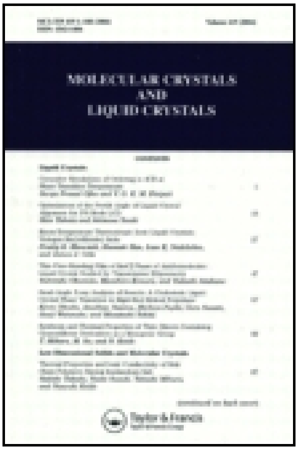

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SUPERCONDUCTIVITY IN ALKALI-AMMONIA COMPLEX FULLERIDES

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Abstract Here we show that low temperature synthesis in liquid ammonia successfully stablied the combination of one Na and two large alkali ions(K and Rb) by incorporating NH_3 molecules.Both $(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xNaRb_2C_{60}$ ($x \sim 0.8$) retained the fcc cell with a=14.37 Å and a=14.52 Å, and superconduct at 11K and 13K, respectively. A Na-NH_3 cluster occupies the octahedral interstice and remaining K or Rb occupies the tetrahedral site.The Na ion is displaced by 0.4-0.6 Å from the center of the octahedral site. The present system thus provides an example of fcc superconductors involving off-centered cations that exhibit different trend in the well known relationship between transition temperature (T_c) and lattice parameter of face-centered cubic A_3C_{60} (A=alkali metals) superconductors .[1-3]

INTRODUCTION

Superconductivity of fullerides occurs in materials with C_{60} molecules at 3- reduction state.[4] One of the current important issues of superconductivity in alkali doped C_{60} is search for materials with large lattice parameters, since the empirical rule predicts that further increase of lattice parameter increases T_c. Zhou et al. showed that ammoniation of Na_2CsC_{60} (a= 14.132 Å and T_c = 10.5 K) produced $(NH_3)_4Na_2CsC_{60}$ (a=14.47Å and T_c=29.7K)[5]. Reaction of K_3C_{60} (T_c=19K) with NH_3, on the other hands, resulted in a orthorhombic distortion of the fcc structure with off-centered K and NH_3 in the octahedral site and disappearance of superconductivity[6]. The low temperature reaction in liquid ammonia yielded Cs_3C_{60}, which does not superconduct ambient pressure, but does under pressure at T_c of 40K.[7] Motivated by these efforts, we searched for novel materials by using ammoniation techniques, and succeeded to stablize the composition NaK_2C_{60} and $NaRb_2C_{60}$ by incorporating NH_3 molecules. Here we report synthesis, structure, and superconductivity of $(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xNaRb_2C_{60}$ ($x\sim0.8$),the T_c of which considerably differs from the empirical relation.

EXPERIMENT AND RESULTS

$(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xNaRb_2C_{60}$ was synthesized by a reaction of stoichiometric amount of alkali metals and C_{60} powders in liquid ammonia.[7]An evacuated glass tube alkali metals and C_{60} inside are cooled by a dry-ice/aceton slush. Dry liquid ammonia was condensed into the tube through a vacuum line. The tube was shaken until when both alkali metals and C_{60} powders completely dissolved into liquid ammonia. After thirty minutes, ammonia was slowly evaporated from the solution,followed by a dry process under vacuum for half an hour.Then the obtained powder was evacuated to 2×10^{-6} torr andsealed under He of 150 torr. This sample was annealed at 100℃ for about a week.

^{1}H- and ^{13}C-NMR technique was used to determine the ammonia composition x. It was 0.6 and 0.7 for $(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xNaRb_2C_{60}$, respectively. This x value is unexpectedly small in comparison with $(NH_3)_4Na_2CsC_{60}$,[5] when one considers that the new compounds were synthesized in liquid ammonia.

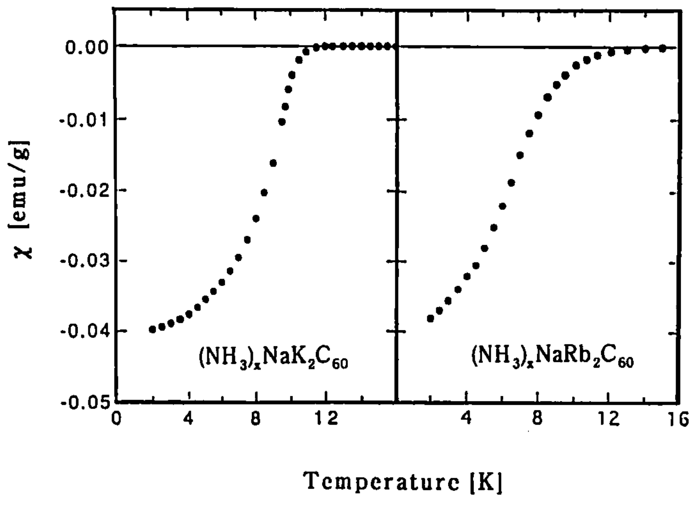


FIGURE 1 Temperature dependence of zero-filed-cooled susceptibility for $(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xNaRb_2C_{60}$.

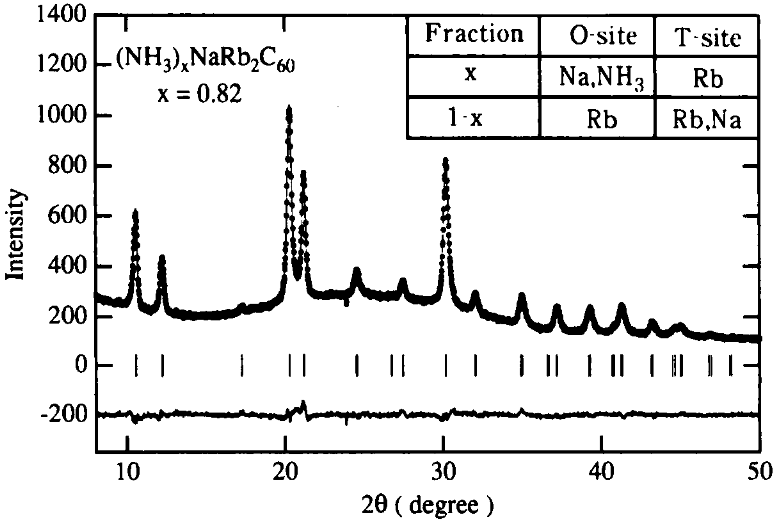
Figure 1 shows the temperature dependence of magnetization of $(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xNaRb_2C_{60}$ measured at a filed of 10 Oe using a superconducting quantum interference device. Both samples show superconductivity signals with the onset temperature of 11K and 13K, respectively. The shielding fraction at 2K were about 100% for both samples, providing unambiguous evidences for a bulk superconductivity.

X-ray diffraction pattern was measured using 12kW Cu-K α radiation, and is shown for $(NH_3)_xNaRb_2C_{60}$ in Fig. 2. All the observed peaks were indexed as fcc with a cell parameter of a=14.52 Å. $(NH_3)_xNaK_2C_{60}$ also showed a single phase fcc diffraction pattern of a=14.37 Å. These x-ray results indicate that less than one molecule of NH_3 per C_{60} stabilizes the cubic structure of fulleride compounds involving one small Na metal and two large alkali metals, which has never been synthesized by a direct reaction of alkali vapor and C_{60} powders.

The observed lattice parameters are significantly large comparing with those of hypothetical $NaRb_2C_{60}$ (a=14.21 Å) and NaK_2C_{60} (a=14.13 Å) estimated by averaging the a-values of A_3C_{60} and Na_2AC_{60}.[3] Also noteworthy is that the T_c of $(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xNaRb_2C_{60}$ is dramatically lower than the empirical relation between T_c and lattice parameter of fullerene compounds with $(C_{60})^{-3}$ reduction state.[1-3]The empirical relation predicts T_c=28K and 32K for K and Rb compounds,respectively.We note that the T_c vs. a relation of the fcc compound $(NH_3)_4Na_2CsC_{60}$ falls on the empirical curve,[5] indicating that the ammoniation itself is not fatal for the superconductivity. Ammoniation of K_3C_{60}, on the other hands, destroys the superconductivity,forming the orthorhombic $NH_3K_3C_{60}$,[6] although the volume per C_{60} is successfully expanded to the value where T_c of roughly 30K is expected.

We performed the structural analysis of $(NH_3)_xNaRb_2C_{60}$.The intensity profile of the diffraction pattern of $(NH_3)_xNaRb_2C_{60}$ is similar to that of $(NH_3)_4Na_2CsC_{60}$, in which the octahedral interstitial site is occupied by a tetrahedron of four NH_3 molecules with Na at the center,and the remaining Na and Cs occupy the tetrahedral site.[5]Thus we modeled that Na and NH_3 occupy the octahedralsite and Rb occupies the tetrahedral sites.

Rietveld refinement was carried out by the RIETAN program (F. Izumi) in space group $Fm\bar{3}m$ for a model tabulated in the inset of Fig. 2. Since the NMR measurement tells us that ammonia composition x is smaller than 1, x value was also refined. The octahedral site is occupied by 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. We note that the model where all the Na^+ ions remain in the octahedral site with NH_3 vacancies did not give low R-factors. In the refinement, NH_3 molecules are replaced by Ne atom having the same electron counts, and placed at the 32(f)(x,x,x) positions on the corner of the cubes. Since, in the monoammoniated K_3C_{60}, the octahedral potassium ion is off-centered, we allowed Na ion to be off-centered[6] and placed at the 32(f)(y,y,y) positions. Thus the Na-NH_3 cluster along the body diagonal of the cube occupies the eight equivalent disordered orientations.Following the refinement of $(NH_3)_4Na_2CsC_{60}$,[5] we fixed the Ne-Na (octahedral) distance at 2.5 Å, which is a typical distance of betweem Na ion and N atom of ammonia. Carbon positions were allowed to vary only radially to preserve the shape of C_{60} molecule.



Fraction	O-site	T-site
x	Na,NH_3	Rb
1-x	Rb	Rb,Na

Figure 2 300K powder x-ray diffraction patterns of $(NH_3)_xNaRb_2C_{60}$ collected with Cu K α radiation produced by a rotating anode source. The closed circles are experimental points and the solid line is a Rietveld fit 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 Bragg reflections taking the K α_1 and K α_2 radiations into account. The table shows the site occupation of alkali ions and ammonia molecules.

The refinement converged to R factors of R_{wp}=2.92% and R_p=2.25% and to S=0.441. It is noted that the shift of Na ion from the center of octahedral site gave a sharp minimum of R-factors at 0.59 Å with R_{wp}=2.92%, while the refinement with Na ion fixed at the center gave R_{wp}=3.33%. Although the shift of cations from the center of the octahedral siteis suggested by several experiments such as NMR,[8] no XRD evidence has ever been reported. For instance,according to Zhou and Cox,[9] the refinement of XRD pattern of Rb_3C_{60}

was not improved by shifting alkali metals from the center of the interstices. The displacement 0.59 Å of the octahedral Na is considerably smaller than that of the octahedral K in $NH_3K_3C_{60}$ (1.42 Å).[6] The refinement gave the x value of 0.82, which is slightly larger than that estimated from NMR. Structural parameters obtained from the refinement are given in Table I. The refinement on $(NH_3)_xNaK_2C_{60}$ converged to R_{wp}=3.18%, R_p=2.45%, and S=0.465 with the displacement of Na^+ ion from the center of octahedral site of 0.41 Å and x= 0.90. These results confirm that the new compounds are the examples of the fcc superconductors with the off-centered alkali ions in the octahedral sites.

TABLE 1 Refined structural parameters for $(NH_3)_xNaRb_2C_{60}$. NH_3 molecules are approximated by Ne in the refinement.

	cite	x	y	z	N	B
C(1)	96(j)	0.0	0.04972	0.24116	0.5	0.67
C(2)	192(l)	0.21051	0.08039	0.09925	0.5	0.67
C(3)	192(l)	0.17974	0.16077	0.04975	0.5	0.67
Na(1)	8(c)	0.25	0.25	0.25	0.0895	2.3
Na(2)	32(f)	0.47670	0.47670	0.47670	0.1026	5.0
Rb(1)	8(c)	0.25	0.25	0.25	0.9105	2.1
Rb(2)	4(b)	0.5	0.5	0.5	0.1789	17.0
Ne	32(f)	0.57610	0.57610	0.57610	0.1026	5.0

DISCUSSION

The low T_c materials having large fcc cells are suggestive about the mechanism of fullerene superconductivity. We find two common features in the three low T_c materials including $NH_3K_3C_{60}$. First is the ammonia composition that is close to 1 and the second is the presence of off-centered alkali ions in the octahedral site. About 0.6 Å displacement of alkali ion from the center of the octahedral site makes the local potential on the C_{60} anion noncubic. Since the noncubic local field removes the degeneracy of t_{1u} orbital of C_{60}, the electronic structures and thus superconductivity are significantly modified. On the other hands, a disorder due to the off-centered alkali ion may suppress the superconductivity. The finding of low T_c materials indicates that the T_c of cubic fullerene superconductors are controlled not only by the cell size but also other parameters such as the position of alkali metals. Synthesis of multinary complex fullerides might give opportunities to extract essential factors for the superconductivity of doped C_{60}.

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