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Structural and electronic properties of $(NH_3)_x K_3C_{60}$

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We have investigated the synthesis, structure, and electronic properties of $(NH_3)_xK_3C_{60}$ by exposing preformed K_3C_{60} to NH_3 vapor. Measurements were made on bulk powders and films with a variety of techniques including *in-situ* x-ray diffraction and monitoring of NH_3 pressure, Raman scattering and ac susceptibility. The reaction of NH_3 with K_3C_{60} is completely reversible and leaves the $(C_{60})^{3-}$ charge state intact, while allowing the distance between the C_{60} molecules to vary. We observe two different crystallographic structures at $x=1$ and $x=8-10$. The $x=1$ structure is face-centered orthorhombic with a single NH_3 on the octahedral interstitial site. It is single phase at 100 °C and NH_3 pressures ≥ 400 torr and remains single phase at 0 torr if the temperature is reduced to 25 °C. Although $(NH_3)K_3C_{60}$ exhibits no superconductivity at ambient pressure, superconductivity can be induced by hydrostatic pressure with an onset at 28 K. The details of the $x=8-10$ structure are uncertain, however it appears that this phase is body-centered tetragonal with NH_3 on both the octahedral and tetrahedral sites. It occurs at room temperature and NH_3 pressures ≥ 500 torr, but is not stable at lower NH_3 pressures. Resistivity measurements of NH_3-doped K_3C_{60} films show that the formation of the new structure results in a rapid increase of the resistivity to values exceeding 1 Ω cm.

I. INTRODUCTION

Since the report of superconductivity in K_3C_{60},[1] the crystal structures and the electronic properties of the superconducting alkali-metal fullerides have been studied in detail.[2] The transition temperature T_c of superconducting A_3C_{60} compounds scales with the size of the unit cell,[3,4] with no evidence of T_c saturation at the larger unit cells.

Synthesis of A_3C_{60} with still larger unit cells is desirable to determine if higher T_c's can be obtained and to investigate the eventual metal-insulator transition, which is expected to occur as the conduction bandwidth becomes smaller than the on-site Coulomb repulsion. However, structural expansion using alkali metals alone in the interstitial sites is limited by the size of the metal ions available for intercalation.[5] Recently, we demonstrated that additional structural expansion can be obtained by using alkali atoms for charge transfer with neutral molecules, such as ammonia, as structural "spacers."[6,7] The expanded compounds were synthesized by exposing preformed A_3C_{60} to NH_3 gas followed by a gentle anneal and subsequent measurement in sealed, He-filled ampules. Our results indicate that in at least one case the fcc lattice can be expanded without disturbing the fcc symmetry or charge transfer. In this example, exposing Na_2CsC_{60} to 380 torr of NH_3, results in an expansion of the fcc lattice parameter from $a=14.13$ to 14.47 Å, and a near tripling of T_c from 10.5–29.7 K.[6] The enhanced T_c of the resulting $(NH_3)_4Na_2CsC_{60}$ agrees with the expected value from the T_c vs a correlation,[3] however, this is not a universal feature of ammoniation of A_3C_{60} superconductors. Ammoniation of K_3C_{60} under similar conditions yields $NH_3K_3C_{60}$. Despite evidence of full charge transfer and a $(C_{60})^{3-}$ oxidation state, the ammonia induces a symmetry reduction from fcc to face-centered orthorhombic and a nonsuperconducting compound above 4 K.[7]

In this paper we further explore the ammoniation of K_3C_{60} by varying both the measurement conditions, e.g., temperature or pressure, as well as the reaction conditions such as synthesis temperature and NH_3 pressure. We report *in-situ* measurements under NH_3 pressure as well as measurements under zero NH_3 vapor pressure. We find that a diversity of structures and physical properties can be obtained by ammoniation of K_3C_{60}. First, we report that $NH_3K_3C_{60}$ prepared as in our earlier report[7] is superconducting only when applying hydrostatic pressure up to 14 kbar. This situation is similar to Cs_3C_{60}, where superconductivity was only observed under hydrostatic pressure.[8] $NH_3K_3C_{60}$ remains face-centered orthorhombic under pressure with no observable pressure or temperature-induced structural changes. Second, using resistivity measurements of K_3C_{60} films and *in-situ* x-ray diffraction of K_3C_{60} exposed to NH_3, we show that an additional phase with a higher ammonia stoichiometry can be formed at NH_3 pressures in excess of 500 torr. Comparison of x-ray data with structural models indicates that the higher NH_3 pressure material may have NH_3 around both alkali-atom sites, in contrast to the other ammoniated fullerides, which only contain NH_3 on the octahedral sites.

Unlike NH_3-K-graphite ternaries,[9] ammoniation of K_3C_{60} is completely reversible. No potassium amide or H_2 formation was observed indicating that ammoniation does not affect the C_{60} valence state. Deintercalation of $(NH_3)_xK_3C_{60}$ to $NH_3K_3C_{60}$ occurs when the NH_3 pressure is kept below 500 torr at room temperature. Further

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deintercalation to fcc K_3C_{60} can be achieved by raising the temperature above room temperature at low NH_3 pressure.

II. EXPERIMENTAL PROCEDURES

Controlled ammoniation of K_3C_{60} films and powder was carried out on a stainless-steel vacuum line with absolute pressure gauges (MKS Instruments) covering 0–5000 torr. Before use, the NH_3 was dried by condensing it into sodium metal in a glass flask held at dry-ice temperature. Subsequently, the NH_3 vapor pressure was controlled by varying the temperature of the Na-NH_3 solution. The volume of each section of the vacuum line was calibrated such that the amount of ammonia uptake could be calculated from the change in NH_3 pressure. The NH_3 pressure could be reduced to zero by cooling a separate trap to liquid-nitrogen temperature. Observation of the residual pressure after condensing the NH_3 gave a measure of any noncondensible, gas, e.g., H_2 or N_2, present in the gas volume. No residual gas pressure was observed during the course of the experiments described here.

In-situ x-ray-diffraction studies of the effects of NH_3 on K_3C_{60} powder were performed by loading K_3C_{60} powder into a 5-mm-diam Pyrex tube with one end drawn into a thin-walled capillary. The glass tube was connected to a high vacuum stopcock by a Cajon Ultra-Torr fitting in a helium-filled dry box and attached to the same vacuum line described above. A Cu K_α rotating-anode x-ray source with a singly bent graphite monochromator and flat graphite analyzer was used for structural measurements. The x-ray powder pattern of $NH_3K_3C_{60}$ was obtained at 10–300 K using powder sealed in a glass capillary under a helium atmosphere using a closed-cycle refrigerator.

A Dilor *XY* Raman spectrometer with 5154-Å-incident Ar^+-ion laser and liquid-nitrogen-cooled charge-coupled device (CCD) detector was used to measure the pressure-induced frequency shifts of the ruby R_1 and R_2 lines for pressure calibration, and also to measure the $C_{60}A_g$ mode under pressure. The data were collected in backscattering geometry with 1 mW of laser light focused to approximately a 16-μm spot. The instrumental resolution was typically about 3 cm^{-1}.

High-pressure powder x-ray-diffraction and Raman measurements were made in a Merrill-Bassett-type diamond-anvil cell with predried mineral oil as the pressure medium. A 200-μm-diam hole was drilled in a spring-steel gasket and filled with $NH_3K_3C_{60}$ powder and a ruby chip (Cr^{3+}-doped Al_2O_3). The pressure cell was loaded in a He-filled glove box and was sealed by applying a small pressure before removing it from the glove box. X-ray-diffraction measurements on the diamond-anvil cell were carried out on a Mo K_α rotating-anode x-ray diffractometer equipped with a flat graphite monochromator and analyzer. The $NH_3K_3C_{60}$ used in the pressure studies had a minority second phase of unreacted K_3C_{60}. The coherence length of the ammoniated phase, as determined from the x-ray peak widths, was about 300 Å, as compared to 350 Å for the K_3C_{60}. The minority K_3C_{60} phase was useful as an additional pressure standard in the susceptibility measurement.

The glass apparatus used earlier[10] for the four-point electrical resistivity measurement of A_xC_{60} films was modified by adding a magnetically operated break seal so that NH_3 gas could be introduced to the system without exposing the film to air. In addition to a C_{60} film, the glass chamber contained a potassium effusion cell and an electrically controlled getter pump. The granular K_3C_{60} film, prepared prior to exposure to NH_3, had a thickness of 2150 Å and a room-temperature resistivity of 2.3 mΩ cm. After attaching the glass chamber to the vacuum line and opening the break seal, the NH_3 pressure was increased step wise. The film resistance was allowed to stabilize before recording the value and increasing the pressure again.

ac susceptibility of the $NH_3K_3C_{60}$ powder was measured between 0.1 and 14.8 kbar using a clamp-type cell[11] with the mineral oil as pressure medium. The cell contained a primary coil outside the pressure cell that generated an ac magnetic field of 0.1 Oe at 88 Hz and two counter-wound secondary coils inside the cell. About 5 mg of sample sealed in an evacuated Pyrex capillary was inserted in the pick-up coils inside a Teflon cup filled with dried mineral oil. A Pb chip inside a second unbalanced pick-up coil was used for pressure calibration. The Pyrex capillary was crushed at seal pressure and the pressure was then transmitted to the sample by the mineral oil.

III. RESULTS

A. Phase formation and crystallographic structure

In earlier experiments[7] single-phase $NH_3K_3C_{60}$ was prepared by heating K_3C_{60} in 450 torr of NH_3 at 100 °C followed by cooling to room temperature and evacuating the remaining gaseous NH_3. Here, we use *in-situ* x-ray diffraction of NH_3-K_3C_{60} to investigate the conditions for obtaining single-phase material. We find that after annealing at 100 °C for about an hour at NH_3 pressures of 200 torr,[12] $NH_3K_3C_{60}$ initially appears at room temperature as a second phase with K_3C_{60}. $NH_3K_3C_{60}$, estimated from the x-ray intensity ratios, grows at the expense of K_3C_{60} as the NH_3 pressure is increased. At pressures between 400 and 1000 torr, $NH_3K_3C_{60}$ is single phase at 100 °C. Once formed, $NH_3K_3C_{60}$ remains even at 0 torr if the temperature is reduced to 25 °C. At temperatures higher than 200 °C and NH_3 pressure < 1000 torr, NH_3 is evolved and the structure reverts the K_3C_{60}. All the gas evolved from $NH_3K_3C_{60}$ on heating is condensible at LN_2 temperature showing that no H_2 is formed at any stage of the intercalation or deintercalation. The amount of NH_3 condensed, determined by measuring the pressure after expanding into a known volume, was found to be 0.95 ± 0.05 NH_3/C_{60}. The x-ray-diffraction pattern taken after deammoniation shows single-phase fcc K_3C_{60}. The fitted lattice parameters at 400 torr NH_3 pressure are $14.97\times14.89\times13.65$ Å, the same as those measured after removing the NH_3 pressure.[7] The unit-cell volume of 761 Å^3/C_{60} is 5% larger than that of the fcc K_3C_{60}. In the ammoniated compound, each octahedral K is coordinated with one NH_3 and displaced away from the center of the octahedral site, which induces a structural distortion from cubic to orthorhombic. No NH_3 is associated with the potassium atom on the tetrahedral site.

Further NH_3 uptake and a structural transformation were observed when the NH_3 pressure was raised above 500 torr, as shown in the lower x-ray pattern of Fig. 1(a). This pattern was obtained at room temperature with NH_3 pressures in the range 500–1000 torr. The intensities of the peaks at 19.6 and 20.69° 2θ (marked with arrows) were found to decrease with increasing NH_3 pressure at room temperature, while the relative intensities and d spacings of the other reflections remained the same. This behavior indicates that the system is multiphase under these conditions and contains a new phase together with one or more additional phases.[13] At a fixed pressure, no significant change in the x-ray powder pattern was observed over 24 h. Heating the sample to 110 °C at a fixed NH_3 pressure of 500 torr, shown in Fig. 1(a) produced a release of NH_3 and the formation of predominately $NH_3K_3C_{60}$. Further heating the sample to 200 °C at 500 torr results in complete NH_3 deintercalation and fcc K_3C_{60}.

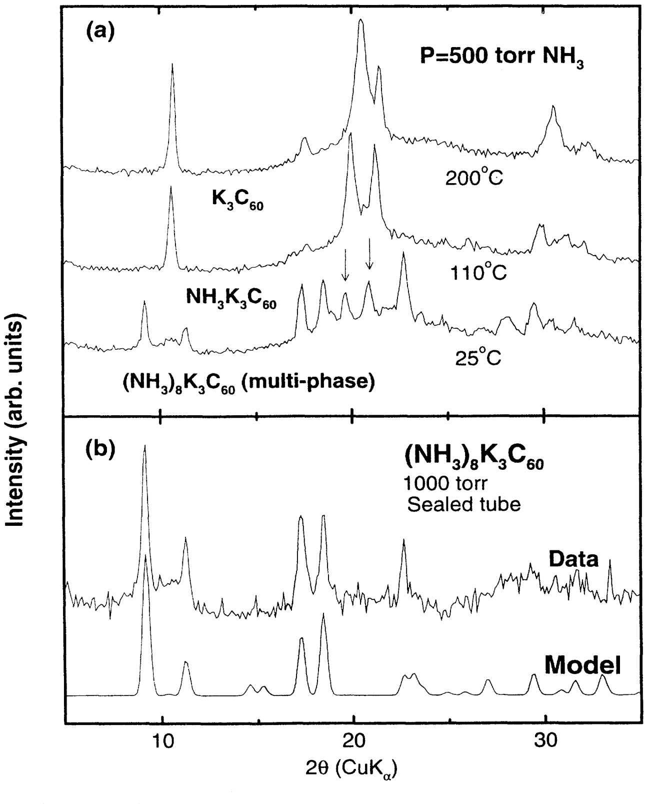

FIG. 1. (a) Powder x-ray-diffraction patterns of NH_3-K_3C_{60} collected at 25, 110, and 200 °C at a fixed NH_3 pressure of 500 torr. The 25 °C pattern is predominately from $(NH_3)_8K_3C_{60}$. The arrows indicate peaks from one or more additional phases. (b) A powder x-ray-diffraction pattern of $(NH_3)_8K_3C_{60}$ sealed at room temperature and 1000 torr of NH_3 taken after annealing at 100 °C for 10 h. The lower curve is a simulated diffraction pattern calculated from a preliminary model structure for $(NH_3)_8K_3C_{60}$.

In-situ annealing for 2 h at pressures up to 1000 torr did not result in single-phase material of the new, higher NH_3 pressure phase. We were successful, however, in obtaining a pattern that could be indexed as single phase by annealing for 10 h in a tube *sealed* at 1000 torr NH_3. (Unlike the *in-situ* experiments, this is not a fixed-pressure measurement, since reaction of NH_3 with K_3C_{60} will reduce the pressure of NH_3 in the tube.) After 10 h at 100 °C, the x-ray pattern evolved from one similar to the lower curve of Fig. 1(a) to the data shown in Fig. 1(b), where the diffuse background due to the glass capillary has been subtracted. Figure 1(b) can be indexed as a single phase with a number of different unit cells: two body-centered tetragonal cells with lattice parameters of 13.58×15.7, 13.51×9.64, or 12.15×15.7 Å, as well as an orthorhombic cell of $13.28\times11.09\times9.68$ Å. Two of these cells have c-axis parameters are smaller than the C_{60} van der Waals diameter [if one excludes K-C_{60} bonding as proposed for RbC_{60} (Ref. 14)], while the 13.58×15.7 bct cell gives an unreasonably large unit-cell volume per fullerene molecule. The 12.15×15.7 Å bct cell was therefore chosen as the most likely candidate. Intensity calculations were carried out using the LAZY-PULVERIX (Ref. 15) program using a spherical shell of charge to model the C_{60} molecule and Ne atoms (10 electrons each) to model ammonia molecules. In a separate experiment, monitoring the pressure change during NH_3 uptake, the NH_3 stoichiometry was calculated to be 10 ± 2 NH_3/C_{60}. Using $I4/mmm$ symmetry, a number of different orientations of NH_3 consistent with this approximate stoichiometry were attempted. Approximate agreement of a model with the data were obtained using the model shown in Fig. 2(a). For comparison, a schematic drawing of the model of $NH_3K_3C_{60}$ used in Ref. 7 is also shown in Fig. 2(b). In Fig. 2(a), ammonia molecules are located at sites $(8j)$ $(x,1/2,0)$ and at $(8g)$ $(0,1/2,z)$ giving a composition of $(NH_3)_8K_3C_{60}$. A simulated x-ray powder pattern using the structural model is shown in Fig. 1(b) along with the data (with the diffuse background from the glass capillary subtracted). Fixing the all potassium-ammonia distances at 2.7 Å, the same as in $NH_3K_3C_{60}$ (Ref. 7) gives $x=0.28$ and $z=0.42$. This model gives a rather short ammonia-ammonia distance across the (0,1.2,0) site of 2.5 Å, however, the quality of the data requires that this model be taken as preliminary. All the model calculations do strongly suggest, however, that a structure with NH_3 in both the octahedral and the tetrahedral sites is required.

B. Electronic properties at low pressure

In our previous paper[7] we reported that $NH_3K_3C_{60}$ is noncubic and nonsuperconducting. Here, we first address the electronic properties of $(NH_3)_xK_3C_{60}$ at low NH_3 pressure and correlate the results with the structural results reported above. As shown in Fig. 3, the room-temperature resistivity (ρ) of K_3C_{60} films increases slowly with increasing NH_3 pressure, from 2.3 mΩ cm at 0 torr to about 10 mΩ cm at 400 torr. The resistivity increases rapidly above 500 torr to 2200 mΩ cm at 840 torr. Upon reducing the pressure at room temperature, the resistivity exhibits a large hysteresis and stabilizes at 30 mΩ cm at 0 torr, about ten times higher than the value before NH_3 exposure. Heating at 150 °C under dynamic vacuum for a few hours recovers the original resistivity of the K_3C_{60} film, consistent with complete loss of ammonia. Resistivity measurements at 100 °C give a different result. At 100 °C, ρ increases continuously with increasing pressure up to 1000 torr, the highest pressure of the experiment. The rapid resistivity increase observed at 25 °C and 500 torr is absent. Lowering the temperature to room temperature at a fixed pressure above 500 torr results in an increase of ρ.

The above transport data can be rationalized on the basis of the phase formed in bulk samples under comparable conditions. On exposure to NH_3 at conditions known to produce single phase $NH_3K_3C_{60}$ (100 °C at 500 torr), the resistance of the metallic K_3C_{60} film increases by a factor of 5–10. An insulating state is obtained *only* under conditions that have been shown to produce a sample that is predominately the high NH_3 pressure structure (25 °C at $\geq$ 500 torr). The increase in the resistance as the film was cooled from 100 °C to room temperature at constant pressure is likely the result of the slow conversion of the film to the high pressure phase. One concludes from these data that the high NH_3 pressure structure is insulating, however, our data do not exclude the possibility that $NH_3K_3C_{60}$ could be metallic. A definitive test of the metallic character of $NH_3K_3C_{60}$ is difficult, however, since all samples have some contamination with metallic K_3C_{60}.

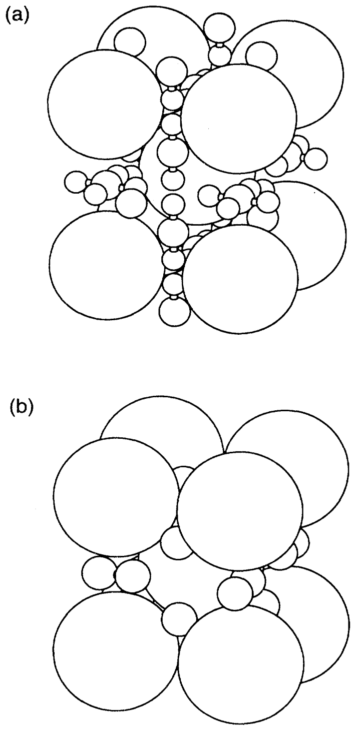

FIG. 2. (a) A schematic diagram of a 12.15×15.7 Å bct cell (*I4/mmm*) consistent with the higher NH_3 pressure phase showing probable location of C_{60} molecules (large circles) at 2*a*, (0,0,0), as well as potassium atoms (intermediate circles) at 2*b*, (0,0,1/2) (octahedral site) and 4*d*, (0,1/2,1/4) (tetrahedral site). The ammonia atom ordering shown (small circles) gives a stoichiometry of $(NH_3)_8K_3C_{60}$ and the calculated diffraction pattern shown in Fig. 1(b). (b) A schematic diagram of the structure of $NH_3K_3C_{60}$ described in detail in Ref. 7. The unit cell has been rotated by 45° about the *c* axis to allow viewing of the octahedral and tetrahedral sites. One potassium atom and one ammonia molecule occupy each octahedral site and are depicted as two adjacent circles. The position of K and NH_3 within each octahedral site is random among four equivalent sites.

C. Electronic properties at hydrostatic pressure

The lack of superconductivity in $NH_3K_3C_{60}$ despite chemical evidence of a half-filled band is surprising.[7] Possible reasons for this fact could be either the occurrence of a Mott transition brought about by the increased in the intermolecular distances in the expanded unit cell or by suppression of the superconductivity due to granularity of the material. Either of these effects could be negated by the application of hydrostatic pressure. Our measurements show that, indeed, $NH_3K_3C_{60}$ is superconducting under hydrostatic pressures. No observable change in the orthorhombic face-centered structure occurs in x-ray measurements at similar pressures. The temperature dependence of the ac susceptibility of $NH_3K_3C_{60}$ measured between 0.1 and 14.8 kbar is shown in Fig. 4. At 1 bar, the data show a flat background and two small but sharp transitions at 19 and 7.2 K, from the minority K_3C_{60} phase (as determined by x-ray diffraction)

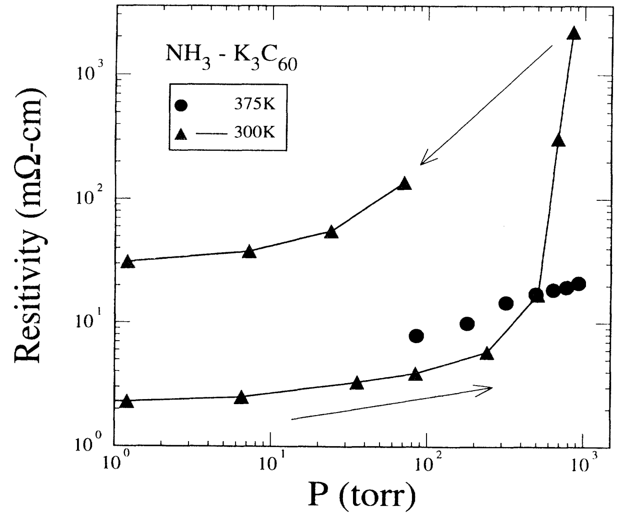

FIG. 3. The electrical resistivity of a $(NH_3)_xK_3C_{60}$ film measured as a function of the NH_3 pressure at room temperature and at 100 °C.

and the Pb chip, respectively. Upon applying pressure, a broad transition appears at a higher temperature. The shielding fraction and the apparent onset temperature of this transition increase with increasing pressure, to 5% and 28 K at 14.8 kbar, respectively. At low pressure, the exact T_c is difficult to determine because of the low shielding fraction and the breadth of the transition. The signal is completely reversible upon pressure cycling. The superconducting transition temperature of the small amount of K_3C_{60} in the sample decreases with increasing pressure with a slope of -0.62 K/kbar in agreement with previous measurements.[16,17]

Room-temperature powder diffraction patterns collected at 0.6 and 8 kbar are shown in Fig. 5, along with a calculated 1-bar pattern obtained using the 1-bar $NH_3K_3C_{60}$ orthorhombic cell parameters[7] and LAZY-PULVERIX.[15] There is no observable change in the symmetry of the structure with pressure. Both patterns are consistent with the orthorhombic structure at 1 bar and neither can be indexed as cubic. The 8-kbar powder pattern is very similar to that obtained at 0.6 kbar, except the peaks are shifted to higher 2θ's and the intensities of the (202) and (022) peaks have increased. Due to the small number of broad, overlapping peaks, reliable unit cell parameters under pressure cannot be obtained from the present data. The Bragg peaks in Fig. 5 are broad because of the small particle size, rather than instrumental resolution. The widths are pressure independent over the pressure range studied. Approximate lattice parameters of a fit of the limited number of observed peaks to a *tetragonal* cell give $a = 14.7$ Å and $c = 13.7$ Å at 8 kbar, a contraction from 1 bar of $\Delta V/V \approx 3\%$. A separate x-ray measurement using Cu K_α radiation shows that the room-temperature face-centered orthorhombic structure of $NH_3K_3C_{60}$ is sustained at temperatures as low as 10 K.

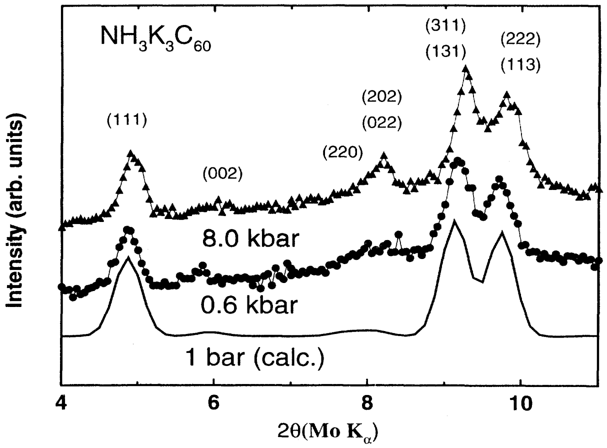

FIG. 5. 300-K powder x-ray-diffraction patterns of the $NH_3K_3C_{60}$ collected at 0.6 and 8 kbar with a diamond-anvil cell and Mo rotating-anode x-ray diffractometer. The solid line is a calculated atmospheric-pressure powder pattern based on the face-centered orthorhombic unit-cell parameters.

Raman spectra measured at 1 bar from a sample sealed in a glass capillary, and at 0.6 kbar and 16 kbar from the powder in the diamond-anvil cell are shown in Fig. 6. At atmospheric pressure, the sample has a simple sharp A_g mode centered at 1448.5 cm^{-1}, nearly the same as that reported for K_3C_{60},[18] indicating that C_{60} in the

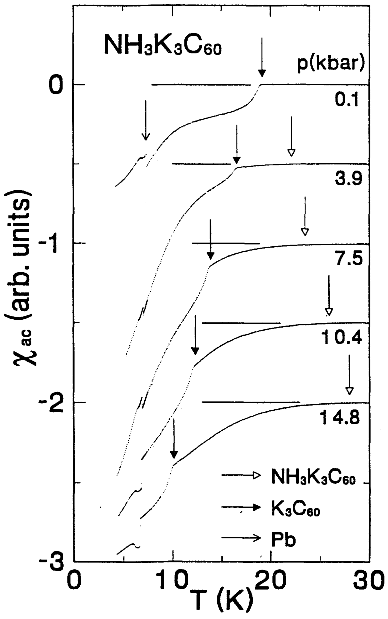

FIG. 4. Temperature dependence of the ac susceptibility of $NH_3K_3C_{60}$ measured between 0.1 and 14.8 kbar in a clamp-type pressure cell. The arrows indicate the superconducting transitions of $NH_3K_3C_{60}$, a minority K_3C_{60} phase identified by x-ray diffraction, and a Pb chip for pressure calibration.

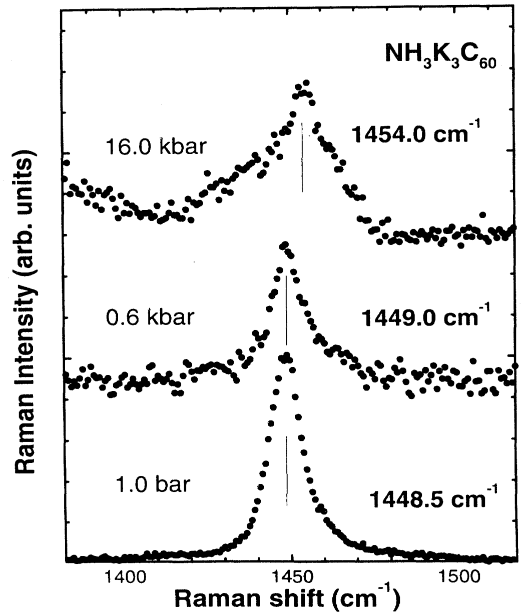

FIG. 6. The Raman-active A_g mode of $NH_3K_3C_{60}$ measured at 1 bar, 0.6 kbar, and 16 kbar. The atmospheric pressure data was collected from a sample sealed in a glass capillary, and the spectra under pressure were collected from the same sample batch in a diamond-anvil cell.

$NH_3K_3C_{60}$ phase is in the 3-oxidation state. This result confirms our previous conclusion that ammoniation does not affect the charge transfer from alkali metal to C_{60}. Under pressure the A_g mode is upshifted, to 1454 cm^{-1} at 16 kbar. As in the case of pristine C_{60},[19] the A_g mode is broad and asymmetric at high pressure. The shift in the frequency of the A_g mode is due to pressure-induced stiffening rather than phase separation or change in the C_{60} valence state. Assuming that the frequency of the A_g mode shifts linearly with the applied pressure, as in the case for all the vibrational modes of pristine C_{60}, one obtains a positive pressure slope of 0.31 cm^{-1}/kbar, larger than the 0.17 cm^{-1}/kbar slope reported for pristine C_{60}.[19] The results from both x-ray diffraction and Raman measurements therefore indicate that at room temperature there is no phase separation or structural transition under pressure. We do not expect the results to be different at low temperature and high pressure, as excess pressure compensates the temperature term in the free energy.

IV. CONCLUSIONS

Resistivity measurements of K_3C_{60} films in gaseous NH_3 and *in-situ* x-ray measurements of K_3C_{60} powder under NH_3 have revealed new details about the NH_3-K_3C_{60} phase diagram. $NH_3K_3C_{60}$ initially appears as a second phase at room temperature and 200 torr. The fraction of $NH_3K_3C_{60}$ increases to 100% at 400 torr and 100 °C. Once formed, $NH_3K_3C_{60}$ remains at room temperature and 0 torr. (The slow kinetics associated with NH_3 intercalation and deintercalation makes the precise determination of the equilibrium NH_3-K_3C_{60} phase diagram difficult.) At room temperature and NH_3 pressures 500–1000 torr, a new phase with 8–10 NH_3 molecules per K_3C_{60} formula unit becomes the dominant phase. This structure appears to become single phase after heating K_3C_{60} sealed with 1000 torr NH_3 to 100 °C. The data were not clean enough to refine a structural model, however, preliminary results indicate that the new structure contains NH_3 on both the octahedral and tetrahedral interstitial sites, in contrast to $NH_3K_3C_{60}$ and $(NH_3)_4Na_2CsC_{60}$. At room temperature, the high NH_3 pressure phase appears to be electrically insulating.

The results reported in this paper show that in $NH_3K_3C_{60}$ the charge transfer is unchanged from that of K_3C_{60} and that the orthorhombic structure is stable at low temperature. This raises the question as to why ammoniation causes the loss of superconductivity in $NH_3K_3C_{60}$ and why hydrostatic pressure recovers the superconductivity. We suggest as a possible reason the vicinity of the Mott limit. The Mott limit has been estimated to be near 2 mΩ cm for these materials,[20] which is close to the measured resistivity of K_3C_{60} thin films. After taking up one NH_3 per C_{60} to form $NH_3K_3C_{60}$, the resistivity increases by a factor of 5 to about 10 mΩ cm at room temperature. We note that, although the unit-cell volume of $NH_3K_3C_{60}$ is comparable to that of the metallic Rb_2CsC_{60}, the intermolecular distances are anisotropic. In an $\{hk0\}$ plane, the nearest-neighbor center-to-center intermolecule distance is 10.56 Å, substantially larger than the value of 10.25 Å in Rb_2CsC_{60}. We suggest that the additional expansion in $\{hk0\}$ planes in $NH_3K_3C_{60}$ could result in electron localization and induces a metal-insulator transition. As hydrostatic pressure causes primarily volume reduction in the *a* and *b* axes, this could consequently delocalize the t_{1u} electrons.

A second possibility that is not excluded by the data is a suppression of superconductivity because of the small grain size of the ammoniated material. It is possible that $NH_3K_3C_{60}$ is intrinsically a superconductor at 1 bar, but the fine grain size suppresses the bulk superconductivity. In this model, hydrostatic pressure may decrease the intrinsic T_c at about 1 K/kbar as in A_3C_{60}, but at the same time it increases the connectivity of the material, resulting in a detectable signature of superconductivity. The x-ray measurements under pressure show that the broad peak widths due to finite-sized grains are unchanged by hydrostatic pressure, however, the size of a grain defined by x-ray coherence is not necessarily correlated with coupling of superconductivity across a grain boundary.

Nevertheless, our results show that superconductivity can be achieved in alkali-metal fulleride with a noncubic crystal structure. $NH_3K_3C_{60}$ may well be the first of a new family of noncubic fullerene superconductors. The role of hydrostatic pressure on the occurrence of superconductivity can, in principle, be eliminated by chemical substitution at 1 bar.

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