveld refinement was performed by using a Rietan 94 program. The lattice constants a, b, c, and β, were determined to be 11.24(1), 11.71(1), 10.25(1) Å, and 96.08(4)°, respectively, in good agreement with those reported previously. The occupancy factors of the Na atoms at 4h and 4i were 0.99(3) and 0.92(2), respectively. Therefore, the sample used in this study is Na$_{3.82}$C$_{60}$ comparable to the sample used by Oszlanyi et al., Na$_{3.72}$C$_{60}$. In this analysis, the isotropic displacement parameter B for Na and C atoms were fixed to the previous ones. The atomic coordinates of C atoms were not refined, but these were adjusted to the new a, b, c, and β to maintain the first molecular geometry. Though we tried to determine the exact C$_{60}$ geometry by taking into account the distortion of C$_{60}$ mol-

TABLE I. Structural parameters from Rietveld analysis for Na$_{3.82}$C$_{60}$ at 1 bar and 300 K. The space group is I2/m. The lattice parameters are $a = 11.24(1)$, $b = 11.71(1)$, and $c = 10.25(1)$ Å, and $β = 96.08(4)°$. The final weighted pattern $R$ factor $R_{wp} = 0.061$, and the final integrated intensity $R$ factor $R_I = 0.024$.

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<th>z</th>
<th>Occupancy</th>
<th>B (Å$^2$)</th>
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FIG. 1. (a) Raman peak of the C$_{60}$ intramolecular Ag(2) mode, and (b) the x-ray-diffraction pattern at 300 K under a pressure of 1 bar [$\lambda = 0.6904(1)$ Å]. The observed data are denoted by the data points (+ symbols), and the calculated plots are by the solid lines. In (b), the allowed peak positions and the difference between the observed and calculated patterns are drawn by ticks and the solid line, respectively. Two peaks due to the sample holder are shown by asterisks. In the Rietveld refinement shown in (b), the final weighted pattern $R$ factor $R_{wp} = 0.061$, the final integrated intensity $R$ factor $R_I = 0.024$, and the goodness of fit $S = 1.7$; $S$ is the ratio of $R_{wp}$ to the expected $R$ factor, $R_{exp}$, and a measure of the adequacy of the model used in the refinement.
The position of C\textsubscript{60} molecules are denoted by small white balls in (a) and by C atoms in (b). (c) [100] and (d) [001] projections of the unit cell; Na atoms are denoted by balls. The black and gray balls refer to the Na atoms at 4\textit{h} and 4\textit{i}, respectively.

FIG. 2. (a) The bcm unit cell, and (b) the view along the [001] direction of the unit cell; C\textsubscript{60} molecules are denoted by white balls in (a) and by C atoms in (b). (c) [100] and (d) [001] projections of the unit cell; Na atoms are denoted by balls. The black and gray balls refer to the Na atoms at 4\textit{h} and 4\textit{i}, respectively.

The center-to-center distance between C\textsubscript{60} molecules along the molecular symmetry of C\textsubscript{60} was not taken into account in this analysis. Consequently, the lowering in the molecular symmetry of C\textsubscript{60} was not taken into account in this analysis. Finally, for Na atoms, y at 4\textit{h}, and x and z at 4\textit{i} were refined. The final structural parameters are listed in Table I.

Figures 2(a) and 2(b) show the bcm unit cell of Na\textsubscript{4}C\textsubscript{60}. The position of C\textsubscript{60} molecules are denoted by small white balls in Fig. 2(a). The arrangement of the C\textsubscript{60} molecules viewed along the [001] plane. The nearest center-to-center distance between the C\textsubscript{60} molecules is 9.28 Å, which is slightly larger than those for 1D polymeric AC\textsubscript{60} formed by [2 + 2] cycloaddition (9.14 Å for RbC\textsubscript{60} and 9.11 Å for KC\textsubscript{60}).

However, the distance in Na\textsubscript{4}C\textsubscript{60} is slightly smaller than that in AC\textsubscript{60} dimer and Na\textsubscript{2}RbC\textsubscript{60} polymer phases with a single C-C bond [9.34 Å for RbC\textsubscript{60} and KC\textsubscript{60} and 9.35 Å for Na\textsubscript{2}RbC\textsubscript{60} (Ref. 14)]. The center-to-center distance between C\textsubscript{60} molecules along the \{111\} directions in the (101) plane is 9.91 Å, which implies van der Waals contacts. The value is smaller than that of monomeric Na\textsubscript{2}C\textsubscript{60} (10.02 Å) (Refs. 31 and 32).

Figures 2(c) and 2(d) show the [100] and [001] projections, respectively, of the bcm unit cell in which Na atoms at 4\textit{h} and 4\textit{i} are denoted by black and gray balls, respectively. The first nearest distance between Na atoms, 4.54(8) Å, is found between the Na atoms at 4\textit{i} in the (010) plane. The value is close to the sum of van der Waals radius (2.27 Å) (Ref. 34) of the Na atom. The second-nearest Na- Na distance is 4.81(7) Å between Na atoms at 4\textit{h} in the (100) plane. The bonds formed between the C\textsubscript{60} molecules are shown for two possible orientations in Figs. 3(a) and 3(b). The C- C distance between C\textsubscript{60} molecules is 2.18 Å for both orientations. The long C-C distance is caused because the distortion of C\textsubscript{60} molecule is not taken into account in this Rietveld refinement. If the exact C\textsubscript{60} geometry can be determined, the C-C distance would become short as that determined in the Na\textsubscript{3}RbC\textsubscript{60} polymer phase, ~1.7 Å. The molecular conformations around the C- C bonds are reasonable for both orientations. These results mean that the polymer chain can be formed between the C\textsubscript{60} molecules with two possible orientations which are randomly distributed with 50% probability in the unit cell. The first and the second nearest C- C distances between the C\textsubscript{60} molecules in the (101) plane are 3.24 and 3.26 Å, respectively, for the same orientation while 3.01 and 3.20 Å for the different orientation. These values are comparable to the first nearest C- C distances in the monomeric Na\textsubscript{2}C\textsubscript{60} (3.15 Å), K\textsubscript{5}C\textsubscript{60} (3.14 Å), Rb\textsubscript{3}C\textsubscript{60} (3.32 Å), and C\textsubscript{60} (3.15 Å). The ESR spectra were analyzed by a least-squares fitting with a single Lorentzian function from 16 to 290 K. The \(\chi_{\text{spin}}\), the peak-to-peak linewidth \(\Delta H_{\text{pp}}\), and the g factor were estimated to be \(1.4 \times 10^{-4}\) emu/mol, 1.7 G, and 2.0012 at 290 K, respectively. The value of \(\chi_{\text{spin}}\) is consistent with that reported previously, \(1.7 \times 10^{-4}\) emu/mol.\textsuperscript{18} The density of state \(N(e_F)\) is 2 state/eV-spin-C\textsubscript{60}, suggesting a broad bandwidth. \(N(e_F)\) is smaller than the densities of states of monomeric fullerides (14 state/eV-spin-C\textsubscript{60} for K\textsubscript{2}C\textsubscript{60} and 19 state/eV-spin-C\textsubscript{60} for Rb\textsubscript{2}C\textsubscript{60}).\textsuperscript{37} The broad bandwidth in Na\textsubscript{4}C\textsubscript{60} can be explained by the small C\textsubscript{60}-C\textsubscript{60} distance due to the formation of the polymer chain. However, the \(N(e_F)\) of Na\textsubscript{4}C\textsubscript{60} is smaller than that of the polymeric Na\textsubscript{2}RbC\textsubscript{60} with single C-C bonds (11 state/eV-spin-C\textsubscript{60} from \(\chi_{\text{spin}}= 9.5 \times 10^{-4}\) emu/mol).\textsuperscript{38} Though the center-to-center distance between C\textsubscript{60} molecules is almost the same between Na\textsubscript{4}C\textsubscript{60} and Na\textsubscript{2}C\textsubscript{60}.}
Na$_2$RbC$_{60}$, as described previously, two dimensionality in
Na$_4$C$_{60}$ may result in band broadening, i.e., samll N($\epsilon_p$).

Figures 4~a, 4~b, 4~c, and 4~d show the temperature
dependence of the $\chi_{\text{spin}}$, $\Delta H_{\text{pp}}$, $g$ factor, and $\Delta H_{\text{pp}}/(\Delta g)^2$,
respectively: $\Delta g = g - 2.0023$. The $\chi_{\text{spin}}$ shows a slight
decrease with an increase in temperature above 100 K, suggesting
that the phase is metallic (a Pauli-paramagnetic state).
The $\chi_{\text{spin}}$ increases rapidly with a decrease in temperature
from 80 to 40 K, and decreases abruptly below 40 K. Such a
temperature dependence can also be found in a figure (Fig. 4)
of Ref. 18 though Oszlanyi et al. did not comment on it. The values of $\Delta H_{\text{pp}}$ and $\Delta H_{\text{pp}}/(\Delta g)^2$ decrease rapidly when de-
creasing temperature from 300 to 200 K [see the insets of
Figs. 4(b) and 4(c)], and decrease slightly with a decrease in
temperature from 200 to 100 K. Further, slopes of the plots of $\Delta H_{\text{pp}}$ and $\Delta H_{\text{pp}}/(\Delta g)^2$ versus temperature change at 100
K. The $g$ factor is constant above 80 K, and shows a rapid
decrease below 100 K. These results suggest a transition of the
Pauli-paramagnetic state below 100 K. The temperature
dependence of $\Delta H_{\text{pp}}$ below 100 K is different from that of the
1D polymeric phase of RbC$_{60}$, in which $\Delta H_{\text{pp}}$ increases
rapidly with a decrease in temperature below the transition
temperature (50 K). The ground state in RbC$_{60}$ is interpreted
as an antiferromagnetic state, like that below 30 K in
CsC$_{60}$. On the other hand, the transition observed in
Na$_2$C$_{60}$ may be attributed to the charge-density-wave
(CDW)-type dimerization (spin singlet) because the tempera-
ture dependence of $\chi_{\text{spin}}$ and $\Delta H_{\text{pp}}$ decreases rapidly with a
decrease in temperature below 50 K. A (spin-Peierls) non-
magnetic ground state is realized below 13.8 K in the 1D
polymeric CsC$_{60}$, and the nonmagnetic state coexists with
the magnetic ordered state which is realized below 30 K. If

FIG. 4. Plots of (a) $\chi_{\text{spin}}$, (b) $\Delta H_{\text{pp}}$, (c) the $g$
factor, and (d) $\Delta H_{\text{pp}}/(\Delta g)^2$ vs temperature.

FIG. 5. X-ray-diffraction patterns at (a) 70 K and (b) 12 K under
a pressure of 1 bar [\(\lambda = 1.1002(2) \text{ Å}\)]. The observed data are de-
noted by the data points (+ symbols), and the calculated plots are
by the solid lines. The weak peak at \(-12.5^\circ\) found in (a) and (b)
was assigned to pristine C$_{60}$ (<5%). The pristine C$_{60}$ was found
only in a batch used for temperature-dependent x-ray-diffraction
measurement. The allowed peak positions and the difference be-
tween the observed and calculated patterns are drawn by ticks and
solid lines, respectively.

$R_{wp}$ = 0.089, $R_I$ = 0.036, and $S$ = 1.8 at 70
K, and $R_{wp}$ = 0.086, $R_I$ = 0.028, and $S$ = 1.7 at 12 K.
the transition in Na$_4$C$_{60}$ can be assigned to CDW-type dimerization through the electron-phonon interaction, the structural change may be observed around 50 K. Recently, a structural anomaly was observed around 14 K in CsC$_{60}$. Figures 5(a) and 5(b) show x-ray-diffraction patterns at 70 and 12 K as typical examples observed in a low-temperature region at 1 bar. The x-ray-diffraction patterns were analyzed according to the same procedure as that at 300 K, except for that B’s for Na atoms were refined. All x-ray-diffraction patterns from 12 to 280 K can be indexed with $I_{2/m}$. The temperature dependence of $a$, $b$, $c$, and $\beta$ and the unit-cell volume $V$, are shown in Figs. 6(a)–6(e). The temperature dependence of $a$, $b$, and $V$ show a discontinuity at 50 K which corresponds to the temperature exhibiting the maximum in $\chi_{\text{spin}}$. The plots of $c$ also show a decrease below 50 K. These results are similar to those observed for lattice constants in the 1D polymeric phase of CsC$_{60}$. The structural anomaly observed below 14 K for CsC$_{60}$ is interpreted as an indication of a spontaneous strain which appears along the polymer chain axis and the interchain direction. Further, the strain was related to the appearance of a nonmagnetic state and magnetoelastic coupling between the localized spin on C$_{60}$ and the (spin-Peierls) phonon degrees of freedom. The anomaly of the lattice constants observed in Na$_4$C$_{60}$ around 50 K may also be assigned to such a spontaneous strain that is expected in CDW-type dimerization. Therefore, this structural anomaly may be related to a transition from the Pauli-paramagnetic state suggested by ESR. Plots of $b$, $c$, and $V$ in Na$_4$C$_{60}$ show a small and continuous increase with a decrease in temperature below 100 K. To confirm the discontinuous variation of $V$ around 50 K, curve fitting was performed by a Grüneisen relation within the Debye approximation [Fig. 6(e)]. $V$ below 50 K could not be fitted by the Grüneisen relation, as seen from Fig. 6(e). This also suggests a structural change around 50 K. However, $\beta$ decreases monotonically with a decrease in temperature in the temperature region below 200 K. Further, new Bragg reflections were not found below 100 K, as in Cs$_3$C$_{60}$. Consequently, these data do not allow one to conclude the structural transition around 50 K clearly. Further study on the structure in the low-temperature region should be performed by single-crystal x-ray diffraction and neutron diffraction.

Negative thermal expansion below 100 K can result in an increase in $N(\varepsilon_F)$ with a decrease in temperature because of the decrease in the transfer integral $t$ between the C$_{60}$ molecules, leading to an increase in $\chi_{\text{spin}}$. However, the large increase in $\chi_{\text{spin}}$ observed in ESR from 80 to 40 K cannot be explained by such a lattice expansion, because the difference
FIG. 7. Plots of the center-to-center distance between the C_{60} molecules in (a) (10\bar{1}) and (b) (101) planes vs the temperature.

in V between 50 and 120 K is very small [1347.6(4) Å² for V at 50 K and 1347.1(4) Å² at 120 K].

The plots of the center-to-center distances between C_{60} molecules in the (10\bar{1}) and (101) planes are shown in Figs. 7(a) and 7(b). The center-to-center distance in the (10\bar{1}) plane, which is associated with the polymer chain, increases slightly with an increase in temperature above 200 K, and is constant from 120 to 200 K. Further, the value increases with a decrease in temperature below 120 K, and shows a maximum at 50 K. The value at 50 K is larger than that at 280 K. The value shows a discontinuous and rapid decrease at 40 K. On the other hand, the center-to-center distance in the (101) plane shows a large increase above 140 K and a discontinuous and rapid decrease at 40 K. These results also reflect the structural anomaly below 100 K. The center-to-center distances between the C_{60} molecules in the (10\bar{1}) and (101) planes at 12 K are 9.296(1) and 9.911(1) Å, respectively. Further, β does not reach 90° even at 12 K [β=95.88(1)° at 12 K]. These results imply that the possibility of the 3D polymerization can be neglected in the temperature region studied at 1 bar.

Figures 8(a) and 8(b) show x-ray-diffraction patterns under pressures of 22 and 51 kbar, respectively, at 300 K, which can be indexed with \#12/m as in the x-ray-diffraction pattern at 1 bar. All x-ray-diffraction patterns under pressure were analyzed according to the same procedure as that at 1 bar, except for that B’s for Na atoms were refined. The pressure dependence of a, b, c, β, and V are shown in Figs. 9(a)–9(e). The linear compressibility \( \kappa \) was determined for Na_{4}C_{60} because the linear extrapolation is applicable for the pressure dependence of the lattice constants in the pressure region below 53 kbar studied here. The \( \kappa \)'s of a \([2.16(1) \times 10^{-4}\text{ kbar}^{-1}]\), b \([3.38(2) \times 10^{-4}\text{ kbar}^{-1}]\), and c \([8.8(1) \times 10^{-4}\text{ kbar}^{-1}]\) in Na_{4}C_{60} are smaller than those of monomeric fullerenes \([1.7 \times 10^{-3}\text{ kbar}^{-1}\text{ for Na}_{2}C_{60}, 1.20(9) \times 10^{-3}\text{ kbar}^{-1}\text{ for K}_{3}C_{60}, 1.52(9) \times 10^{-3}\text{ kbar}^{-1}\text{ for Rb}_{3}C_{60}, 2.3(2) \times 10^{-3}\text{ kbar}^{-1}\text{ or } 2.7 \times 10^{-3}\text{ kbar}^{-1}\text{ for C}_{60}\text{ (Refs. 42–44)}]\). Further, the \( \kappa \) of V of Na_{4}C_{60} \([1.37(3) \times 10^{-3}\text{ kbar}^{-1}\text{ for Na}_{2}C_{60}, 41 1.20(9) \times 10^{-3}\text{ kbar}^{-1}\text{ for K}_{3}C_{60}, 42 1.52(9) \times 10^{-3}\text{ kbar}^{-1}\text{ for Rb}_{3}C_{60}, 42 and 2.3(2) \times 10^{-3}\text{ kbar}^{-1}\text{ or } 2.7 \times 10^{-3}\text{ kbar}^{-1}\text{ for C}_{60}\text{ (Refs. 42–44)}]\), is smaller than the \( \kappa \)'s of Na_{2}CsC_{60} (6.4 \times 10^{-3}\text{ kbar}^{-1}), 43 and Li_{2}CsC_{60} (2.6 \times 10^{-3}\text{ kbar}^{-1}), 46 which polymerize through 1D C-C single bonds. It can be deduced as a first approximation that the values of \( \kappa \) in Na_{4}C_{60}, smaller than those of monomeric and 1D polymeric fullerenes, originate from the formation of the 2D polymer chains.

The \( \kappa \) of c in Na_{4}C_{60} is larger than the \( \kappa \)'s of a and b. The small \( \kappa \) of b may be ascribed to the formation of a polymer chain. However, the difference in \( \kappa \) between c and a cannot be explained by the formation of polymer chains between C_{60} molecules because the effect contributes almost equally to a and c. The small \( \kappa \) of a can be ascribed to the close Na···Na contact along the [100] direction in the (010) plane \([4.54(8) \text{ Å at 1 bar and } 300 \text{ K}]\). The Na···Na distance along the [001] direction \([10.25(8) \text{ Å at 1 bar and } 300 \text{ K}]\) is twice as large as that along the [100] direction. Thus the small repulsion between Na atoms along the [001] direction results in the large \( \kappa \) of c. Further, the second close Na···Na distance along the [010] direction \([4.81(7) \text{ Å at 1 bar and } 300 \text{ K}]\) can contribute to the small \( \kappa \) of b. In fact, the values of \( \kappa \) increase with an increase in the Na···Na distance. On the other hand, the closest Na···C distances between the Na
atom and the C\textsubscript{60} molecule along the [100], [010] and [001] directions are 2.80(4), 2.70(4) and 2.71(4) \AA, respectively, at 300 K under a pressure of 1 bar. These values are close to the sum of the ionic radius of Na\textsuperscript{+} (1.16 \AA for a coordination number of 6),\textsuperscript{47} and the van der Waals radius of the C atom (1.70 \AA).\textsuperscript{34} The difference in the Na\textsuperscript{+}-C distance cannot be related to the difference in the \(k\) of \(a\), \(b\), and \(c\).

The pressure dependence of the Na\textsuperscript{+}-Na distance in the (010) plane is shown in Fig. 10(a). The Na\textsuperscript{+}-Na distance shows a substantial linear decrease with an increase in pressure up to 53 kbar. The distance is 3.8(2) \AA at 49 kbar, which is larger than that of the Na\textsubscript{12} cluster in Na\textsubscript{12}C\textsubscript{60}, 2.78 \AA.\textsuperscript{48} Figure 10(b) shows the pressure dependence of the center-to-center distances between the neighboring C\textsubscript{60} molecules in the (101) and (010) planes. The distances in the (101) and (010) planes are dominated by the chemical bond forming the polymer chains and the van der Waals contacts between the C\textsubscript{60} molecules, respectively. The distance in the (101) plane shows a rapid decrease in comparison with that in the (101) plane. \(k\) of the center-to-center distance between the C\textsubscript{60} molecules in the (101) plane \(2.11(1) \times 10^{-4}\) kbar\textsuperscript{-1} is \(\sim \frac{1}{2}\) smaller than that \(6.55(7) \times 10^{-4}\) kbar\textsuperscript{-1} in the (101) plane. The small \(k\) can be directly related to the formation of the polymer chain.

As seen from the inset in Fig. 10, the extrapolation with the Murnaghan EOS,\textsuperscript{49,50} which can be applied in a high-pressure region, for the plots of the C\textsubscript{60}···C\textsubscript{60} center-to-center distances in the (10\overline{1}) and (010) planes versus pressure, shows that these distances approach each other with an increase in pressure. The center-to-center distance in the (010) plane at 150 kbar is estimated from the extrapolation to be 9.28 \AA which is consistent with the distance in the (10\overline{1}) plane at 1 bar. This result implies the formation of polymer chains in both planes at 150 kbar. On the other hand, the C\textsubscript{60}···C\textsubscript{60} distance in the (10\overline{1}) plane is estimated to be 8.95 \AA at 150 kbar. Consequently, a 3D anisotropic polymeric phase, with two types of polymer chains, may be realized above 150 kbar. As seen from Fig. 9(d), \(\beta\) decreases straightforwardly up to 53 kbar. This corresponds to the fact that both distances approach each other with an increase in pressure. However, \(\beta\) is expected not to reach to 90° at 150 kbar, judging from the extrapolation for the C\textsubscript{60}···C\textsubscript{60} distances. The C-C distances at 150 kbar are expected to be 1.9 \AA in the (10\overline{1}) plane and 2.6 \AA in the (010) plane. The distances realized at 150 kbar should be shorter than the above values because in this analysis the distortion of C\textsubscript{60} molecule from \(I_h\) symmetry is not considered. However, the C-C distance in
The temperature dependence of $x_{\text{spin}}$, $\Delta H_{\text{pp}}$, the $g$ factor, and $\Delta H_{\text{pp}}/(\Delta g)^2$ estimated from ESR showed a clear change below 100 K. The structural anomaly around 50 K, indicated from the temperature dependence of lattice constants, may be related to the change in the ESR. If the ground state below 50 K is a CDW-type nonmagnetic state, as expected from ESR, the structural change accompanied by the transformation from a polymer to a dimer may be observed in the powder x-ray-diffraction pattern. Though a structural anomaly is indicated around 50 K, definitive evidence for a structural transition, such as the appearance of new Bragg reflections, was not found from the x-ray diffraction.

The pressure dependence of lattice constants showed a smaller $\kappa$ than those of monomeric and 1D single C-C polymeric fullerides.\textsuperscript{41–43,45,46} It was found that the $\kappa$ of lattice constants was governed by the Na$\cdots$Na repulsion. The $\kappa$ of the center-to-center distance between C$_{60}$ molecules in the polymer chain was $\sim \frac{1}{2}$ smaller than that between the $\kappa$’s in contact with the van der Waals interaction. The formation of two types of polymer chains in Na$_4$C$_{60}$ around 150 kbar is expected from the extrapolation with the Murnaghan EOS for the pressure dependence of the C$_{60}$·C$_{60}$ center-to-center distances in (101) and (101) planes. Further, the 3D isotropic polymer phase may also be realized through a structural transition. If the 3D polymerized phase of Na$_4$C$_{60}$ can be realized, the phase should exhibit a metallic behavior and an extremely small $N(\varepsilon_f)$. This phase is very interesting from the viewpoint of a comparative study of the monomeric bct phase (metallic) of Na$_4$C$_{60}$, which is realized above 500 K.\textsuperscript{23}

**IV. CONCLUSIONS**

The authors acknowledge Y. Iwasa and T. Mitani of JAIST for the opportunity to use Raman equipment. We are grateful to K. Ishii and A. Fujiwara of University of Tokyo, and to Y. Murakami and H. Nakao of KEK-PF, for their valuable discussion in x-ray-diffraction measurements under high pressure. The x-ray-diffraction study was performed under a proposal of KEK-PF (99G032). This work was supported by a Grant-in-Aid (11165227) from the Ministry of Education, Science, Culture and Sports, Japan.

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