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Metal-insulator transition in ammoniated K_3C_{60}

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Magnetic susceptibility, electron spin resonance, and ^{13}C nuclear-magnetic-resonance data on $NH_3K_3C_{60}$ reveal that $NH_3K_3C_{60}$ is a narrow-band metal with a transition to an insulating ground state at 40 K. This transition suppresses the superconductivity that is expected to occur at around 30 K according to a simple empirical relation between T_c and the cell volume in alkali-metal-doped C_{60} superconductors.

Soon after the discovery of the superconductivity of alkali-metal-doped C_{60},[1] a simple relation between T_c and lattice parameters has been established: T_c increases with lattice parameter.[2,3] This trend suggests that the superconductivity of fullerenes are in the framework of the weak-coupling Bardeen-Cooper-Schrieffer mechanism, where T_c is controlled by the density of states $N(\epsilon_F)$ at the Fermi level ϵ_F which increases with increasing intermolecular separation due to band narrowing. This simple empirical rule has motivated many efforts in the synthesis of high-T_c fullerides with large lattice parameters.

The most successful results are obtained by ammoniation of Na_2CsC_{60} (fcc cell parameter $a=14.132$ Å, $T_c=10.5$ K).[4] Exposing preformed Na_2CsC_{60} to about 400 torr NH_3, followed by 100 °C anneal yields $(NH_3)_4Na_2CsC_{60}$ which shows a cell expansion to $a=14.47$ Å and an almost tripled T_c of 29.7 K. In this case, neutral NH_3 molecules are intercalated as a spacer and successfully increased the cell dimension without symmetry lowering.

In other cases, intercalation of NH_3 causes structural distortion from fcc.[5] Reaction of K_3C_{60} with NH_3 under the condition similar to that for Na_2CsC_{60} produced $NH_3K_3C_{60}$, which has an orthorhombic structure. The unit cell volume of the $NH_3K_3C_{60}$ compound is 763 Å^3/C_{60}, which is comparable to Rb_2CsC_{60} ($T_c=31$ K). However, no superconductivity was observed above 2 K at ambient conditions. Later on, the superconductivity of $T_c=28$ K was found under pressure above 10 kbar.[6] These properties suggest that $NH_3K_3C_{60}$ is at the verge of the superconductor-nonsuperconductor boundary.

Synthesis routes using NH_3 produced several other materials which retain the $(C_{60})^{3-}$ state but do not superconduct at ambient pressure. Ammoniation of K_3C_{60} at high NH_3 pressure results in $(NH_3)_xK_3C_{60}$ ($x=8$–10), which is insulating due to too much lattice expansion.[6] Cs_3C_{60} was synthesized from liquid ammonia and found to exhibit superconductivity at 40 K only under hydrostatic pressure similar to the case of $NH_3K_3C_{60}$.[7] These findings indicate that the lattice expansion yields nonsuperconductors rather than high-T_c superconductors at ambient pressure. The electronic properties of these nonsuperconductors are important issues for the full understanding of the phase diagram of fullerides with $(C_{60})^{3-}$ states.

Among the nonsuperconductors with large lattice parameters, $NH_3K_3C_{60}$ is a key material because it is easy to synthesize in a single phase and well characterized. To investigate the reason for the absence of superconductivity in $NH_3K_3C_{60}$, we performed the electron spin resonance (ESR), magnetic susceptibility, and ^{13}C nuclear-magnetic-resonance (NMR) measurements at ambient pressure. Here we report these experimental results and show that $NH_3K_3C_{60}$ undergoes a metal-insulator transition at 40 K that prevents an occurrence of superconductivity.

$NH_3K_3C_{60}$ was prepared following the previous works.[5,6] Starting K_3C_{60} was synthesized by a direct reaction of K vapor and C_{60} powders and following a one-month anneal at 400 °C. Thus obtained single phase K_3C_{60} powders (20–50 mg) were loaded in a glass tube (5 mm in diameter), evacuated to 10^{-3} torr, and exposed to ammonia gas of 0.5 atom at room temperature for 20 min. After the reaction, the glass tube was sealed under 0.5 atom NH_3. The samples were annealed at 100 °C for one month. In this method, we usually obtained NH_3-poor samples, which show the single-phase x-ray-diffraction (XRD) pattern of $NH_3K_3C_{60}$, but exhibit residual superconductivity from

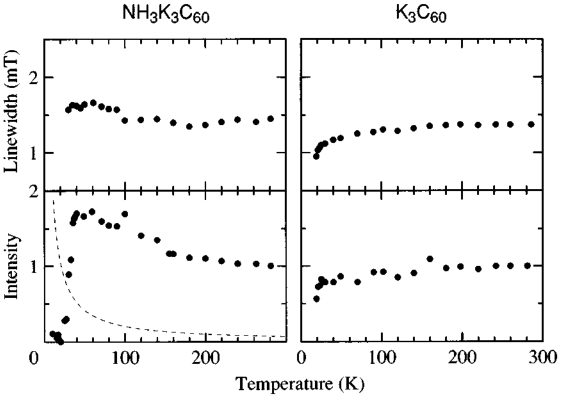

FIG. 1. Temperature dependence of ESR linewidth and intensity for $NH_3K_3C_{60}$ (left) and K_3C_{60} (right). The intensity is normalized by the room-temperature value for K_3C_{60}. The thin solid line in the bottom panel of $NH_3K_3C_{60}$ shows a Curie component from the narrow impurity line.

K_3C_{60} with a volume fraction of a few percent. When we exposed the NH_3-poor samples to NH_3 gas under the same condition as the first exposure, NH_3-rich samples were made. The XRD data of this sample shows the majority is $NH_3K_3C_{60}$ with a slight amount of $(NH_3)_8K_3C_{60}$ as an impurity phase. The residual superconductivity disappeared. Analysis by H- and ^{13}C-NMR showed that a typical NH_3-rich sample contains 1.14 NH_3 molecules per C_{60}. We measured ESR and magnetic susceptibility both on NH_3-poor and rich samples, and obtained quantitatively the same results, indicating that the properties reported below are intrinsic to $NH_3K_3C_{60}$. NMR measurements were performed on NH_3-rich samples.

9 GHz ESR data were collected on typically 2–5mg samples loaded in quartz tubes. The spin susceptibility was estimated from the areas of the ESR signal, which were calibrated by a standard tetramethylpiperidinooxy sample using Mn^{2+}/MgO as an internal standard. K_3C_{60} shows a single Lorentzian ESR signal at room temperature. The spin susceptibility at room temperature determined by the ESR was 4.3×10^{-4} emu/mole for K_3C_{60}, which is smaller than the reported values.[8,9] The g value ($g=2.0004$), and the peak-to-peak linewidth (δH=1.4 mT) are consistent with the literature.[9]

The ESR signal (g value and peak-peak linewidth) of $NH_3K_3C_{60}$ is very similar to that of K_3C_{60} at room temperature. The relative integrated intensity for $NH_3K_3C_{60}$ and K_3C_{60} was carefully measured using several samples. This experiment lead us to a conclusion that the intensity of $NH_3K_3C_{60}$ is the same as that of K_3C_{60} within an experimental error at room temperature.

At low temperatures we observed different behaviors in $NH_3K_3C_{60}$ and K_3C_{60}. In $NH_3K_3C_{60}$, a sharp impurity line (~0.1 mT in width) appears below 150 K in addition to the intrinsic broad line (δH~1.5 mT). The integrated intensity of the sharp line approximately follows the Curie law drawn by a thin broken line in Fig. 1. The estimated spin concentration was about 2% per C_{60} molecule. The broad intrinsic signal suddenly decreases at 40 K and disappears leaving the narrow impurity line below 20 K. The contribution of impurity signal in K_3C_{60} was roughly one order smaller than that in $NH_3K_3C_{60}$. Figure 1 shows the temperature dependence of peak-to-peak linewidths and integrated intensities for $NH_3K_3C_{60}$ and K_3C_{60}. For $NH_3K_3C_{60}$, the broad intrinsic component is plotted by solid circles. The intensity is normalized by the room-temperature value of K_3C_{60}. While the intensity for K_3C_{60} is almost temperature independent, showing a slight decrease at low temperature, the intensity increases with decreasing temperature followed by a sharp drop at 40 K in $NH_3K_3C_{60}$. The ESR linewidth slightly decreases with temperature in K_3C_{60}, whereas, the width is almost constant in $NH_3K_3C_{60}$. However, we must note that the width data for $NH_3K_3C_{60}$ involves large experimental errors ($\pm0.2\sim0.3$ mT) at temperatures lower than 100 K, due to the narrow and strong impurity line.

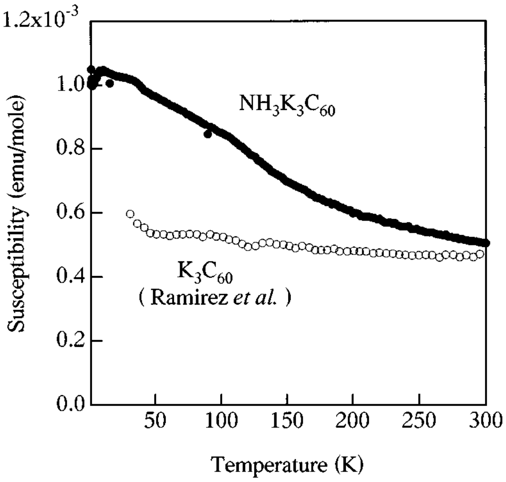

FIG. 2. Magnetic susceptibility of $NH_3K_3C_{60}$ and K_3C_{60}. The Curie tail attributable to impurities are subtracteD from the raw data. The data for K_3C_{60} was taken after Ref. 11.

First we focus on the high-temperature phase of $NH_3K_3C_{60}$. The increase in the ESR intensity upon cooling is in a sharp contrast to the behavior of A_3C_{60}, typically shown in Fig. 1 for K_3C_{60}. Here A is alkali metals. The slight decrease in the intensity of K_3C_{60} is explained by the reduction of $N(\epsilon_F)$ due to the lattice contraction.[9] The increase in the ESR intensity upon cooling observed in $NH_3K_3C_{60}$ is rather exceptional for conventional A_3C_{60} compounds. Only from the ESR data, we cannot tell whether $NH_3K_3C_{60}$ is metallic or not. However, taking account of the susceptibility and NMR data shown below, we conclude that the high-temperature state is metallic. The temperature dependence of ESR linewidth is another useful means to investigate the metallic states of alkali intercalated C_{60} materials.[9] The observed temperature dependence in $NH_3K_3C_{60}$ is very similar to that of A_3C_{60} materials with large lattice parameters and with high T_c such as Rb_3C_{60}.[10,9] This result indicates that $NH_3K_3C_{60}$ is a narrow-band metal.

Below 40 K, the intrinsic broad signal suddenly disappears leaving the sharp impurity component. The disappearance of the conduction ESR signal suggests a drastic change in electronic properties, such as a metal-insulator transition.

Figure 2 shows the magnetic susceptibility of $NH_3K_3C_{60}$ and K_3C_{60}. The data for the ammoniated compounds were collected using a superconducting quantum in-

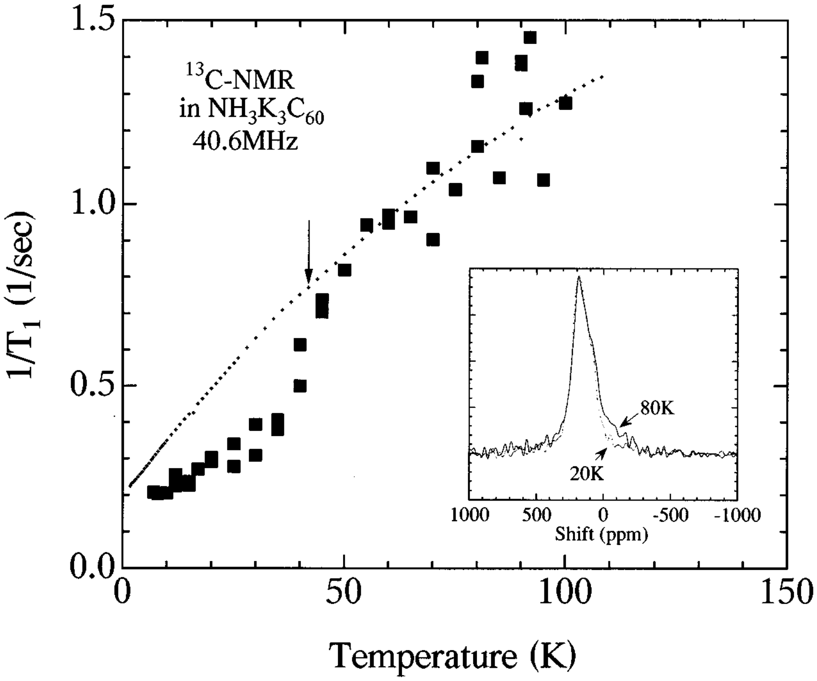

FIG. 3. Temperature dependence of T_1^{-1} for ^{13}C NMR for $NH_3K_3C_{60}$. The full squares are experimental results, and the dots are calculated data using Eq. (1) from the static susceptibility. The inset shows the NMR spectra at 80 and 20 K.

terference device susceptometer on 50 mg powder samples sealed in NMR tubes. The contribution from the tubes were subtracted by an independent measurement of the empty tube. We did not see any evidence for ferromagnetic impurities which are sometimes observed in alkali doped C_{60} materials. The raw data involved the Curie tail at low temperature that is approximated by the formula $1.0\times10^{-2}/(T+\theta)$ [emu/mole], which corresponds to 2.6% spins per C_{60} (here, $\theta=1$ K). The concentration of impurity spins agrees with the ESR data. In Fig. 2, the Curie part was subtracted from the raw data. The diamagnetic contribution from C_{60}, potassium ion, and ammonia was not subtracted. Both NH_3-rich and poor samples showed similar behaviors, indicating the observed features in Fig. 2 are intrinsic to $NH_3K_3C_{60}$.

The susceptibility χ at room temperature is 5.0×10^{-4} emu/mole. This value is close to that for K_3C_{60} (4.7–5.9 $\times10^{-4}$ emu/mole after Ramirez *et al.*[11]). Thus we conclude that ammoniation does not change static susceptibility χ at room temperature, in a fair agreement with the ESR results. The χ increases with decreasing temperature in contrast with the almost temperature-independent χ of K_3C_{60}. The χ value at low temperature reaches 1×10^{-3} emu/mole, which is comparable to the raw data for Rb_3C_{60}.[11] The enhancement of χ at low temperature is qualitatively consistent with the ESR. This behavior may suggest that the electron correlation effect is stronger in $NH_3K_3C_{60}$ than in K_3C_{60}.

In a marked contrast with the ESR, the susceptibility does not show any anomaly around 40–45 K. The nonvanishing susceptibility at the lowest temperature implies that the magnetic excitations remain in the low-temperature state.

To confirm the phase transition and investigate the high- and low-temperature states, we measured ^{13}C NMR for $NH_3K_3C_{60}$ at 40.6 MHz. 50-mg powder samples were sealed in NMR tubes of 5 mm in diameter. The ^{13}C spin-lattice relaxation time T_1 was determined by a conventional saturation recovery method, using the relation $M(t)=M_1[1-C\exp\{-(t/T_1)^{\alpha}\}]$. Here $M(t)$ is time-dependent magnetization and M_1, C, T_1, and α are fitting parameters. The ^{13}C NMR spectra was obtained by a pulse Fourier transformation.[12] The peak position was measured as a shift from that of tetramethylsilane standard. The spectra of $NH_3K_3C_{60}$ has a sharp single peak with the shift of 195 ±2 ppm at room temperature, ensuring the purity of the sample. This shift is slightly larger than that of K_3C_{60} (187 ±2 ppm). The sharp spectra (13 ppm in width) indicates that C_{60} molecules rotate at room temperature. The signal becomes broader below 150 K, implying the freezing of molecular rotation. The detailed features of ^{13}C NMR and ^{1}H NMR are reported in a separate paper.

Figure 3 shows the T_1^{-1} against temperature below 100 K. To test the metallic nature above 40 K, the data are compared with the calculated curve of

$$1/T_1=A\chi_s^2T+B. \tag{1}$$

Here, χ_s is the spin susceptibility computed from the data in Fig. 2 using the relation that $\chi_s=\chi-\chi_{\mathrm{core}}$, where the orbital magnetism is neglected.[11] χ_{core} is the sum of contribution from K_3C_{60} $(-3.05\times10^{-4}$ emu/mole$)$[11] and NH_3 $(-1.8\times10^{-5}$ emu/mole$)$.[13] Assuming that the B term $(=0.2$ $s^{-1})$ is attributed to the paramagnetic impurities, the concentration of impurities is roughly estimated to be 3%, which is not far from the paramagnetic impurities found in magnetic susceptibility and ESR. Since the observed NMR relaxation rate $1/T_1$ (full squares) is well fitted by Eq. (1) between 40 and 100 K, the intrinsic relaxation rate is explained by the Korringa law. Although ESR, magnetic susceptibility, and resistivity[6] cannot be definitive tests for the electronic properties above 40 K, the NMR result provides an unambiguous evidence for the metallic state. It is noted that T_1^{-1} of $NH_3K_3C_{60}$ is larger than that of K_3C_{60} at each temperature. This is explained by the difference in χ of the two materials shown in Fig. 2.

A clear deviation from the Korringa relation is observed at about 40 K (indicated by an arrow), corroborating the occurrence of the phase transition. The deviation from the Korringa law and disappearance of conduction-electron spin resonance strongly indicate that this phase change is a metal-insulator transition.

As to the nature of the low-temperature phase, experimental results are controversial. NMR results imply that the low-temperature state is nonmagnetic. First, we did not observe any enhancement of ${T_1}^{-1}$ which is frequently found at the antiferromagnetic or spin density wave (SDW) transition in organic conductors.[14] Second, if the low-temperature phase is the antiferromagnetically ordered states, the linewidth should be broadened due to the inhomogeneity of the internal field. The inset of Fig. 3 shows the ^{13}C NMR spectra at 80 and 20 K. Neither the line shape nor the intensity change very much across 40 K, implying that the magnetic moment is smaller than the detection limit. The ESR results also suggest that the low-temperature phase is nonmagnetic. If the low-temperature state is antiferromagnetically ordered, the ESR linewidth is usually broadened as was found in Rb_1C_{60}.[15] The observed linewidth, however, does not show much change around the transition temperature, although the accurate measurement is hindered by the impurity line. The absence of ESR line broadening does not support the magnetic ground states.

However, it is impossible to understand the nonvanishing static susceptibility at the low-temperature phase (Fig. 2) in terms of the nonmagnetic insulator model. In this model, the temperature dependence of static susceptibility should be similar to that of the ESR intensity. A possible explanation for this contradiction is the antiferromagnetic insulating state with an extremely small magnetic moment. This hypothesis does not contradict the absence of broadening of ESR and NMR lines characteristic to antiferromagnetic transition because the internal field should be also small. Small moment, for example in the order of $10^{-3}\mu_B$, cannot be easily detected by standard techniques. In the antiferromagnetically ordered state, the magnetic susceptibility perpendicular to the easy axis is not zero, resulting in a nonvanishing susceptibility at low temperature in powder samples. On the other hand, since the conditions for the antiferromagnetic resonance are very different from that for the paramagnetic resonance, the ESR signal disappears at the transition temperature. All the observed features so far are understood by the antiferromagnetic insulator model with the small moment. This insulator might be related to the Mott-insulating state predicted by Rosseinsky *et al.*[5] However, the reason for the moment shrink remains to be explained. Experiments using better samples might help to solve the puzzle.

It is noted that the results of ESR intensity and susceptibility of $NH_3K_3C_{60}$ are similar to those of Rb_1C_{60}. In the latter material, the ESR intensity dramatically decreases at 50 K, while the susceptibility exhibits only a small knee at this temperature.[16] The ESR linewidth, on the other hand, is considerably broadened below 50 K, so that the antiferromagnetic transition was unambiguously confirmed.[15]

In summary, we have shown that lattice expansion and symmetry reduction of K_3C_{60} by ammoniation cause a serious change in electronic properties. $NH_3K_3C_{60}$ retains a narrow-band metallic state at high temperature, but undergoes a metal-insulator transition at 40 K instead of superconductivity.

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