Antiferromagnetism and Phase Diagram in Ammoniated Alkali Fulleride Salts

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Intercalation of neutral ammonia molecules into trivalent face-centered-cubic (fcc) fulleride superconductors induces a dramatic change in electronic states. Monoammoniated alkali fulleride salts $(NH_3)K_{3-x}Rb_xC_{60}$, forming an isostructural orthorhombic series, undergo an antiferromagnetic transition, which was found by the electron spin resonance experiment. The Néel temperature first increases with the interfullerene spacing and then decreases for $(NH_3)Rb_3C_{60}$, forming a maximum at 76 K. This feature is explained by the generalized phase diagram of Mott-Hubbard transition with an antiferromagnetic ground state.

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Fullerere C_{60} is known to form a vast variety of compounds including superconductors, by intercalation of alkali (A), alkaline earth, and rare earth metals. It has been pointed out that the experimentally estimated on-ball Coulomb repulsion energy ($U = 1.0 - 1.5$ eV) is fairly large compared to the bandwidth ($W \sim 0.5$ eV), leading to a conjecture that the fullerene compounds are highly correlated electron systems [1]. In fact, the spin density wave (SDW) state found in the polymeric A_1C_{60} is an example of electron correlation effects combined with the low dimensionality [2]. By contrast with higher valency fullerides, particularly A_3C_{60}, this feature has not been explicitly demonstrated until recently.

Recent investigations on the trivalent compounds revealed that slight modification of the fcc structure which affords various superconductors dramatically changes the electronic properties. First, the intercalation of ammonia into the K_3C_{60} superconductor induces a slight structural distortion from cubic to orthorhombic, forming $(NH_3)K_3C_{60}$ [3], where superconductivity (SC) is replaced by an antiferromagnetic (AF) insulating state [4,5]. This result provided unambiguous evidence for the existence of strong correlation effect even in the trivalent compounds. The second interesting system found very recently is $Na_2Cs_xRb_{1-x}C_{60}$, which is a superconductor at about 10 K with the simple cubic ($Pa\bar{3}$) structure. The slow cooling of the crystal induces a spontaneous polymerization of fullerene molecules and an SDW ground state [6]. This SDW is another example of the magnetic ground state due to the correlation effect in the vicinity of fullerene superconductors.

In previous papers, we have clarified the physical properties of $(NH_3)K_3C_{60}$ through several methods. This compound adopts a pseudotetragonal (orthorhombic) structure, which is derived by a slight deformation of the fcc structure. NH_3 molecules are inserted into octahedral sites, forming K-NH_3 pairs. The resulting AF state with a Néel temperature (T_N) of 40 K is confirmed by electron paramagnetic resonance (EPR) [4,7], muon spin relaxation (μSR) [8], and nuclear magnetic resonance (NMR) experiments [9]. The moment at the ordered state is $1.0\mu_B$ as determined by NMR. Moreover, a structural phase transition was found at 150 K in $(NH_3)K_3C_{60}$. While the octahedral K-NH_3 group rotates at higher temperature, the orientation of this group is ordered in an antiferroelectric fashion below 150 K, associated with the unit cell doubling [10].

In this paper we report synthesis and EPR experiments of a new series of the $(NH_3)K_3C_{60}$ type compounds, in order to uncover the nature of the AF state. We found that T_N systematically changes, and has a maximum as a function of the interfullerene distance. These results are explained by the generalized phase diagram of the Mott-Hubbard system, indicating that the intercalation of ammonia into fcc superconducting fullerides results in highly correlated electron systems.

The newly synthesized compounds in this study have chemical formulas of $(NH_3)K_2RbC_{60}$, $(NH_3)KRb_2C_{60}$, and $(NH_3)Rb_3C_{60}$. While the standard $(NH_3)K_3C_{60}$ is synthesized by exposing the preformed K_3C_{60} to ammonia gas, the Rb including compounds were obtained by the deintercalation of ammonia from the ammonia rich phase. After dissolving a stoichiometric amount of C_{60} and alkali metals into dry liquid ammonia kept at -65 °C, ammonia was evaporated very slowly over about one week. The main part of the as-evaporated powders is an unidentified ammonia rich phase, which can be indexed to an orthorhombic cell of $a = 12.633(3)$ Å, $b = 11.669(2)$ Å, $c = 10.909(1)$ Å for $(NH_3)_yKRb_2C_{60}$ ($y > 1.4$). Ammonia was removed by a ten-minute annealing at 100 °C to obtain high quality samples $(NH_3)_yK_{3-x}Rb_xC_{60}$ ($y \sim 1$). The final concentration of ammonia was estimated as $y = 1.15 \pm 0.05$ for $(NH_3)_yKRb_2C_{60}$ by pressure changes upon heating the sample. This concentration, slightly larger than the stoichiometric value ($y = 1$), is consistent with the x-ray diffraction data showing that a small amount of the ammonia rich phase remains even in the best sample so far obtained.

Figure 1 displays a synchrotron x-ray diffraction pattern of the nominal $(NH_3)_yK_{3-x}Rb_xC_{60}$ ($y \sim 1, x \sim 2$) sample at $\lambda = 1.0$ Å collected on the BL1B beam line at the Photon Factory, KEK. Most of the peaks index to the

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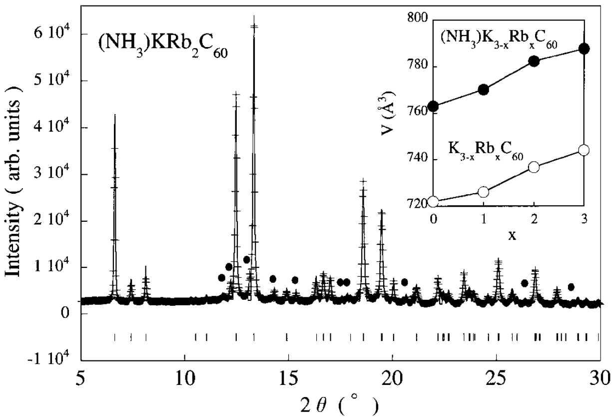

FIG. 1. X-ray diffraction pattern of $(NH_3)KRb_2C_{60}$. The crosses are experimental points and the solid line is a Rietveld fit to the model described in the text. Ticks mark the positions of the allowed reflection and dots on the pattern indicate the reflections of the ammonia rich impurity phase, which was excluded in the present refinement. The inset shows the relation between the volume V per C_{60} and the Rb concentration.

$(NH_3)K_3C_{60}$-type orthorhombic unit cell, and the refined cell parameters are tabulated in Table I. Several weak reflections indicated by marks are attributed to the ammonia rich phase. In order to determine the site occupancy of alkali metals, we have made a preliminary Rietveld fit using the FULLPROF software (J. Rodriguez-Cavajal, Laboratoire Leon Brillouin, 1998), excluding the peaks from the unknown ammonia rich phase. Since the chemical analysis allows us to fix the ammonia concentration at one per C_{60} molecule, we adopted the same structural model with the space group of $Fmmm$ as that of $NH_3K_3C_{60}$ [3,10], where a single A-NH_3 group occupies every octahedral site, and the remaining alkali atoms occupy tetrahedral sites. The A-NH_3 group in the octahedral site lies on the basal plain with disorder over the four equivalent orientations. In the refinement, the K/Rb concentration ratio and their occupancies have been refined, neglecting the hydrogen atom. The goodness of the fit was $R_{wp} = 13.9\%$ and $R_I = 8.2\%$. The obtained Rb composition was $x = 2.00(19)$, in fair agreement with the nominal value. The occupation of alkali atoms in the octahedral site was found to be selective, though not exclusive: The octahedral occupancy of K was found to be 1.8 times larger than that of Rb. From the chemical point of view, the larger occupancy of K in the octahedral site is reasonable, since the larger rubidium is expected to be less strongly coordinated with NH_3. More detailed refinement is in progress in parallel with efforts to remove the ammonia rich phase completely.

For $(NH_3)K_2RbC_{60}$ and $(NH_3)Rb_3C_{60}$, the observed x-ray pattern agreed fairly well with the simulation by the LAZY-PULVERIX software [K. Yvon, W. Jeitschko, and E. Parthe (unpublished)] on the same structural model. Their refined cell parameters by the Le Bail fit is summarized in Table I. The inset of Fig. 1 shows the volume/C_{60} against the nominal Rb concentration x for $K_{3-x}Rb_xC_{60}$ and $(NH_3)_yK_{3-x}Rb_xC_{60}$. The volume expansion upon replacing K with Rb is successfully made in the new ammoniated series. The constant expansion of the unit cell on ammonia intercalation indicates that the concentration of ammonia is one per C_{60} for all the ammoniated compounds.

EPR spectra of 9 GHz have been measured from 40 to 300 K using a JEOL EPR spectrometer equipped with a flow-type cryostat. The EPR signals of $(NH_3)K_2RbC_{60}$, $(NH_3)KRb_2C_{60}$, and $(NH_3)Rb_3C_{60}$ consist of two components. Through a Lorentzian fit, we deduced the integrated intensities which are proportional to the spin susceptibility, the full width at half maximum linewidths $\Delta H_{1/2}$, and the g values for the two components. Since the intensity of the narrow line [$\Delta H_{1/2} = 3.2$ mT at 300 K for $(NH_3)KRb_2C_{60}$] displays a Curie-type temperature dependence throughout 40–300 K, the narrow line is ascribed to a paramagnetic impurity possibly due to lattice imperfections. The linewidth and g value of the broad intrinsic component at room temperature are summarized in Table I for the four $(NH_3)K_{3-x}Rb_xC_{60}$ $(0 \le x \le 3)$ compounds. It is useful to compare this result with the case of fcc $K_{3-x}Rb_xC_{60}$ compounds, where the linewidth increases with Rb concentration accompanied with the increase of the g-value shift $\Delta g = |g_e - g|$ from the free electron value $g_e = 2.002\,32$. This behavior has been understood in terms of the Elliott mechanism of conduction electron EPR [11,12]. In $(NH_3)K_{3-x}Rb_xC_{60}$ compounds, the $\Delta H_{1/2}$ and Δg increase with the Rb concentration between $x = 0$ and $x = 2$ in a similar manner to $K_{3-x}Rb_xC_{60}$. Particularly, the $\Delta H_{1/2}$ values do not essentially change upon ammoniation. These features indicate that the Elliott mechanism still holds at least for $x \le 2$ at room temperature, and that the electronic states of these

TABLE I. Cell parameters, the EPR g value, and linewidth for the orthorhombic series of monoammoniated fullerides at room temperature. Cell parameters for $(NH_3)K_3C_{60}$ are from Ref. [10]. Errors for the g value were estimated from the repeated measurements on several different samples.

	$(NH_3)K_3C_{60}$	$(NH_3)K_2RbC_{60}$	$(NH_3)KRb_2C_{60}$	$(NH_3)Rb_3C_{60}$
a (Å)	14.971(10)	15.004(2)	15.0998(5)	15.236(3)
b (Å)	14.917(10)	14.924(2)	15.0557(5)	15.170(3)
c (Å)	13.692(4)	13.758(2)	13.7663(3)	13.662(2)
g value	2.0011 ± 0.0003	1.9992 ± 0.0004	1.9985 ± 0.0012	2.0017 ± 0.0020
$\Delta H_{1/2}$ (mT)	2.8	15.4	38.6	66.0

compounds are not dramatically different from those of A_3C_{60}. $(NH_3)Rb_3C_{60}$ ($x = 3$), however, displays a rather large g value, which is close to g_e. This gives a small Δg, which is not sufficient for explaining the large $\Delta H_{1/2}$ by the same Elliott mechanism, indicating an occurrence of dramatic change of electronic state, such as a metal-insulator transition.

The temperature dependences of the integrated intensity, normalized by the room temperature value, and $\Delta H_{1/2}$ are displayed in Fig. 2 for $(NH_3)KRb_2C_{60}$. Dramatic anomalies were observed at 145 ± 5 K and at 76 ± 1 K. The susceptibility shows an increase at around 145 K, followed by a sharp decrease at 76 K. Corresponding anomalies are also observed in $\Delta H_{1/2}$. Two phase transitions are known to take place in the isostructural $(NH_3)K_3C_{60}$, namely, the antiferroelectric transition of the K-NH_3 groups at $T_S =$ 150 K and the AF transition of C_{60} spins at $T_N = 40$ K. Hence, the two transitions observed in $(NH_3)KRb_2C_{60}$ are likely attributable to the analogous phase transitions.

In $(NH_3)KRb_2C_{60}$, the transition at 76 K is characterized by the decrease of EPR intensity, and a sharp increase of $\Delta H_{1/2}$. The rapid broadening of the EPR line across 76 K is a strong evidence for an AF transition, because this phenomenon is a sign of buildup of internal fields due to the magnetic ordering. Importantly, almost identical temperature dependent EPR data are obtained for the standard compound $(NH_3)K_3C_{60}$, where the AF transition has been confirmed by other measurements. In this example, the drop in intensity does not necessarily mean the decrease of spin susceptibility, but that the signal becomes invisible due to the huge magnetic broadening, as observed in $(NH_3)K_3C_{60}$ [4,7]. Taking into consideration the close correlation of chemical, structural, and EPR properties with those of $(NH_3)K_3C_{60}$, we conclude that an AF phase transition takes place in $(NH_3)KRb_2C_{60}$ at $T_N = 76$ K. It is also to be pointed out that polymeric fulleride Rb_1C_{60} exhibits similar features in the EPR behaviors at T_N [2]. The intensity drop accompanied with the line broadening is a common feature of fulleride antiferromagnets. Various other experiments, such as antiferromagnetic resonance at higher magnetic field [7], will provide more refined and detailed information on the AF state of this compound.

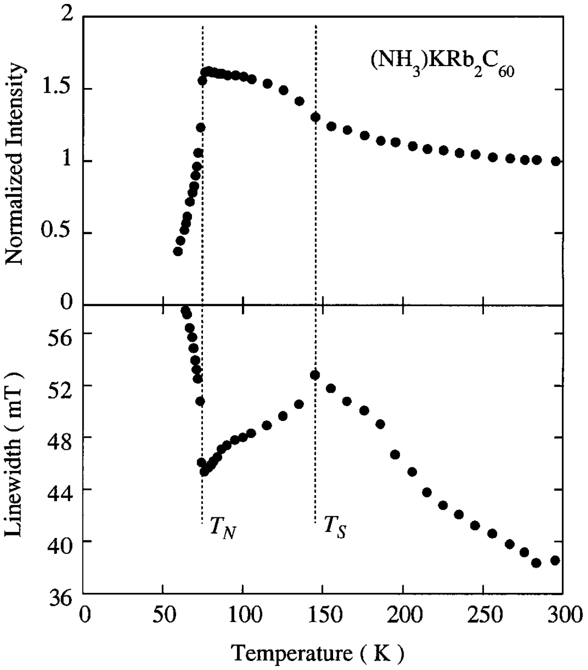

FIG. 2. Temperature dependence of integrated intensity (normalized by the room temperature value) and $\Delta H_{1/2}$, for the EPR signals of $(NH_3)KRb_2C_{60}$.

We found that all the four compounds ($x = 0$, 1, 2, and 3) display a drop in EPR intensity at low temperature, which is attributable to the AF ordering, indicating that the AF state is the common electronic ground state for the monoammoniated series of compounds. It is noted that T_N is strongly dependent on the Rb concentration. Figure 3 shows the plots of T_N against the volume V per C_{60}. T_N first increases with the concentration of Rb until $x = 2$, but decreases to 58 K for $x = 3$. The observed change of T_N is totally different from what is expected from a simple localized moment model, since this model predicts that the increase of interfullerene distance causes the decrease of the exchange interaction J and thus the reduction of T_N. However, the present results remind us of a phase diagram of the Mott-Hubbard system, theoretically presented by Moriya and Hasegawa [13], and experimentally demonstrated in various materials [14], where T_N shows a crossover behavior from the itinerant to localized picture against U/W. T_N increases with U/W in the metallic regime (small U/W), while T_N decreases in the localized regime (large U/W). This feature closely resembles Fig. 3, since the V is a good parameter for $1/W$. In other words, the electronic states of the $(NH_3)A_3C_{60}$ system should be explained not by a simple localized model, but in terms of the Hubbard model.

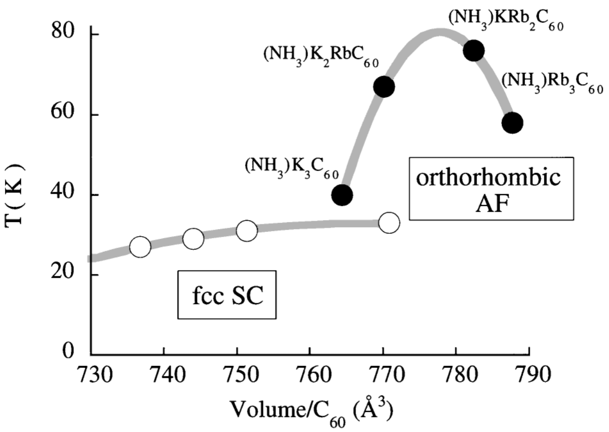

FIG. 3. T-V phase diagram of the orthorhombic $(NH_3)A_3C_{60}$ (filled circle) and the fcc A_3C_{60} (open circles) fullerides. The horizontal axis V represents the volume/C_{60}. Two shaded lines are quadratic fits for guiding eyes.

The metallicity of the paramagnetic state above T_N even in $(NH_3)K_3C_{60}$ has been severely controversial. While the latest EPR experiment suggests a metallic behavior above 40 K [7], NMR experiments showed that the relaxation rate T_1^{-1} and the Knight shift are accounted for by a localized moment model [9]. One possible explanation of the EPR result is that the metallic state is maintained up to $x = 2$ from the argument on the g value and $\Delta H_{1/2}$, and a metal-insulator transition seems occurring at $x = 3$. This is consistent with the theoretical phase diagram of the Mott-Hubbard system, where the paramagnetic states above T_N are expected to be metallic and insulating for the small and large U/W values, respectively. Low temperature resistivity measurements, which have not been reported so far because of the air sensitivity and the absence of single crystals, are urgently required for all the $(NH_3)A_3C_{60}$ systems to resolve this issue.

In Fig. 3, T_c's of superconductivity in the fcc compounds are also plotted for comparison. An important question arises from this plot: What is the origin of such a dramatic change of electronic properties on ammoniation? The transition from a phonon-mediated superconductivity to a Mott-Hubbard state induced simply by the intercalation of ammonia is an interesting issue from the viewpoint of the competition of electron-phonon interaction and the electron-electron interaction [15]. Since $(NH_3)K_3C_{60}$ is expected to be a superconductor according to an empirical correlation between T_c and V, we postulate that this transition is not caused by a simple lattice expansion, but that the symmetry reduction from fcc to orthorhombic crystal plays a crucial role. While the triple degeneracy of the lowest unoccupied molecular orbital of C_{60} is maintained in the fcc structure, this degeneracy is removed in the structure of lower symmetry, such as orthorhombic. According to Lu [16] and Gunnarsson [17], the doped C_{60} is essentially a strongly correlated electron system, and the triple degeneracy of molecular orbital is crucially important to maintain the metallic state. The effective transfer energy is larger than the apparent value when the molecular orbital is degenerate, because the additional electron hopping channel between the different molecular orbitals are allowed. Ammoniation causes the symmetry reduction in the crystal structure and, consequently, reduction of effective hopping energy. In this sense, the phase diagram, Fig. 3, should be understood in terms of the Mott transition of the degenerate Hubbard model.

To summarize, we have synthesized an orthorhombic series of alkali ammonia trivalent fulleride compounds, and showed that the AF transition T_N exhibits a systematic change against the interfullerene spacing. The change of T_N, forming a peak as a function of V, is possibly explained in terms of the phase diagram of the Hubbard model. The present finding clearly demonstrates that the ammoniation emphasizes the electron correlation effect possibly via crystal symmetry reduction [17]. The Mott transition in the ammoniated system provides novel problems on the orbital states in the insulating states and on the crossover from superconductivity to antiferromagnetic states.

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