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Rapid and Efficient Synthesis of Alkali Metal–C_{60} Compounds in Liquid Ammonia

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Abstract: The reaction of stoichiometric amounts of alkali metals with C_{60} in liquid ammonia provides a rapid and quantitative route to M_xC_{60} superconductors ($M_x = K_3$, Rb_3, $CsRb_2$, $RbCs_2$, KRbCs). Annealing of the samples for 24–48 h at 375 °C is required to obtain large superconducting fractions. ^{13}C and ^{87}Rb NMR line shapes are reported for Rb_3C_{60}. The ^{13}C line shapes show the degree of rotational motion of the C_{60} ions varies considerably from sample to sample and is dependent on the method of preparation and subsequent heat treatment. A correlation between the degree of rotational motion and the superconducting fraction is noted and attributed to the amount of disorder in the sample. ^{87}Rb NMR shows three peaks indicating that Rb_3C_{60} actually contains three different cation sites, rather than the two suggested by X-ray powder diffraction data. The third site is occupied by approximately 15% of the Rb ions in Rb_3C_{60} and is shown to be a subset of the tetrahedral sites in the cubic close-packed C_{60} lattice. Although the exact nature of the distortion required to produce the third site is unknown, it appears to be unrelated to the orientations of the C_{60} ions creating the site.

The discovery of superconductivity in alkali metal–C_{60} salts has generated a considerable amount of experimental and theoretical interest.[1–7] One of the limitations encountered in gaining a clearer understanding of these materials has been the difficulty in preparing good quality, single phase samples for physical measurements. Although the procedure for the preparation of alkali metal M_3C_{60} salts is simple and only involves the heating of stoichiometric amounts of the metal or M_6C_{60} and C_{60} in a sealed tube,[1,8] it is time consuming and often results in a mixture of products. Additionally, the procedure is applicable only to metals that exhibit fairly high vapor pressures ($\sim 10^{-2}$ Torr and above) at temperatures below the point at which they attack the quartz reaction container, typically less than ~600 °C. Solution routes to M_3C_{60} (M = K, Rb) have been reported,[9–11] but residual solvent and the need for excess alkali metal which must be separated from the product have limited the utility of these methods. We report here that the preparation of M_3C_{60} salts by the reaction of alkali metals and C_{60} in liquid ammonia circumvents these problems and provides a rapid and quantitative route to alkali metal–C_{60} compounds. It is also potentially applicable to the preparation of compounds containing other metals that are soluble in liquid ammonia (alkaline earth metals, Yb, and Eu).

Experimental Section

C_{60} was prepared from soot generated by a 4.0 kW dc carbon arc in a water-cooled vacuum chamber maintained at ~200 Torr of He pressure.[12] C_{60} was extracted from the soot with toluene and purified on a graphite/silica gel column with toluene as the eluent.[13] The C_{60} was dried under dynamic vacuum at 300 °C for 24 h to remove any residual solvent. The purity of the C_{60} was verified by mass spectrometry. Alkali metals (Strem Chemicals, 99.9+%) were used as received. Liquid ammonia (AGA Specialty Gas, 99.99%) was dried over sodium metal immediately prior to use. All of the alkali metals and alkali metal–C_{60} compounds were handled under vacuum or inert atmosphere conditions.

Rb_3C_{60} was prepared by the condensation of approximately 5 mL of liquid ammonia on stoichiometric amounts of C_{60} and Rb metal (65.0 and 23.1 mg, respectively) in an evacuated quartz tube at −78 °C. The reaction was carefully warmed to −55 °C and held for 30–60 min with occasional stirring with a quartz encapsulated stir bar. The ammonia was slowly removed over several hours to prevent bumping and then gently heated (<100 °C) under dynamic vacuum to remove any residual ammonia. The product was scraped from the tube in an inert atmosphere glovebox, pressed into a pellet, sealed in an evacuated silica tube, and then annealed for 24 h at 375 °C. Rb_3C_{60} was the only phase detected by X-ray powder diffraction. A standard C, H, and N analysis showed H and N levels to be below the detection limits (<0.5%), suggesting the amount of residual ammonia was negligible. The superconducting onset temperature was about 29 K, and a shielding fraction of approximately 80% was observed. We have prepared more than half a dozen samples of Rb_3C_{60} by this procedure with highly reproducible results. Rb_2Cs-, $RbCs_2$-, K_3-, and $KRbCsC_{60}$ have been prepared in a similar fashion with stoichiometric amounts of reactants with comparable results. Reactions to prepare alkaline earth, Eu, and Yb–C_{60} salts are in progress.

For purposes of comparison, Rb_3C_{60} was also prepared with the more conventional technique of heating stoichiometric amounts of Rb_6C_{60} and

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C_{60} in a sealed quartz tube for 24 h at 225 °C followed by 4 days at 350 °C.[8] X-ray powder diffraction and low temperature magnetic susceptibility measurements verified the presence of Rb_3C_{60} (T_c = 29 K, 60% shielding fraction). The Rb_6C_{60} was obtained by the reaction of excess Rb and C_{60} at 225 °C for 3 days. Cooling of the reaction in a small temperature gradient separated the excess Rb from the desired product.

Low-temperature magnetic susceptibility measurements were made in a 10 Oe field with a Quantum Design SQUID magnetometer. ^{13}C and ^{87}Rb NMR measurements were acquired on static samples in an 8.8 T field with a Techmag Libra spectrometer with a homebuilt probe. NMR line shapes were produced by Fourier transform of the spin-echo. ^{13}C and ^{87}Rb line shapes were referenced to C_{60} and saturated RbCl(aq), respectively. The narrow C_{60} resonance is located at 143 ppm relative to the conventional ^{13}C reference of TMS. In the ^{87}Rb NMR spectra only the $+^1/_2$, $-^1/_2$ Zeeman transition was observed.

Results and Discussion

The preparation of M_3C_{60} superconducting compounds proceeds readily in liquid ammonia with a variety of alkali metals. Although the reaction on paper appears to be a low temperature intercalation with the alkali metal diffusing into the face-centered cubic C_{60} lattice, the actual reaction is more complicated and involves not only M^+ ions and solvated electrons in solution but also C_{60}^{n-} ions. C_{60} is not soluble in NH_3(l) and does not react with ammonia under the reaction conditions.[14] Initial condensation of liquid ammonia on the reactants produces a dark blue solution characteristic of solvated electrons, which on warming to −55 °C and stirring changes to an intensely colored dark brown solution. Previous electrochemical and spectrophotometric studies of C_{60}^{n-} ions (n = 1, 2, 3, 4, 5) in a number of solvents including liquid ammonia have shown the dark brown color can be attributed to the presence of C_{60}^{n-} anions.[14,15] Evaporation of the ammonia leaves a black, largely amorphous powder. Low-temperature magnetic susceptibility measurements of the powder show essentially no superconducting fraction (<0.1%), although a very slight decrease in the susceptibility is observed beginning ~29 K. Annealing of the material in powder or pressed pellet form at 375 °C for 24 h produces a crystalline sample with an X-ray powder diffraction pattern that shows only Rb_3C_{60}. Superconducting fractions tend to be about a factor of 2 larger in samples annealed in pressed pellet form than those annealed in powdered form. Low-temperature magnetic susceptibility data show the annealed material contains a significant superconducting fraction (~80%) with an onset temperature of ~29 K. A very slow decrease in susceptibility occurs in the region just below T_c, but becomes much more rapid below ~23 K. This type of behavior has been attributed to weak links between the superconducting grains.[8] An additional 24 h of annealing sharpens the transition and increases the superconducting fraction to ~100%. Magnetic susceptibility data for three samples prepared from the same reaction but annealed in pressed pellet form for different periods of time are shown in Figure 1.

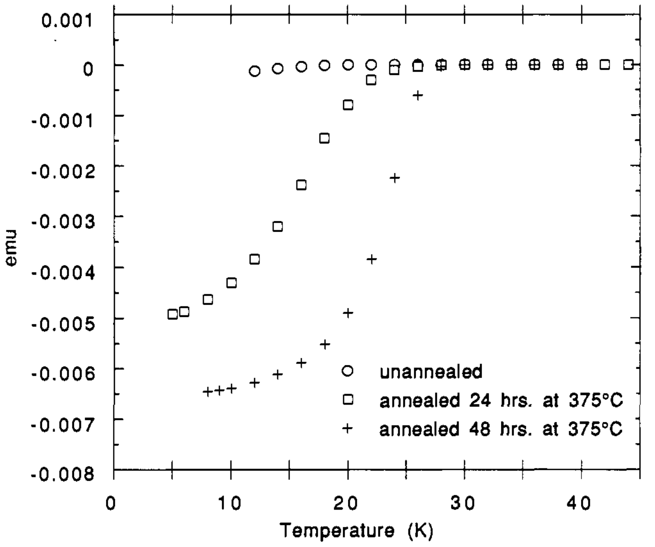

Figure 1. Plot of magnetic susceptibility data for three samples of Rb_3C_{60} prepared in liquid ammonia and annealed for different periods of time at 375 °C. All samples were cooled in zero field.

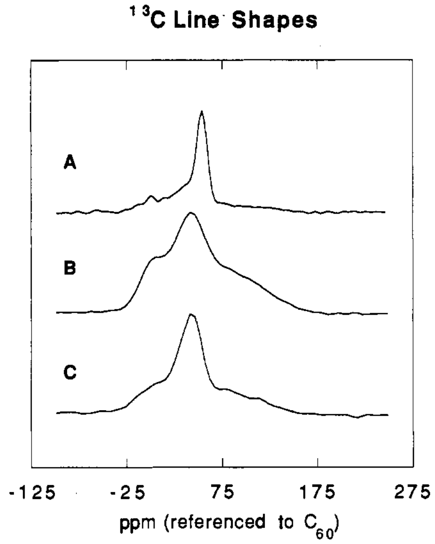

Figure 2. Plot of ^{13}C NMR line shapes for three samples of Rb_3C_{60}. Sample A was prepared in liquid NH_3 and has not been annealed. Sample B was prepared in NH_3 and annealed for 24 h at 375 °C. Sample C was prepared by heating Rb_6C_{60} and C_{60} for 4 days at 350 °C. Shifts are relative to C_{60}.

Concerns about residual ammonia prompted us to examine the reaction product in some detail. A standard C, H, and N analysis showed H and N levels to be less than 0.5 wt %. This translates into fewer than 0.3 N atoms/C_{60}. A proton NMR spectrum of a saturated solution of Rb_3C_{60} in CD_3CN showed no resonances that could be attributed to any species other than residual protons in the deuterated solvent. Ammonia associated with the alkali metal ions or trapped in the lattice should have been detectable with this approach. We suspect any residual ammonia is removed prior to the annealing process when the sample is gently warmed under vacuum. This is consistent with the behavior of $Na(NH_3)_4NaCsC_{60}$ which readily loses ammonia at relatively low temperatures under vacuum.[7] Weight changes observed during the annealing process, even on samples as large as 225 mg, were considered less than our experimental error, ~2 mg. Considering the lack of experimental evidence for ammonia in our samples and the large superconducting fractions, we conclude the amount of residual ammonia is negligible.

^{87}Rb and ^{13}C NMR line shapes were obtained for two Rb_3C_{60} samples prepared in liquid ammonia and also for a sample prepared by heating the Rb_6C_{60} and C_{60}. The latter sample was prepared to further substantiate the equivalence of the products prepared in liquid ammonia and those prepared by heating. The Rb_3C_{60} sample prepared in liquid ammonia was split into two samples once the ammonia was removed and subjected to different thermal treatments to examine the effects of annealing. Figure 2 shows the ^{13}C line shapes obtained for Rb_3C_{60} prepared in ammonia (samples A and B, annealed for 0 and 24 h, respectively) and a sample prepared by heating Rb_6C_{60} and C_{60} (sample C). A single peak is observed in all three spectra with a center of mass at ~50 ppm, measured from the line position of pure C_{60}. The ^{13}C line shapes for samples B and C are identical in gross detail and are comparable with those previously reported for Rb_3C_{60} and

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K_3C_{60}.[9,16] The resonance observed for sample B is somewhat broader than that in C, particularly around the base. The ^{13}C line shape obtained for the unannealed sample of Rb_3C_{60} prepared in ammonia, A, shows a much sharper resonance with the same center of mass as was observed for samples B and C. The ^{13}C line shape is also an excellent indicator of the presence of unreacted C_{60} which shows up as a peak at 0 ppm with a much longer spin–lattice relaxation time (T_1). None of the samples showed any unreacted C_{60}.

The differences in the ^{13}C NMR spectra of samples A, B, and C can be interpreted in terms of varying degrees of rotational motion of the C_{60} ions in the lattice. The narrow line shape observed for sample A (NH_3 prep., unannealed) is indicative of rapid rotational motion of the C_{60} ions. The broader resonance seen for sample C (Rb_6C_{60} and C_{60} prep.) suggests hindered rotational motion of the C_{60} ions. This suggestion has been confirmed by variable-temperature measurements which show the peak broadens further on cooling. The broadest peak, that observed for sample B (NH_3 prep., annealed), is marginally narrower than the ^{13}C line shapes obtained for sample C at temperatures where the rotational motion of the C_{60} ions has ceased on the NMR time scale (≤ 150 K). Apparently, rotation of the C_{60} ions is much more hindered in sample B at room temperature than in the other two samples.

Interestingly, the superconducting fraction appears to be inversely correlated with the degree of C_{60} rotational motion. It is also likely that the degree of motional narrowing seen for the C_{60} resonance is closely related to the amount of disorder or number of defects in the sample. The narrowest resonance is seen in the unannealed, essentially amorphous sample prepared in liquid ammonia (A). It is also the sample which presumably has the largest amount of disorder. The annealed sample prepared in liquid ammonia (B) shows the broadest resonance. Prior to annealing, the ions were presumably mixed on an atomic level and hence any diffusion of ions required to eliminate the disorder was probably quite short. The short annealing period at 375 °C provided the requisite energy for diffusion to occur and largely eliminated the disorder. The degree of disorder in Rb_3C_{60} sample prepared from Rb_6C_{60} and C_{60} (C) is more difficult to estimate. Clearly, the diffusion distances required for Rb ions are orders of magnitude longer than those in sample B. In addition, reorganization of the C_{60} ions previously in Rb_6C_{60} is also required. Although the annealing time was longer, it is not difficult to imagine that diffusion was incomplete and the disorder was not entirely eliminated.

The ^{87}Rb line shapes for the same three samples are shown in Figure 3. As observed for the ^{13}C spectra, the line shapes for the three samples are identical in gross detail. Three peaks are observed at −149, −26, and 62 ppm with relative areas of approximately 3.5:5 :1.5, respectively. Increases in annealing or reaction time tend to accentuate the small shoulders on the peak centered at −149 ppm, but even these are visible in the unannealed sample.

The presence of three peaks in the ^{87}Rb spectrum of Rb_3C_{60} is surprising considering the structure deduced from diffraction studies[3,17] which has Rb ions occupying all the tetrahedral and octahedral sites in a cubic close-packed array of C_{60} ions. This structural model would result in two peaks in the ^{87}Rb NMR spectrum with relative areas of 2:1. The fact that the same peak positions and ratios are observed for three different samples prepared by two different methods strongly suggests that we are observing an intrinsic feature of Rb_3C_{60} and not an impurity phase or artifact of the preparative method. Simply on the basis of relative areas, the two peaks centered at −26 and 62 ppm probably correspond to "tetrahedral sites", while the peak at −149 corresponds to the octahedral site. To confirm our assignment and the parentage of the additional resonance, we have prepared $CsRb_2C_{60}$.[8] In $CsRb_2C_{60}$, Rb ions are expected to be found almost exclusively in tetrahedral sites because the larger Cs ion should preferentially occupy the larger octahedral site. The ^{87}Rb line shape shows two peaks centered at −26 and 62 ppm with the same relative areas as the corresponding peaks in Rb_3C_{60} and a much smaller peak at −149 ppm. The ^{133}Cs spectrum shows the single resonance expected and confirms our previous assignment of the peaks. The Rb ions in "tetrahedral sites" in both Rb_3C_{60} and $CsRb_2C_{60}$ clearly do not all experience the same chemical environment. Although it is clear the "tetrahedral sites" cannot all be the same (at least on the NMR time scale), the exact nature of the structural modification required to produce two types of tetrahedral sites and only one type of octahedral site is not obvious. It is unlikely that the merohedral disorder of two C_{60} orientations seen in the X-ray structure[17] would produce only two types of tetrahedral sites or result in a significant enough change in chemical environment to be responsible for the inequivalence of the tetrahedral sites observed. The varying degree of C_{60} rotational motion for the three samples as deduced from the ^{13}C line shapes above also suggests that the Rb peak positions and shapes are relatively insensitive to the orientation of the neighboring C_{60} ions. Walstedt et al. have recently described similar ^{87}Rb line shapes for Rb_3C_{60}.[18] Further experiments are in progress to determine more precisely the nature of the distortion.

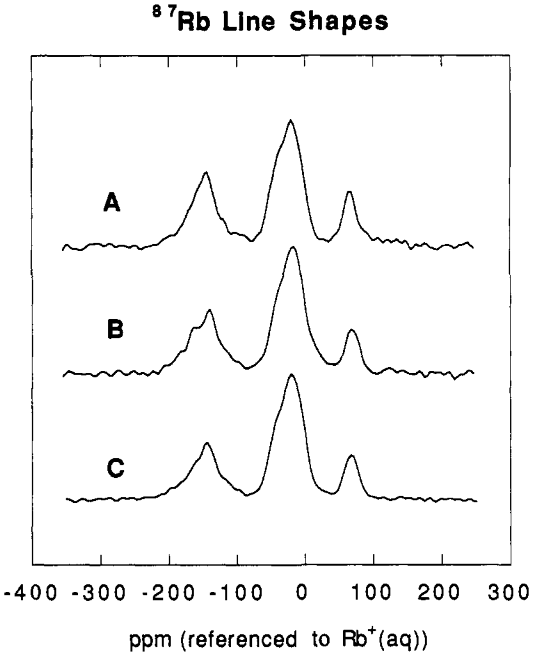

Figure 3. Plot of ^{87}Rb NMR line shapes for three samples of Rb_3C_{60}. Sample A was prepared in liquid NH_3 and has not been annealed. Sample B was prepared in NH_3 and annealed for 24 h at 375 °C. Sample C was prepared by heating Rb_6C_{60} and C_{60} for 4 days at 350 °C. Shifts are relative to Rb^+(aq).

Conclusions

High quality samples of alkali metal–C_{60} superconductors are rapidly and easily prepared by the reaction of stoichiometric amounts of alkali metal and C_{60} in liquid ammonia. Annealing of the product prepared in liquid ammonia for 24–48 h at 375 °C is required to obtain a sizable superconducting fraction. Most samples approach 100% after 48 h of annealing. ^{13}C and ^{87}Rb line shapes confirm the identity of the product, but they also suggest the degree of rotational motion of the C_{60} ions at room

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temperature can vary considerably from sample to sample. The degree of rotational motion is dependent on the method of preparation and subsequent thermal treatment. A correlation between the degree of rotational motion and the superconducting fraction appears to be present and is probably related to the amount of disorder in the sample. ^{87}Rb NMR indicates that Rb_3C_{60} actually contains three different cation sites, rather than the two suggested by X-ray powder diffraction data. The third site is a subset of the tetrahedral sites, although the exact nature of the distortion is unknown.

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