

## Superconductivity of fcc fullerides containing off-centered octahedral cations

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Low-temperature synthesis in liquid ammonia yielded the superconductors  $(\text{NH}_3)_x\text{NaA}_2\text{C}_{60}$  ( $0.5 < x < 1$ ,  $A = \text{K}$  and  $\text{Rb}$ ). These compounds retained the fcc cell with a tunable lattice constant around  $a = 14.37 \text{ \AA}$  and  $a = 14.52 \text{ \AA}$  for  $\text{K}$  and  $\text{Rb}$  compounds, respectively, by controlling the ammonia concentration  $x$ .  $T_c$  of both compounds decreases with increasing lattice parameter, in a striking contrast with the empirical correlation. A  $\text{Na-NH}_3$  cluster occupies the octahedral interstice and remaining  $\text{K}$  or  $\text{Rb}$  occupies the tetrahedral site. The  $\text{Na}$  ion is displaced by  $0.4\text{--}0.6 \text{ \AA}$  from the center of the octahedral site. [S0163-1829(96)52146-6]

$\text{C}_{60}$  is regarded as an element for constructing new solids of interesting properties. Among various kinds of intercalated  $\text{C}_{60}$  compounds, high- $T_c$  superconductivity is observed in alkali metal intercalated materials with  $\text{C}_{60}$  molecules.<sup>1,2</sup> While the observed superconductivity is well explained by the BCS weak coupling theory, a fundamental question remains to be solved; that is, the conditions for the occurrence of superconductivity, in other words, structural and electronic constraint for superconductors. In alkali metal intercalated  $\text{C}_{60}$ , for instance, superconductivity appears only at the 3- reduction state and in face centered cubic (fcc) or simple cubic structures, although there exist various kinds of materials.<sup>3</sup> Meanwhile, superconductivity is observed at highly reduced states when alkali earth metals<sup>4</sup> or rare earth metals<sup>5</sup> are intercalated.

As to the alkali intercalated  $\text{C}_{60}$  superconductors, one of the current important issues is the search for new materials with large lattice parameters and their electronic properties. This is motivated by the well-known correlation between  $T_c$  and cell dimensions;<sup>6-8</sup>  $T_c$  increases with lattice parameters, in accord with the BCS theory. Further expansion of lattice produces a new question: Whether  $T_c$  increases following the empirical relation or electrons are localized due to too much band narrowing. An effective method to expand the unit cell is the intercalation of neutral molecules, which was first demonstrated by Zhou, Rosseinsky, and co-workers. Zhou *et al.* showed that ammoniation of  $\text{Na}_2\text{CsC}_{60}$  increased  $T_c$  from 10.5 to 29.6 K forming  $(\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}$ .<sup>9</sup> Reaction of  $\text{K}_3\text{C}_{60}$  with  $\text{NH}_3$ , on the other hand, resulted in a disappearance of superconductivity.<sup>10</sup> This compound was found to undergo a metal-insulator transition at about 40 K,<sup>11</sup> but the superconductivity recovers by application of high pressure.<sup>12</sup>

These results indicate that ammoniation is useful to study not only high- $T_c$  fullerides but also the superconductor-insulator boundary in a large lattice parameter region. Here we report synthesis and structure of superconductors  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$  ( $x \sim 0.5\text{--}1.0$ ).

$(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$  were synthesized by a reaction of stoichiometric amount of alkali metals and  $\text{C}_{60}$  powders in liquid ammonia.<sup>13</sup> An evacuated glass tube with alkali metals and  $\text{C}_{60}$  were cooled by a dry-ice/acetone slush. Liquid ammonia was condensed into the tube through a vacuum line. The tube was shaken until both alkali metals and  $\text{C}_{60}$  powders completely dissolved into liquid ammonia. After 30 min, ammonia was slowly evaporated from the solution, followed by drying powders under vacuum for half an hour. We found that the ammonia concentration  $x$  and thus the lattice parameters can be changed with varying temperatures at the drying process. Here we denote the three samples of  $\text{Rb}$  compounds by RA, RB, and RC, and the three  $\text{K}$  compounds by KA, KB, KC. The A, B, and C samples were dried at 190 °C, and 120 °C, and room temperature, respectively. Then the obtained powders were evacuated to  $2 \times 10^{-6}$  Torr and sealed under He of 150–200 Torr. Samples A and B were annealed at 100 °C for about a week.

Preliminary estimation of  $x$  was made by  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR). The  $x$  values estimated by NMR, tabulated in Table II, were smaller than or almost equal to 1, being unexpectedly small in comparison with  $(\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}$ ,<sup>9</sup> when one considers that the new compounds were synthesized in liquid ammonia.

X-ray diffraction (XRD) patterns were measured using 12 kW  $\text{Cu-K}\alpha$  radiation, and are shown for three samples of  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$  in Fig. 1. All patterns are indexed as single phase fcc. Three  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  samples also showed fcc patterns. The lattice parameters are summarized in Table II. These x-ray results indicate that less than one molecule of  $\text{NH}_3$  per  $\text{C}_{60}$  stabilizes the cubic structure of fulleride compounds involving one small  $\text{Na}$  metal and two large alkali metals, which have never been synthesized by a direct reaction of alkali vapor and  $\text{C}_{60}$  powders. The observed lattice parameters are significantly large comparing with those of hypothetical  $\text{NaK}_2\text{C}_{60}$  ( $a = 14.13 \text{ \AA}$ ) and

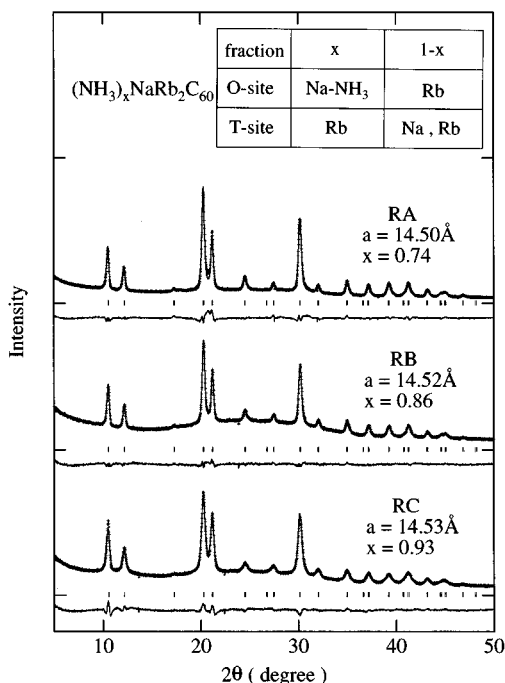


FIG. 1. 300 K powder x-ray diffraction patterns for three samples of  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$  collected with Cu-K $\alpha$  radiation produced by a rotating anode source. The crosses are experimental points and the solid lines are Rietveld fits to the model described in the text, with the differences shown on the same scale beneath the experimental and calculated patterns. Ticks mark the positions of the allowed reflections. The table in the inset shows the site occupation of alkali ions and ammonia molecules.

$\text{NaRb}_2\text{C}_{60}$  ( $a = 14.21 \text{ \AA}$ ) estimated by averaging the  $a$  values of  $\text{A}_3\text{C}_{60}$  and  $\text{Na}_2\text{AC}_{60}$ ,<sup>8</sup> where  $A = \text{K}$  and  $\text{Rb}$ .

Figure 2 shows the temperature dependence of magnetization of  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$ , measured at a field of 10 Oe using a superconducting quantum interference device magnetometer. The shielding fractions at 5 K were larger than 40% for all samples, providing unambiguous evidence for bulk superconductivity. The onset temperature changes with the temperature at which samples were dried.

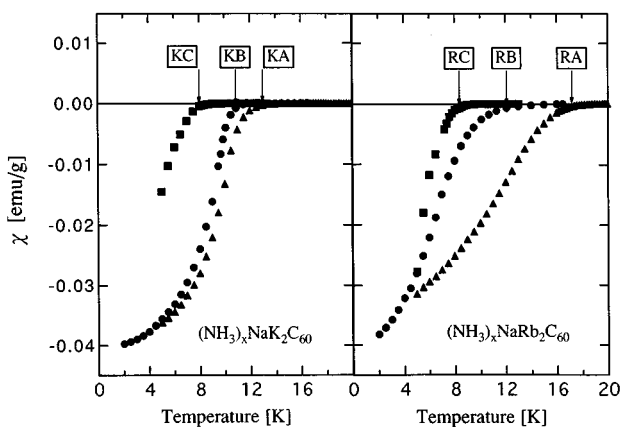


FIG. 2. Temperature dependence of zero-field-cooled susceptibility for  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$ . Three samples for each system have different ammonia composition  $x$ .

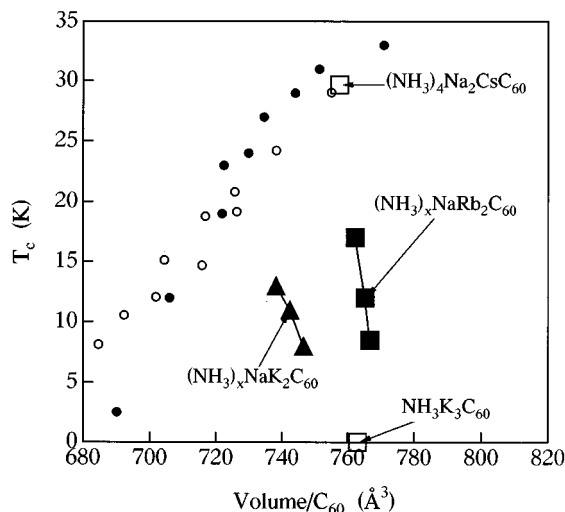


FIG. 3. Relation between  $T_c$  and volume  $V$  per  $\text{C}_{60}$  for fullerene compounds containing ammonia molecules. Small open and filled circles are plots for  $\text{A}_3\text{C}_{60}$  superconductors from Refs. 7 and 8, respectively, showing a conventional relation between  $T_c$  and  $V$ .

The relation between  $T_c$  and volume  $V$  per  $\text{C}_{60}$  is plotted for  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$  in Fig. 3. In this figure, we plotted the conventional  $T_c$ - $V$  relation of fullerene compounds.<sup>6-8</sup> Noteworthy is that the  $T_c$ 's of  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$  are dramatically lower than the empirical relation and that  $T_c$ 's decrease with increasing lattice parameters in sharp contrast with the conventional relation. Open squares in Fig. 3 show the already known ammoniated compounds. The plot for  $(\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}$  falls on the empirical  $T_c$ - $V$  curve.<sup>9</sup> On the other hand, superconductivity is destroyed in orthorhombic  $\text{NH}_3\text{K}_3\text{C}_{60}$ ,<sup>10</sup> although  $V$  is successfully expanded to the value where a  $T_c$  of roughly 30 K is expected.

Let us go back to the XRD pattern in Fig. 1. The pattern of the sample RC is similar to that of  $(\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}$  in which the octahedral interstitial site is occupied by a tetrahedron of four  $\text{NH}_3$  molecules with Na at the center, and the remaining Na and Cs occupy the tetrahedral site.<sup>9</sup> Thus we started from a model of the ideal composition  $(\text{NH}_3)\text{NaRb}_2\text{C}_{60}$ , where Na and  $\text{NH}_3$  occupy the octahedral site and Rb occupies the tetrahedral sites. Another interesting feature is the change in the intensity profile. When the ammonia composition is smaller ( $\text{C} \rightarrow \text{B} \rightarrow \text{A}$ ), the relative intensity of the (111) peak at about  $2\theta \sim 10.5^\circ$  decreases. This change suggests that, when the ammonia fraction  $x$  is smaller than 1, a part of heavy ions (Rb) occupies the octahedral site.

Rietveld refinement was carried out by the RIETAN program (Izumi) in space group  $Fm\bar{3}m$  for a model tabulated in the inset of Fig. 1. Since the NMR measurement tells us that ammonia composition  $x$  is smaller than 1, the  $x$  value was also refined. The octahedral site is occupied by  $\text{NH}_3$  and Na with the probability  $x$ , while the tetrahedral site is occupied by Rb ions (upper column). The remaining octahedral site is occupied by Rb ions with the probability  $1-x$  with the tetrahedral site occupied by Rb and Na (lower column). The whole crystal is regarded as a microscopic mixture (solid solution) of the two configurations. In the refinement,  $\text{NH}_3$  molecules are replaced by a Ne atom having the same elec-

TABLE I. Atomic coordinates, fractional occupancies  $N$ , and thermal factors  $B$ , for the sample RB of  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$ .  $\text{NH}_3$  molecules are replaced by Ne atoms. Space group  $Fm\bar{3}m$ ,  $a=14.520(1)$  Å,  $x=0.86$ .

Site	$x$	$y$	$z$	$N$	$B$ (Å <sup>2</sup> )	
C1	96j	0.0	0.0496	0.241	0.5	0.67
C2	192l	0.210	0.0802	0.0990	0.5	0.67
C3	192l	0.179	0.160	0.0496	0.5	0.67
Na1	8c	0.25	0.25	0.25	0.07(4)	2.4(4)
Na2	32f	0.478	0.478	0.478	0.11(1)	6.8
Rb1	8c	0.25	0.25	0.25	0.93(4)	2.4(4)
Rb2	4b	0.5	0.5	0.5	0.14(8)	15
Ne	32f	0.576	0.576	0.576	0.11(1)	6.8

tron counts, and placed at the  $32(f)(x,x,x)$  position in the corner of the cubes. Since, in the monoammoniated  $\text{K}_3\text{C}_{60}$ , the octahedral potassium ion is off centered, we allowed the Na ion to be off centered<sup>10</sup> and placed at the  $32(f)(y,y,y)$  position. We found that the  $x$  value and the positions of  $\text{Na}^+$  and Ne are strongly correlated. Thus we first fixed the Na-Ne (octahedral) distance at 2.5 Å, which is a typical distance between the Na ion and the N atom of ammonia.<sup>9</sup> Then we removed the constraint of the Na-Ne distance and refined the Na and Ne positions with a fixed  $x$ . Carbon positions were allowed to vary only radially to preserve the shape of the  $\text{C}_{60}$  molecule.

The refinement converged to the results tabulated in Tables I and II, although the thermal factors were unstable except for tetrahedral cations. Only in the case of the sample KC, we fixed the ammonia composition at  $x=1$ . The ammonia content  $x$  estimated by NMR and Rietveld refinement shows the same trend, decreasing with increasing drying temperatures.

Na ions are shifted from the octahedral center by 0.4–0.6 Å with the Na-Ne distance of 2.4–2.6 Å for all samples. Refinement by a model containing on-centered Na ions gives comparable  $R$  factors but with the Na-Ne distance of 1.7–2.1 Å. This value is unreasonably small when one considers the ionic radius of  $\text{Na}^+$  (1.0 Å) and the van der Waals radius of N (1.6 Å). Since the conventional Na-N distance around 2.5 Å is observed in  $(\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}$ ,<sup>9</sup> the off-centered Na is a more likely model. We calculated  $R$  factors as a function of

the position of the octahedral Na for the sample RB with a fixed Na-Ne distance at 2.5 Å. The  $R_{wp}$  value decreased from 3.5% for the on-centered Na to 3.2% for the shifted Na by 0.55 Å, where  $R_{wp}$  forms a sharp minimum as a function of the Na position.

The model structure for the analysis is summarized as follows.  $\text{NH}_3$  molecules are always in the octahedral site accompanied by Na. In the ideal composition  $x=1$  such as sample KC, the octahedral site is occupied by Na- $\text{NH}_3$  clusters, and the tetrahedral site is occupied by Rb or K. In the octahedral site, Na is pushed away from the center position due to the presence of ammonia. When samples are heated under dynamical vacuum,  $\text{NH}_3$  molecules are lost, resulting in an exchange of Na and K(Rb). This is the best possible model within the present experimental data. A physically reasonable structure derived from this model is that Na and  $\text{NH}_3$  exist in the opposite sides keeping the Na- $\text{NH}_3$  distance at approximately 2.5 Å. The Na- $\text{NH}_3$  cluster along the body diagonal of the cube occupies the eight equivalent disordered orientations.

Although the shift of cations from the center of the octahedral site is suggested by several experiments such as NMR,<sup>14</sup> no XRD evidence has ever been reported. For instance, the refinement of the XRD pattern of  $\text{Rb}_3\text{C}_{60}$  was not improved by shifting alkali metals from the center of the interstices,<sup>15</sup> indicating that the shift is not detectable even if it may not be zero. The displacement 0.4–0.6 Å of the octahedral Na is considerably smaller than that of the octahedral K in  $\text{NH}_3\text{K}_3\text{C}_{60}$  (1.42 Å).<sup>10</sup> The small shift might be a part of the reason for the preserved cubic structure in  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$ .

The low  $T_c$ 's in  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$  are suggestive about the mechanism of fullerene superconductivity. There may exist an unknown factor which suppresses high- $T_c$  superconductivity in the compounds with large lattice parameters. High  $T_c$  in  $(\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}$  indicates that the ammoniation itself is not fatal for the superconductivity. We tested valence of the  $\text{C}_{60}$  molecule by means of Raman spectroscopy.  $(\text{C}_{60})^{3-}$  state is preserved within an experimental error for both  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$ , as well as for  $\text{NH}_3\text{K}_3\text{C}_{60}$ .<sup>12</sup> We note that the randomness due to the solid solution of the two configurations in the inset of Fig. 1 does not suppress  $T_c$ . In fact, the lowest  $T_c$  is observed in  $x\sim 1$  samples, where the

TABLE II.  $T_c$  and structural parameters for three samples RA, RB, and RC of  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$ , and three samples KA, KB, and KC of  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$ .  $\text{NH}_3$  molecules are approximated by Ne in the refinement.  $x(\text{NMR})$  and  $x(\text{RR})$  are the ammonia composition estimated by NMR and Rietveld refinement.  $D(\text{Na})$  and  $D(\text{Ne})$  are the distances from the octahedral center of Na ion and Ne atom, respectively, determined by the refinement.

	$T_c$ (K)	$a$ (Å)	$x(\text{NMR})$	$x(\text{RR})$	$D(\text{Na})$ (Å)	$D(\text{Ne})$ (Å)	$R_I$ (%)	$R_{wp}$ (%)	$S$
RA	17	14.500	0.55	0.74	0.40	1.98	1.85	5.67	2.93
RB	12	14.520	0.60	0.86	0.55	1.91	2.80	3.23	1.71
RC	8.5	14.531	1.01	0.93	0.57	1.93	2.34	4.54	2.44
KA	13	14.350	0.67	0.84	0.37	2.13	2.87	3.77	1.83
KB	11	14.369	0.71	0.87	0.44	2.17	2.29	3.53	1.83
KC	8	14.400	1.06	1.00	0.46	2.04	3.47	3.72	1.87

configuration in the upper column is dominant. We find a common feature in the three low- $T_c$  materials including  $\text{NH}_3\text{K}_3\text{C}_{60}$ : the ammonia composition is close to 1 and, as a result, the presence of off-centered alkali ions in the octahedral site.

About 0.5 Å displacement of alkali ion from the center of the octahedral site makes the local potential on the  $\text{C}_{60}$  anion noncubic. The noncubic local Coulomb potential on  $\text{C}_{60}$  from the surrounding alkali ions lifts the triple degeneracy of the  $t_{1u}$  level. This static degeneracy lifting significantly suppresses the pairing mechanism that originates from the triple degeneracy of the LUMO.<sup>16,17</sup> In other words, the low  $T_c$  of the off-centered system suggests that the high symmetry of the molecule is crucial for fullerene superconductivity.

The decrease in  $T_c$  with increasing cell size is also a unique property. This trend completely differs from the conventional one, and thus indicates that the new superconductors are likely beyond the BCS weak coupling regime. In fact, measurements of the NMR Knight shift suggest that the density of states at the Fermi energy for  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $\text{NH}_3\text{K}_3\text{C}_{60}$  is comparable or larger than that for the high- $T_c$  fullerenes with similar lattice parameters;<sup>18</sup> therefore, the normal-state electronic structures of  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$  are of significant interest.

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