Solvent Effects on Superconducting Alkali-Metal Intercalated C_{60} Prepared from Liquid Ammonia Studied by Solid-State NMR

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The directly isolated precipitate of Rb_xC_{60} from liquid ammonia contains solvent molecules, NH_3. Thermal treatment is necessary to remove ammonia solvent molecules from the lattice as well as to homogenize the Rb distribution within the synthetic product, to produce a face-centered cubic (fcc) unit cell. This latter unit cell is the form of Rb_3C_{60} which shows superconductivity. The superconducting transition temperature, T_c, is found to be lower in Rb_3C_{60} samples prepared from liquid ammonia than from those prepared by a conventional vapor transport technique. The depression of T_c can be explained in terms of a large degree of orientational disorder of C_{60} ions, along with effects of a trace amount of residual NH_3, as suggested from solid-state NMR results.

Introduction

Synthesis of superconducting alkali-metal intercalated fullerides A_3C_{60} (A = K, Rb) in liquid ammonia has attracted considerable interest as an alternative technique to complement the conventional vapor-transport technique.[1−5] This method offers the following advantages: (a) it is an efficient and an effective way to produce superconducting A_3C_{60} phases, as compared to the vapor-transport technique; (b) it extends the dopant elements selection, by taking advantage of the fact that most alkali and alkaline-earth metals and some rare-earth metals (Yb, Eu) are soluble in liquid ammonia to form solvated electron solutions; (c) liquid ammonia has a low boiling point (−33 °C) so that the solvent can be easily evaporated after the completion of the reaction, offering better control of stoichiometry of the synthetic product; (d) high-purity ammonia gas (purity 99.999%) is readily available minimizing the effect of solvent impurities; (e) a large number of both organic and inorganic compounds are soluble in liquid ammonia, offering potential of synthesizing new fullerene-based materials.

However, there are several controversial questions regarding the liquid ammonia synthetic method. For example, Murphy[1] reported that the reaction product recovered from liquid ammonia was noncrystalline, and solvent molecules could be removed only after heating the product over 300 °C. In contrast, Buffinger[2] concluded that the amount of residual ammonia was negligible after the product was gently heated (100 °C) under dynamic vacuum, and the superconducting Rb_3C_{60} phase was produced after 2 days annealing at 375 °C. It has also been reported[3] that the synthetic product recovered from liquid ammonia was a mixed phase consisting of a face-centered cubic (fcc) unit cell and a body-centered tetragonal (bct) unit cell after being dried at 100 °C for about 1 h under dynamic vacuum. A single Rb_3C_{60} phase could be obtained only after the product was further heated at 150 °C for a few days under dynamic vacuum.

Experimental evidence has shown that ammonia molecules can be intercalated into vacancy sites of an A_3C_{60} lattice to expand or distort the unit cell of the host lattice and to further affect the superconductivity as well.[5−7] Intercalation of NH_3 into Na_2CsC_{60} results in lattice expansion of the fcc unit cell, with a consequent dramatic increase in the superconducting transition temperature.[5] However, either intercalation of NH_3 into K_3C_{60} or Rb_3C_{60} distorts the original fcc unit cell into $K_3C_{60}(NH_3)$ with a body-centered tetragonal (bct) unit cell[6] or there is a disproportionation of the original Rb_3C_{60} into a mixture of orthorhombic RbC_{60} and a body-centered orthorhombic *Immm* phase of Rb_4C_{60}-

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$(NH_3)_{1.7}$,[7] both compounds showing the absence of superconductivity. Rb_3C_{60} was found to readily absorb gaseous ammonia at room temperature. Intercalation with about one ammonia per C_{60} disrupts the original fcc unit cell of Rb_3C_{60}. Furthermore, X-ray diffraction showed that the formed $Rb_3C_{60}(NH_3)_x$ shared a single basic structure with x values up to 4.[8]

The present work is an attempt to answer two fundamental questions concerning liquid ammonia synthesis. Do solvent molecules participate in the formation of the product, and if they do, how do these ammonia molecules affect the structure as well as the superconductivity? To answer these questions, X-ray diffraction was used to perform detailed structural analysis, and solid-state NMR measurements were applied to probe the electronic states and molecular dynamics.

Experimental Section

C_{60} was purchased from Hoechst with purity > 99% (Gold Grade) and was subjected to dynamic pumping at 200 °C for 2 h prior to use. Rubidium metal (99.8%) was obtained from Aesar and was used without further purification. Ammonia gas (semiconductor grade, purity > 99.999%) was obtained from Matheson & Company. All material transfers were performed in a nitrogen atmosphere glovebox which had an oxygen level controlled below 2 ppm and moisture less than 3 ppm.

A reactor in which Rb metal and C_{60} (75 mg) were stoichiometrically mixed was connected to a vacuum line manifold. The system was kept under a constant nitrogen purge (purity > 99.999%) to avoid oxygen and moisture contamination. About 10 mL of liquid ammonia was purified over potassium before being transferred into the reactor. The reaction chamber was kept at −78 °C (dry ice + acetone) for 60 min with magnetic stirring. An intense blue color appeared initially as liquid ammonia was added to the reactor. Then the solution turned dark reddish-brown as C_{60} powder dissolved into the solution phase. This color change sequence indicated that the reaction between Rb and C_{60} in liquid ammonia was proceeding stepwise. First, a solution forms consisting of solvated electrons from the ammonia reaction with alkali metal, which is a strong reducing agent with a characteristic intense blue color.[9] The second step involves charge transfer between C_{60} and the electron-solvated solution, giving rise to a homogeneous solution phase with a dark reddish-brown color.

At the end of the process, the reactor was slowly warmed (1.5 h) to evaporate ammonia. The reactor was then connected to a vacuum line to be dried under dynamic vacuum at room temperature for 1 h before being transferred into the glovebox where the synthetic product was collected. This “as-made” material was then heated at 125 °C for 3 days under dynamic vacuum, followed by further annealing at 375 °C for an additional 2 days in a sealed glass tube. Various characterization techniques were applied to both the “as-made” material and the product after thermal treatment. X-ray diffraction (XRD) spectra were taken on an INEL powder diffractometer (Cu Kα 1.5406 Å). The magnetic susceptibility was measured using a Quantum Design SQUID magnetometer. Additional electronic properties were evaluated via conventional pulsed NMR measurements.

Results and Discussion

Figure 1 a gives the room-temperature XRD profile of the “as-made” Rb_3C_{60} from liquid ammonia. This “as-made” sample has a nominal composition of $Rb_3C_{60}(NH_3)_x$ with $x = 0.8-1.0$, as determined from ^1H and ^{13}C solid-state NMR measurements. Indexing the sample on the basis of a simple unit cell was unsuccessful due to the low degree of crystallinity, as indicated by broadened diffraction peaks. However, the diffraction pattern in Figure 1a closely resembles those reported by Durand,[8] who observed the same pattern for samples of $Rb_3C_{60}(NH_3)_x$ ($x = 1-4$) obtained by exposing Rb_3C_{60} to either gaseous or liquid ammonia. On the basis of the XRD and inelastic neutron-scattering techniques, the new structure of $Rb_3C_{60}(NH_3)_x$ was described as supercells related to an underlying ideal body-centered $Im3m$ unit cell derived from C_{60}- - -C_{60} distances averaging 10.42 Å for the $x = 0.96$ sample.[10] Thermal treatment (125 °C, 3 days under dynamic vacuum and 2 days additional annealing at 375 °C) greatly improves the degree of sample crystallinity and results in the formation of a single fcc unit cell with a lattice constant of 14.42 ± 0.02 Å, as shown in Figure 1b. This measured lattice constant is in good agreement with those for an Rb_3C_{60} phase obtained via vapor-transport techniques.[11,12] Solid-state NMR measurements indicate that the sample has a nominal composition of $Rb_3C_{60}(NH_3)_{0.08}$ after thermal treatment.

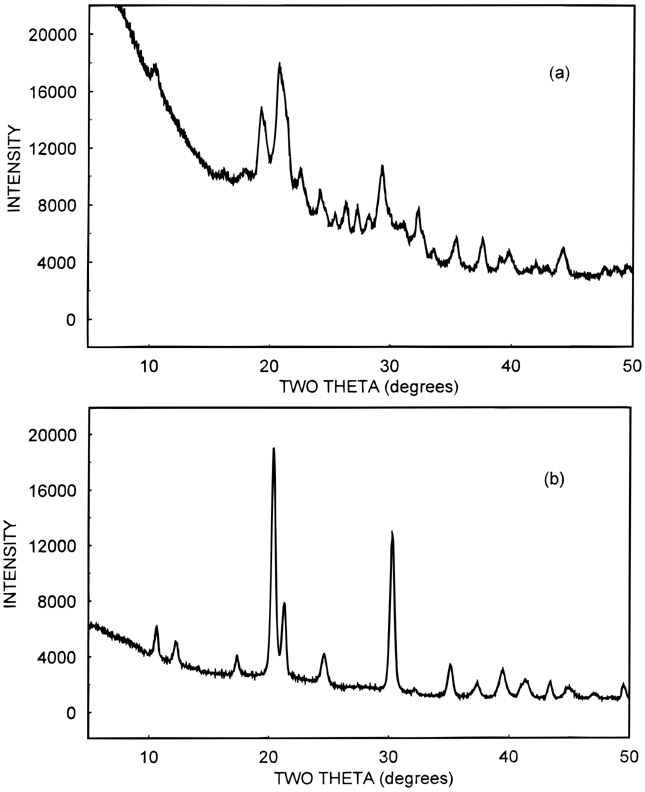

Figure 1. Room-temperature powder XRD patterns of (a) an “as-made”sample of $Rb_3C_{60}(NH_3)_{0.9}$ and (b) a sample of $Rb_3C_{60}(NH_3)_{0.08}$ after thermal treatment (125 °C, 3 days dynamic vacuum and 375 °C, 2 days additional anneal).

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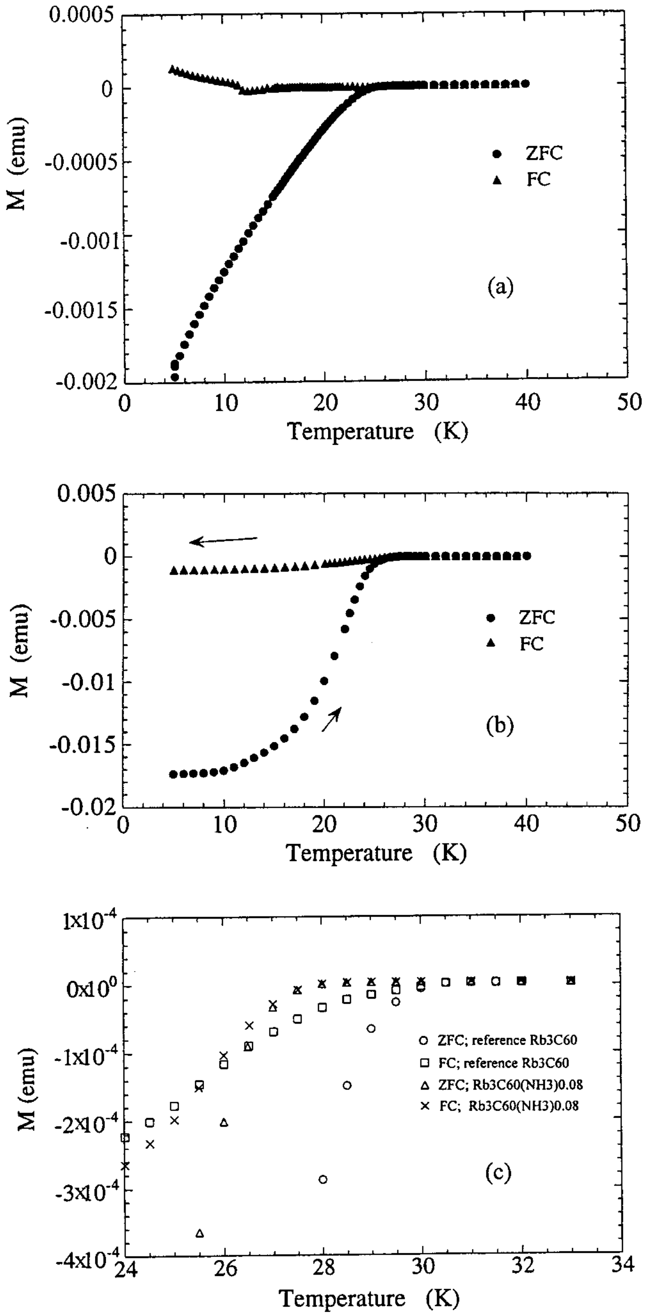

Figure 2. Temperature dependence of diamagnetic susceptibility measured at an applied field of 20 G. (a) An "as-made"sample of $Rb_3C_{60}(NH_3)_{0.9}$, and (b) a sample of $Rb_3C_{60}(NH_3)_{0.08}$ after thermal treatment (125 °C, 3 days dynamic vacuum and 375 °C, 2 days additional anneal), and (c) an expanded view around T_c of a reference Rb_3C_{60} sample, and a sample of $Rb_3C_{60}(NH_3)_{0.08}$ from (b).

The temperature dependence of magnetization of Rb_3C_{60} for different thermal treatments is shown in Figure 2. For comparison, data on a reference Rb_3C_{60} sample prepared by the vapor-transport technique are also shown. The "as-made" sample from liquid ammonia (Figure 2a) shows a weak superconducting signal with T_c at 26 K, and the shielding fraction estimated from its zero-field-cooled (ZFC) magnetization at a temperature of 5 K is about 4% in comparison with a perfect superconductor of cylindrical geometry. After being heated at 125 °C under dynamic vacuum for 3 days, the sample (data not shown) shows an enhanced shielding fraction (about 60%) with a T_c of 27−28 K. The superconducting transition region is broad, however, suggesting that there exist weak links between the superconducting grains.[11] Additional annealing at 375 °C for 2 days produces a sharper transition (onset $T_c \sim 28$ K). The superconducting shielding fraction is estimated to be about 60% (Figure 2b).

The SQUID results clearly show that thermal treatment of Rb_3C_{60} prepared from liquid ammonia plays an important role in the sample's superconducting property. The observed weak diamagnetic signal from the "as-made" powder is probably due to the presence of a small amount of an fcc superconducting phase of Rb_3C_{60}, i.e., the superconducting fraction is very low in this sample. Most of the ammonia solvent can be removed from the sample during 3 days heating at 125 °C under dynamic vacuum, to yield a nominal composition of $Rb_3C_{60}(NH_3)_{0.08}$. The high shielding fraction produced at this stage indicates that the sample undergoes a solid-phase transition to form fcc Rb_3C_{60} as the major phase while ammonia molecules are driven off from the lattice. Apparently, additional annealing at higher temperature (375 °C for 2 days) is necessary to achieve a higher onset critical temperature and a sharper transition region, suggesting that a longer annealing treatment at higher temperature is required to produce an ideal fcc superconducting Rb_3C_{60}. It should be mentioned here that the need for thermal treatment is to homogenize the Rb distribution within the "as-made" product, as well as to remove residual NH_3 solvent. Due to the nature of a solid-phase process, an insufficient thermal treatment will likely result in the formation of a crystal phase with either defects or a distorted unit cell.

These results are in contrast to the conclusions of Boss et al.,[3] who state that the liquid ammonia method produces a precipitate with ammoniated alkali cations in a proper crystal structure and that the primary function of a subsequent thermal treatment is the complete removal of the ammonia, rather than a solid-state reaction. There is also disagreement between these results and those of Zhou et al. in which it was found that the complete removal of ammonia from $(NH_3)_4Na_2CsC_{60}$ can be achieved after a few minutes of gentle heating under dynamic vacuum.[5] A possible reason for the difference is that while intercalation of ammonia into Na_2CsC_{60} causes a volume expansion without disturbing the original fcc unit cell of the host lattice, ammoniated Rb_3C_{60} precipitated from liquid ammonia possesses a different crystal structure than a pure Rb_3C_{60} phase. A substantial difference in the removal of intercalated ammonia is thus anticipated.

There are two side reactions that must be taken into consideration with regard to liquid ammonia synthesis. One is possible amide formation due to the decomposition of a metastable alkali metal solution in liquid ammonia.[13] This reaction can be minimized under the synthetic conditions employed in this work, since (a) the reaction is conducted at −78 °C, therefore reducing the rate of decomposition, and (b) the alkali metal solvated solution appears only during the first few minutes of

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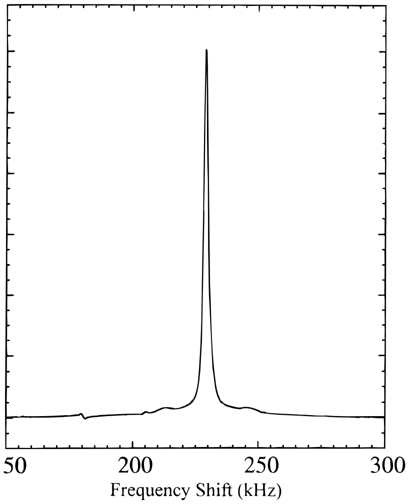

Figure 3. Room-temperature ^{1}H NMR frequency shift (kHz) measured from an "as-made" sample of $Rb_3C_{60}(NH_3)_{0.9}$. Applied field $f = 161.48$ MHz.

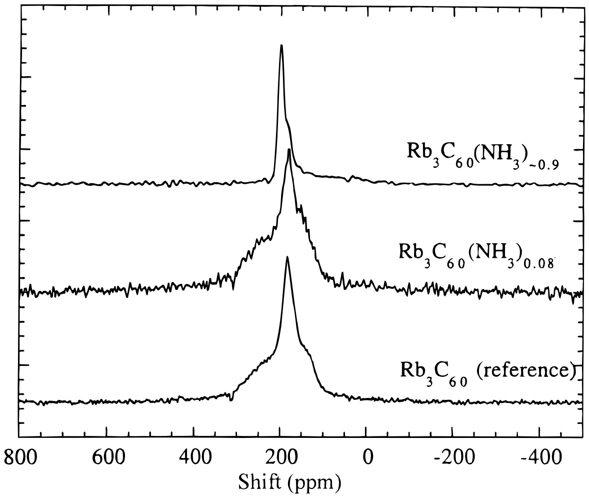

Figure 4. Room-temperature ^{13}C NMR line shapes for samples before thermal treatment ($Rb_3C_{60}(NH_3)_{0.9}$), after thermal treatment ($Rb_3C_{60}(NH_3)_{0.08}$) and a reference sample of Rb_3C_{60}. Frequency shift is relative to TMS (ppm), applied field $f = 40.61$ MHz.

the reaction, followed by a rapid charge-transfer process between the solvated solution and C_{60} powder. The second side reaction is nucleophilic attack. It has been shown that C_{60} reacts with various amines due to its high electron affinity, to form C_{60}-amine adducts.[14−16] This reaction can be neglected in the case of liquid ammonia, since the reaction occurs at a very low temperature, which limits the reaction rate between C_{60} and ammonia. In fact, our study shows that pure C_{60} can be recovered after being kept in liquid ammonia for 2 h, which is a typical time scale for a synthetic reaction in liquid ammonia. In addition, charge transfer between C_{60} and alkali metal solvated solution in liquid ammonia progresses very rapidly. The reaction forms $C_{60}{}^{n-}$ anions in solution,[17,18] which makes further nucleophilic attack very unlikely. Like most of the ammoniated alkali metal salts, the primary synthetic product $Rb_3C_{60}(NH_3)_x$ decomposes to release NH_3 upon vacuum heating. Raman scattering experiments indicate that the oxidation number of C_{60} in this sample is the normal −3 state. All the above evidence strongly suggests that ammonia exists in its molecular form.

There is a decrease of T_c found in samples prepared from liquid ammonia, compared with that of the reference Rb_3C_{60} from the vapor-transport technique (Figure 2). To study the origin of the T_c depression, solid-state NMR experiments were performed. Figure 3 shows a ^{1}H NMR spectrum measured from the "as-made" sample which has a nominal composition of $Rb_3C_{60}(NH_3)_x$ with $x \sim 0.9$ at room temperature. There are two satellite lines appearing at 213 and 246 kHz respectively around the main line at 229 kHz. Such a line shape is indicative of a triangular-shaped NH_3 molecule rotating around a 3-fold axis,[19] confirming that ammonia solvent exists in its molecular form. Figure 4 presents the ^{13}C NMR spectra at room temperature of an annealed sample of $Rb_3C_{60}(NH_3)_{0.08}$, an "as-made" sample of $Rb_3C_{60}(NH_3)_x$ ($x \sim 0.9$) and a reference sample of Rb_3C_{60} ($x = 0$). Compared with those samples with an fcc crystal structure ($x = 0$ and 0.08), the motional narrowing of the ^{13}C resonance from the "as-made" sample indicates that large-amplitude C_{60} ion rotation is taking place at room temperature. This significant difference in the molecular dynamics of C_{60} may be ascribed to the difference in the degree of disorder, as reported by Buffinger et al.[2] However, we suggest an alternative explanation, namely, that the observed sharp line in $Rb_3C_{60}(NH_3)_x$ ($x \sim 0.9$) is due to a different crystal phase observed in the XRD pattern in Figure 1. In fact, the temperature dependence of the sharp line of $Rb_3C_{60}(NH_3)_x$ ($x \sim 0.9$) is different from that of fcc A_3C_{60}: with decreasing temperature the peak position of the ^{13}C resonance measured from $Rb_3C_{60}(NH_3)_x$ ($x \sim 0.9$) moves to the downfield side (~202 ppm at 300 K to ~206 ppm at 250 K). Such a temperature dependence is similar to the case of $K_3C_{60}(NH_3)$ with a bct unit cell, rather than to fcc A_3C_{60} which has a nearly temperature-independent spin susceptibility.[20,21]

Figure 5 shows the ^{87}Rb NMR spectrum measured from an "as-made" sample of $Rb_3C_{60}(NH_3)_x$ ($x \sim 0.9$), an annealed sample of $Rb_3C_{60}(NH_3)_{0.08}$, and a reference Rb_3C_{60}. For fcc Rb_3C_{60} (annealed and reference samples), ^{87}Rb NMR measurement reveals three distinct peaks marked as T, T′, and O, where T and T′ are ascribed to Rb cations located at tetrahedral interstitial sites and O is to those at an octahedral interstitial site.[2,22,23] In

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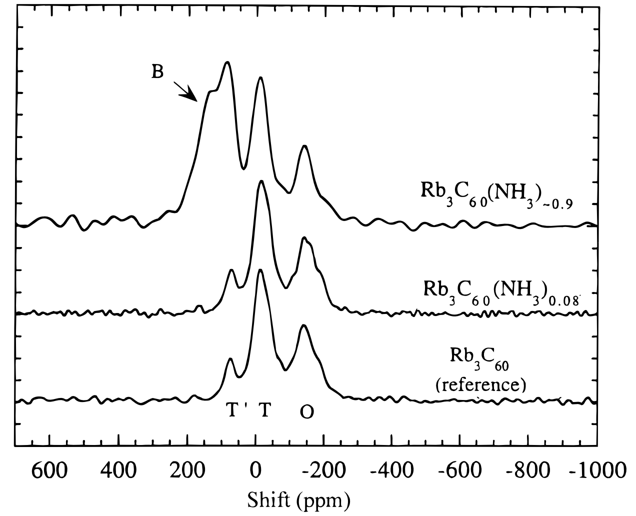

Figure 5. Room-temperature ^{87}Rb NMR line shapes for samples before thermal treatment ($Rb_3C_{60}(NH_3)_{0.9}$), after thermal treatment ($Rb_3C_{60}(NH_3)_{0.08}$) and a reference sample of Rb_3C_{60}. Frequency shift is relative to RbCl (ppm). Applied field $f = 52.84$ MHz.

addition to those peaks from an fcc phase, a new signal B has been found in the "as-made" sample at the lower field side of T′ peak. The origin of peak B is not yet clear. However, it is worth mentioning that a similar signal has been observed in $K_3C_{60}(NH_3)$ with a non-fcc structure.[20]

It should also be noted that ^{87}Rb NMR spectra reported by Buffinger et al.[2] did not show the new peak B in their unannealed Rb_3C_{60}. The lack of the peak B suggests that their unannealed sample is probably different from the present "as-made" sample of $Rb_3C_{60}(NH_3)_x$ ($x \sim 0.9$) in this study, while they reported that the NH_3 contents in their samples were lower than 0.3 N atom per C_{60}. Nevertheless, our solid-state NMR observations, combined with the corresponding XRD patterns in this study, indicate that the "as-made" sample includes NH_3 molecules, which presumably leads to a different crystal structure and to a different electronic state from those of fcc Rb_3C_{60}.

In A_3C_{60} superconductors, where A is an alkali metal, the superconducting transition temperature T_c has been confirmed to be well correlated with the electronic density of states, $N(E_f)$, at the Fermi level, although $NH_3-A_3C_{60}$ violates this relation if one uses $N(E_f)$ at room temperature.[20] To obtain information on $N(E_f)$, the ^{13}C NMR spin−lattice relaxation time T_1 was measured at low temperature, which is expected to follow the Korringa law in metals: $(T_1T)^{-0.5}$ is proportional to $N(E_f)$. T_1 was obtained using a conventional saturation recovery method. The recovery magnetization $M(t)$ could not be expressed by a single T_1 as shown in Figure 6. At low temperature, a metallic $T_1T =$ const law was confirmed, as occurs in other A_3C_{60} superconductors.[24] Interestingly, the average T_1 was found to be shorter in $Rb_3C_{60}(NH_3)_{0.08}$ than in the reference Rb_3C_{60}, which corresponds to $N(E_f)$ of $Rb_3C_{60}(NH_3)_{0.08}$ being larger by 7% than that in the reference sample.

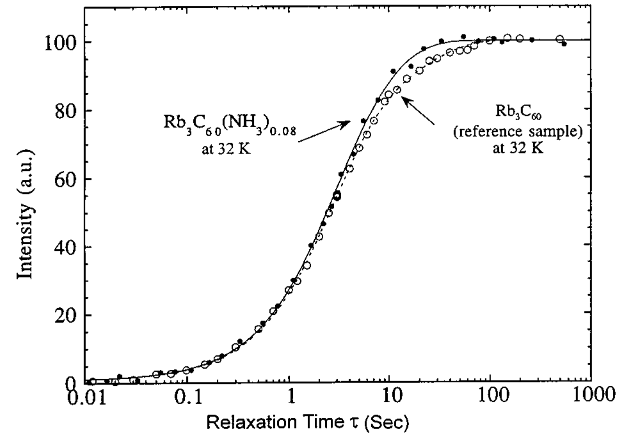

Figure 6. Low-temperature measurement of ^{13}C spin−lattice relaxation time T_1. Solid dots and open circles are experimental data of measured recovery magnetization at delay time τ after the saturation pulses. The solid line and dashed line are the results of a three-component fit on the basis of the following exponential function: $M_{(t)} = M_1 - M_2 \exp(-\tau/T_{1a}) - M_3 \exp(-\tau/T_{1b}) - M_4 \exp(-\tau/T_{1c})$ where T_{1a}, T_{1b}, T_{1c} correspond to those of three carbon sites in a fcc Rb_3C_{60}, and M_i ($i = 1-4$) are fitting parameters. For $Rb_3C_{60}(NH_3)_{0.08}$, T_1 values are 10.7, 4.41, and 1.86 s and in the intensity ratio 1:2:2. For the reference Rb_3C_{60}, T_1 values are 22.6, 4.29, and 1.96, in the intensity ratio of 1:2:2. The average T_1 is taken as $1/\langle T_1\rangle = (1/T_{1a} + 2/T_{1b} + 2/T_{1c})/5$. The calculated average value of T_1 is 2.80 and 3.19 for a sample of $Rb_3C_{60}(NH_3)_{0.08}$ and a reference sample of Rb_3C_{60}, respectively.

This is qualitatively consistent with the slightly larger lattice constant of 14.42 Å found in $Rb_3C_{60}(NH_3)_{0.08}$, as compared to 14.39 Å in the reference sample. However, a quantitative estimate using $dN(E_f)/da = 9.46$ [states/eV/C_{60}/spin][20] gives a value only 3% larger than that of the reference sample. The additional enhancement in $N(E_f)$ is possibly due to the C_{60} orientational disorder, as in Na_2CsC_{60} where the orientational disorder states with an fcc structure above room temperature have $N(E_f)$ larger by 10% than the sample in a simple cubic ordered state.[25] At any rate, the present results of T_c depression cannot be explained by a change in the electronic density of states, $N(E_f)$.

Figure 6 includes another important feature, in which T_1 (that is, the local density of states at each carbon site) is more homogeneous in $Rb_3C_{60}(NH_3)_{0.08}$ than that in the reference sample. In an ideal fcc Rb_3C_{60}, where C_{60} ions are in orientational ordered states within the lattice, there are three different carbon sites with quite different local electronic density of states.[26] Therefore, the origin of the more homogeneous distribution of T_1 observed in $Rb_3C_{60}(NH_3)_{0.08}$ is likely caused by an orientational disorder of C_{60} ions, along with the effect from the residual NH_3 molecules. Both imperfections of crystal structure would smear out the difference in $N(E_f)$ at each carbon site.

The results on $Rb_3C_{60}(NH_3)_{0.08}$ as compared to the reference Rb_3C_{60} can be summarized as follows: (1) the lattice constant is slightly larger, (2) the value of $N(E_f)$ is larger by 7% at low temperature (~32 K), and (3) the distribution of local density of states is more homoge-

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neous. These observations suggest that there exists a larger degree of orientational disorder in $Rb_3C_{60}(NH_3)_{0.08}$, and those intercalated residual NH_3 molecules, as impurities, will probably cause defects to be formed within the fcc lattice.

Thus the T_c depression mechanism can be explained from this point of view: the lattice imperfection, including a higher degree of orientational disorder of C_{60} ions, and residual NH_3 impurities, can cause significant disturbance of the triply degenerate t_{1u} state in C_{60} molecular orbitals, which correspond to the depression of superconductivity in the sample of Rb_3C_{60} synthesized from liquid ammonia. A similar situation was also observed in Na_2KC_{60} and Na_2RbC_{60}, where lattice imperfections or disorder were considered to lead to significant T_c depression.[27] The sensitivity of T_c to the lattice imperfection may be due to the nature of the narrow t_{1u} conduction band in A_3C_{60} superconducting compounds. Also, the triple degeneracy of the t_{1u} orbital can easily be lifted by lowering the crystal field symmetry, by Jahn–Teller splitting, and by rather strong electron correlation effects.

Conclusions

Rb intercalated fullerene C_{60} has been synthesized by utilizing liquid ammonia as a solvent. The sample precipitated from the solvent contains NH_3 molecules with a nominal composition of $Rb_3C_{60}(NH_3)_x$ ($x \sim 0.9$). X-ray diffraction indicates that this "as-made" sample has a low degree of crystallinity and possesses a crystal structure similar to a supercell based on a body-centered $Im3m$ unit cell found by Durand et al.[8] Most of ammonia solvent molecules can be removed from lattice sites by applying thermal treatment at 125 °C for 3 days under dynamic vacuum plus 2 days additional anneal at 375 °C. During this heat treatment, the sample forms a fcc unit cell with a nominal composition of $Rb_3C_{60}(NH_3)_{0.08}$. The superconducting transition temperature T_c, is 28 K for the sample of $Rb_3C_{60}(NH_3)_{0.08}$ after annealing, which is about 2 K lower than a reference sample of Rb_3C_{60} obtained from a conventional vapor transport preparation. Solid-state NMR results suggest that the T_c depression is likely due to a higher degree of orientational disorder of C_{60} ions in the sample $Rb_3C_{60}(NH_3)_{0.08}$, and might be due to the effect of residual NH_3 molecules and other related defects within the fcc lattice structure as well.

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