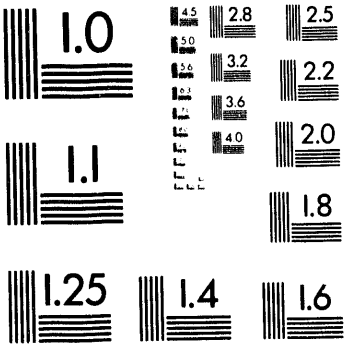

1.0
4.5
2.8
2.5
5.0
3.2
2.2
5.6
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

1 of 1

# A new family of superconducting fullerides, $Na_3(NH_3)_xC_{60}$ ($x \approx 2$-8)

**J. A. Schlueter, J. L. Smart, H. H. Wang,* U. Welp, U. Geiser, J. M. Williams, M. J. Henson, J. D. Dudek, M. A. Caleca, A. C. Cooper, & K. D. Carlson**

Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439, USA

*To whom correspondence should be addressed

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free licence to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

A series of $A_3C_{60}$ fulleride superconductors (A is an alkali metal) with superconducting transition temperatures ($T_c$s) ranging between 2.5 and 33 K has been reported[1-8]. The $T_c$s of these materials are closely correlated to their f.c.c. lattice parameters, with the higher $T_c$ materials having larger unit cell lengths[9, 10]. Recently, the $T_c$ of the superconducting $Na_2CsC_{60}$ has been raised from 10.5 K to 29.6 K by ammonia intercalation[11]. The resulting intercalated compound, $NaCs[Na(NH_3)_4]C_{60}$, has an expanded unit cell compared to the starting material, with a larger cation $Na(NH_3)_4^+$ occupying the octahedral site. The sodium-doped $C_{60}$ with nominal composition $Na_3C_{60}$, however, does not show superconductivity and was reported to undergo a disproportionation reaction into two f.c.c. phases, $Na_2C_{60}$ and $Na_6C_{60}$ below 250 K[7]. Here we report on the ammonia intercalation of $Na_3C_{60}$. Up to four superconducting phases with $T_c$s occurring near 6.7, 11.5, 13.5 and 16.5 K were observed in the intercalated compounds, $Na_3(NH_3)_xC_{60}$ ($x \approx 2$-8). All these phases gave significant superconducting shielding fractions (between 15 and 80% at 5 K). These compounds were characterized by use of AC susceptibility and SQUID measurements, TGA and x-ray powder diffraction.

The sodium doped $C_{60}$ compounds, $Na_nC_{60}$, are known to exist in a wide range of dopant concentrations ($2 \leq n < 11$)[7, 12]. All these compounds can be indexed with a f.c.c. unit cell. For $n = 2$, the sodium atoms fill the two tetrahedral sites, and for $n = 3$ they fill both the tetrahedral and octahedral sites. For $n = 6$, four sodium atoms form a $Na_4$ tetrahedron and occupy the octahedral site. The other two sodium atoms occupy the two tetrahedral sites. Furthermore, for an ideal structure $n = 11$, the octahedral interstitial site contains a $Na_9$ body-centered cluster while the two tetrahedral sites are singly occupied by two sodium atoms[12]. In contrast to other alkali metal doped fullerides, $A_3C_{60}$ (A = K, Rb, and alloys), $Na_3C_{60}$ does not exhibit superconductivity[7, 12]. A low temperature lattice distortion in $Na_3C_{60}$, arising from the mismatch in sizes of the sodium cation and the octahedral site, is thought to suppress superconductivity. At higher sodium doping levels ($n = 6$ and 10) the f.c.c. structures are stabilized at low temperature, and the lack of superconductivity in these materials is attributed to low values of $N(E_F)$, the density of states at the Fermi level[12]. Motivated by the ammonia intercalation into $Na_2CsC_{60}$, and the rise of $T_c$ from 10.5 to 29.6 K[11], we studied the effect of ammonia intercalation on $Na_3C_{60}$.

The $C_{60}$ crystals were prepared by sublimation of high purity $C_{60}$ powders (Norite A/silica gel column) under a helium carrier gas[13-15]. $Na_3C_{60}$ crystals were prepared from direct reaction between $C_{60}$ crystals and three equivalents of Na in a sealed quartz tube at 300°C for 7 days. Similarly prepared $Rb_3C_{60}$ samples had large particle sizes (between 0.5 and 2 mm) and showed sharp magnetic superconducting transitions ($\Delta T_{10\text{-}90} < 1$ K) with a slightly higher $T_c$ (~30.5 K) than powder samples[15]. The AC susceptibilities of $Na_3C_{60}$ crystals indicated no superconductivity above 5 K, consistent with the reported results. To explore the synthesis conditions, $Na_3C_{60}$ samples were repeatedly exposed to 1/2 atm of Ar

and an incremental amount of $NH_3$ gas (AGA, anhydrous grade, 99.99%) from 1/32 to 1/2 atm at room temperature. Each time the sample was evacuated, exposed to Ar/$NH_3$, heat treated, and tested for superconductivity. The heating conditions for four samples (A to D) are listed in Table 1.

**---Table 1 here---**

After the cycle with 1/2 atm Ar and 1/2 atm $NH_3$, sample A was heat-treated at 100°C for 3 days, the AC susceptibility measurements indicated a superconducting transition near 6.7 K and a shielding fraction (uncorrected for demagnetization) of ~15% at 5 K. Sample B initially showed a weak superconducting signal at 7 K and an 1% shielding fraction after the 1/2 atm Ar and 1/4 atm $NH_3$ cycle. The same sample was subject to additional ammonia (1/2 atm Ar and 1/2 atm $NH_3$) and heating (225°C, 2 days). The AC susceptibility measurements of this $Na_3(NH_3)_xC_{60}$ compound (Sample B) indicated a higher $T_c$ at 11.5 K and a 40% shielding fraction at 5 K. The higher $T_c$ in sample B was likely associated with higher ammonia content which could expand the unit cell lattice parameters. Superconductivity was further established with zero-field-cooled (ZFC) and field-cooled (FC) SQUID measurements. In the FC experiment the magnetic flux was expelled from the sample at $T_c$ to give an ~1% Meissner fraction at 5 K. In an impure sample, flux remains pinned (trapped) in the sample and the Meissner signal is usually much smaller than the ZFC-signal as observed in sample B. However, the observation of a Meissner signal, even small, is a proof for a superconducting transition. For sample B, this occurred near $T_c$ = 11.5 K, and the ZFC shielding fraction was ~30% at 5 K. Recently, a sodium-nitrogen-$C_{60}$ compound, $Na_xN_yC_{60}$, prepared from doping $C_{60}$ with $NaN_3$, was reported to be a superconductor with a $T_c$ around 12 K and a low shielding fraction of ~3% at 3 K[16]. Due to the unknown nature of the chemical composition, no comparison between the two compounds can be made at present.

The ammonia-intercalated $Na_3(NH_3)_xC_{60}$ crystals had the same morphology as the pristine $C_{60}$ crystals. Some exfoliation was observed after the doping and heating process, but the crystals generally remained intact. If ammonia gas was introduced directly onto the $Na_3C_{60}$ crystals without argon, the crystalline samples invariably crumbled due to over-saturation with ammonia. No superconductivity has been observed in those samples. In fact, a large excess of ammonia, if liquified, can dissolve $Na_3C_{60}$ and destroy the crystal lattice entirely[17]. Two additional samples were prepared: sample C was heat-treated at 225°C for two months in order to attempt to reach equilibrium, whereas sample D was heated at 225°C for one week. For sample C, which was fully equilibrated, the AC susceptibilities showed a superconducting transition at 13.5 K and a shielding fraction of 55% at 5 K without demagnetization corrections. SQUID measurements of the same sample indicated a slightly higher $T_c$ at 14.2 K and a comparable shielding fraction. For sample D, the AC susceptibilities revealed the highest $T_c$, at 16.5 K, among the four samples. The superconducting shielding fraction was 30% at 5 K. For comparison, the real part ($\chi'$) of the AC susceptibilities of all four samples (A through D) were normalized to their 5 K values and plotted in figure 1.

**---Figure 1 here---**

Four different superconducting onset temperatures at 6.7, 11.5, 13.5, and 16.5 K for $Na_3(NH_3)_xC_{60}$ samples A through D, respectively, are clearly evident. Sample D was not equilibrated to a single phase, as indicated by the stepwise AC-derived superconducting transition curve. The imaginary part ($\chi''$) of the AC susceptibility of sample D was plotted in figure 1 inset. Four distinct local maxima were observed at temperatures approximately corresponding to the four different superconducting transitions. The multiple local maxima in $\chi''$ suggested the presence of multiple superconducting phases in sample D. The

nonequilibrated nature of sample D was further revealed in the lower superconducting onset temperature during a SQUID measurement 7 days later, which is shown in figure 2.

**---Figure 2 here---**

In the ZFC transition, a series of steps at 7 K, 12 K, and the onset of diamagnetism near 15.5 K was clearly observed. These features approximately correlated with the features in the inset of Figure 1. Steps in a ZFC transition can be caused by decoupling phenomena in granular or multiply connected samples (see ref.18 for a detailed discussion). However, the observation of similar steps in the Meissner signal (Figure 2 inset) showed that the sample contained multiple phases with distinct $T_c$ values. After 17 days, second AC susceptibility measurements on sample D showed that the superconducting onset temperature decreased to 15 K, the multi-step transition became very obvious, and the shielding fraction increased to ~80% at 5 K. Assuming the highest $T_c$ corresponds to the maximum amount of ammonia intercalation, the lowering of the onset transition temperature from 16.5 to 15 K in sample D, might be associated with reaching equilibrium among different superconducting phases in the sample.

At room temperature, $Na_3C_{60}$ has a f.c.c. structure containing $Na^+$ cations in all the tetrahedral and octahedral holes. The 14.19 Å unit cell parameter is large enough to be within the range where superconducting salts are found, but disproportionation occurs below 250 K to form $Na_2C_{60}$ and $Na_6C_{60}$, preventing the occurrence of superconductivity[7]. It is established that $NH_3$ molecules coordinate with the $Na^+$ cations to form $Na(NH_3)_4^+$ cations in the octahedral holes because the tetrahedral holes are too small to accommodate any $Na(NH_3)_x^+$ cations[11]. The $Na(NH_3)_4^+$ cations in $NaCs[Na(NH_3)_4]C_{60}$ compound are disordered. Based on the size of the octahedral site, it can accommodate the eight-coordinate cation,

$[Na(NH_3)_8]^+$.[11] The size argument sets the upper limit for $x$ in $Na_3(NH_3)_xC_{60}$ to 8. Preliminary x-ray powder diffraction data indicated the f.c.c. lattice of $Na_3C_{60}$ was approximately maintained upon intercalation of $NH_3$, with a small lattice expansion from 14.19 Å to 14.21±0.02 Å in sample D and 14.26±0.02 Å in sample C. Because sample D was not a single phase material, this 14.21 Å unit cell was the average length of several stoichiometries. Compared to other known f.c.c. $A_3C_{60}$ fulleride superconductors, the unit cell lengths between 14.21 and 14.26 Å corresponded to $T_c$s between ~14 to 19 K[7, 8], which are consistent with the observed values (13.5 to 14.2 K for sample C and 15 to 16.5 K for sample D) in these samples. Apparently, the larger $Na(NH_3)_x^+$ cations stabilized the f.c.c. structure against the low-temperature disproportionation, and thus, superconductivity could be observed in these materials. The lower limit of $x$ in $Na_3(NH_3)_xC_{60}$ was approximately 2 since the $Na(NH_3)^+$ cation was expected to be disordered in the octahedral site and might not stabilize the f.c.c. structure. The related $K_2[K(NH_3)]C_{60}$ compound exhibited an orthorhombic distortion and did not indicate superconductivity[19]. The structure model we propose for $Na_3(NH_3)_xC_{60}$ ($x$≈2-8) is similar to the structure of $Na_{11}C_{60}$[12], where the eight corners of the $Na_9$ cluster are replaced by ammonia molecules. Detail structural analysis awaits further study.

In order to measure the amount of $NH_3$ intercalated in these compounds, thermal gravimetric analyses (TGA) were carried out on samples C and D. The samples were heated in a nitrogen (99.9985%) purged chamber at a ramping rate of 20°C/min from ambient to 700°C. The weight loss and its derivative with temperature for sample C (thermally equilibrated sample) are plotted against the temperature in figure 3.

**---Figure 3 here---**

As shown in figure 3, the first derivative peak centered at 61°C is attributed to the loss of ammonia. Based on the formula, $Na_3(NH_3)_xC_{60}$, the 9.8±0.6% weight loss corresponded to $x$ = 5.0±0.3. The second and third peaks at 212 and 298°C, respectively, are assigned to weight loss due to sodium evaporation. The assignment was qualitatively verified by checking the TGA of a $Na_3C_{60}$ sample. The calculated (vs. measured) total weight loss for three equivalents of sodium was 7.88 (vs. 7.81)%. Sample D contained multiple phases; thus the ammonia content was the weighted average of several components. The weight loss occurring around 60°C was ~7.5%, which corresponds to $x$ = 3.8. Both samples showed ammonia content in the expected range between 2 and 8, and are consistent with the proposed structural model. Thus ammonia intercalation is a viable route for the expansion of a f.c.c. crystal lattice to make new superconductors or to increase $T_c$ in $C_{60}$ based systems. Discovery of other ammonia intercalated sodium or lithium containing fulleride superconductors is quite likely.

ACKNOWLEDGMENT Work at Argonne National Laboratory is sponsored by the US Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences, under Contract W-31-109-ENG-38 and the NSF-Office of Science and Technology Center under contract STC-91-20000 (UW). JLS, MJH, and ACC are undergraduate student research participants sponsored by the Argonne Division of Educational Programs from Western Montana College, Dillon, MT; Kalamazoo College, Kalamazoo, MI; and Alma College, Alma, MI, respectively.

**References**


1. Hebard, A.F., *et al. Nature* **350**, 600–601 (1991).
2. Rosseinsky, M.J., *et al. Phys. Rev. Lett.* **66**, 2830–2832 (1991).
3. Holczer, K., *et al. Science (Washington, D.C.)* **252**, 1154–1157 (1991).
4. Wang, H.H., *et al. Inorg. Chem.* **30**, 2962–2963 (1991).
5. Chen, C., Kelty, S.P. & Lieber, C.M. *Science* **253**, 886-888 (1991).
6. Tanigaki, K., *et al. Nature* **352**, 222–223 (1991).
7. Rosseinsky, M.J., *et al. Nature* **356**, 416-418 (1992).
8. Tanigaki, K., *et al. Nature* **356**, 419-421 (1992).
9. Fleming, R.M., *et al. Nature* **352**, 787-788 (1991).
10. Zhou, O., *et al. Science (Washington, D.C.)* **255**, 833–835 (1992).
11. Zhou, O., *et al. Nature* **362**, 433-435 (1993).
12. Yildirim, T., *et al. Nature* **360**, 568-571 (1992).
13. Scrivens, W.A., Bedworth, P.V. & Tour, J.M. *J. Am. Chem. Soc.* **114**, 7917-7919 (1992).
14. Liu, J.Z., *et al. Appl. Phys. Lett.* **62(5)**, 531-532 (1993).
15. Schlueter, J.A., *et al. Physica C* **216**, 305-314 (1993).
16. Imaeda, K., *et al. Solid State Commun.* **87**, 375-378 (1993).
17. Zhou, F., Jehoulet, C. & Bard, A.J. *J. Am. Chem. Soc.* **114**, 11004-11006 (1992).
18. Thompson, J.R., *et al.* in *Magnetic Susceptibility of Superconductors and Other Spin Systems*, eds. Hein, R.A., et al. Plenum Press, New York, 157-176 (1991).
19. Rosseinsky, M.J., Murphy, D.W., Fleming, R.M. & Zhou, O. *Nature* **364**, 425-427 (1993).

Table 1. Heating conditions and $T_c$s for four samples treated with 1/2 atm Ar and 1/2 atm $NH_3$.

| | Heating | AC susceptibility[a] | | SQUID[a] | |
|---|---|---|---|---|---|
| $Na_3(NH_3)_xC_{60}$ | °C (days) | $T_c$ (K) | Fraction(%) | $T_c$ (K) | Fraction(%) |
| A | 100 (3) | 6.7 | 15 | – | – |
| B | 225 (2) | 11.5 | 40 | 11.5 | 30 |
| C | 225 (~60) | 13.5 | 55 | 14.2 | 45 |
| D | 225 (7) | 16.5[b] | 30 | 15.5[c] | 43 |
| | | 15[d] | 80 | | |

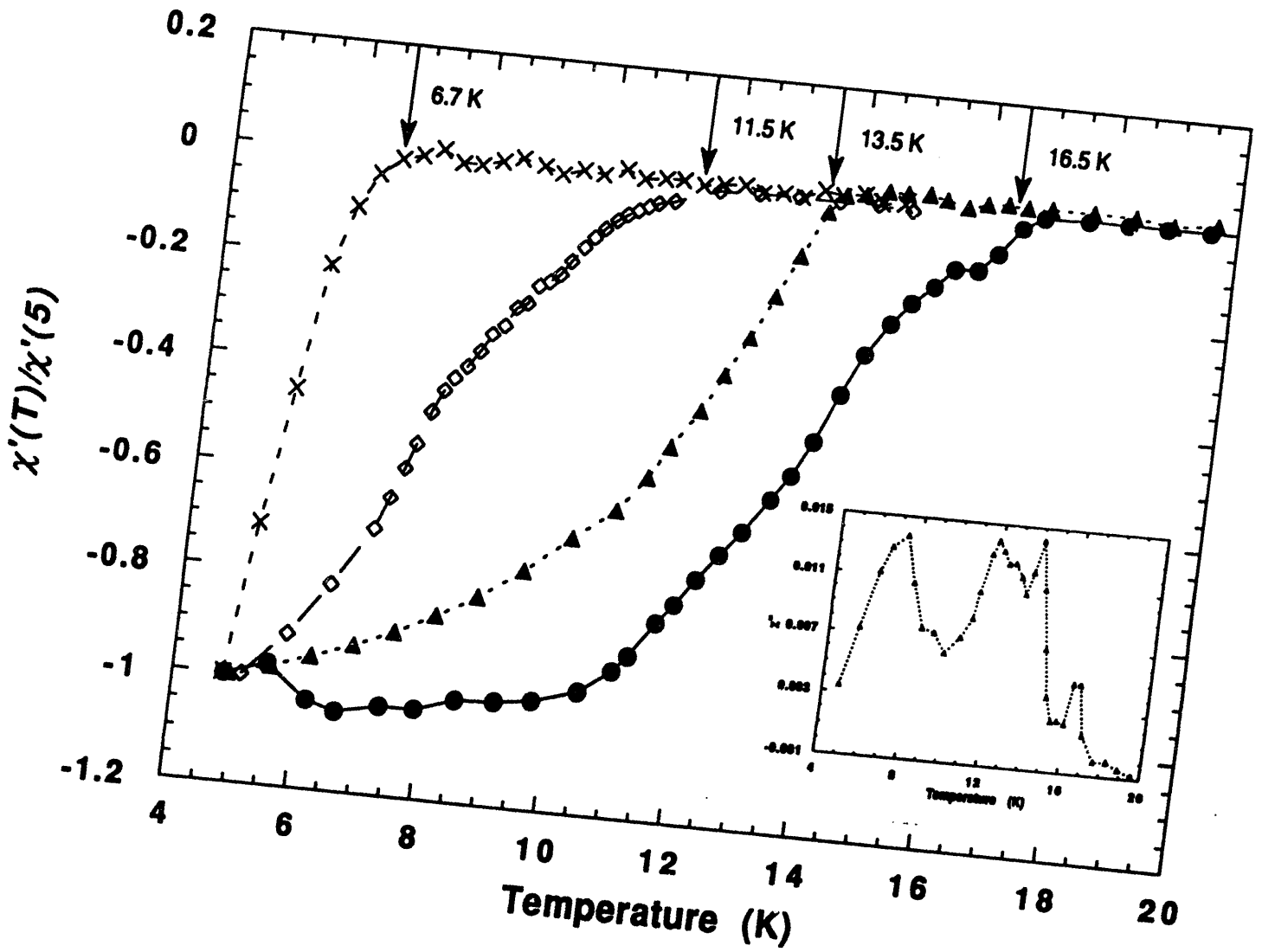
[a]Shielding fractions at 5 K without demagnetization correction [b]Initial measurements [c]measurements after 7 days [d]measurements after 17 days

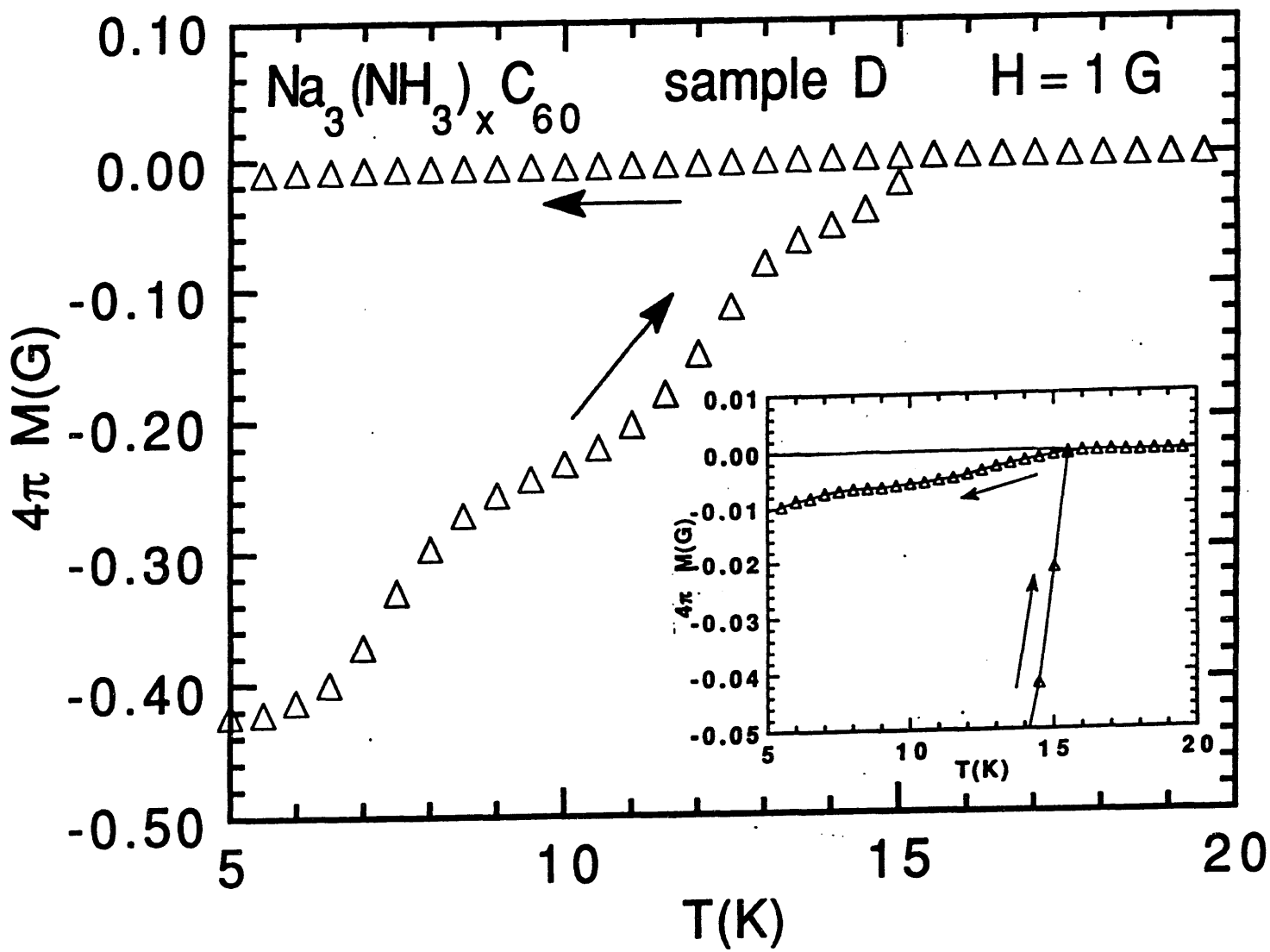
Figure Captions

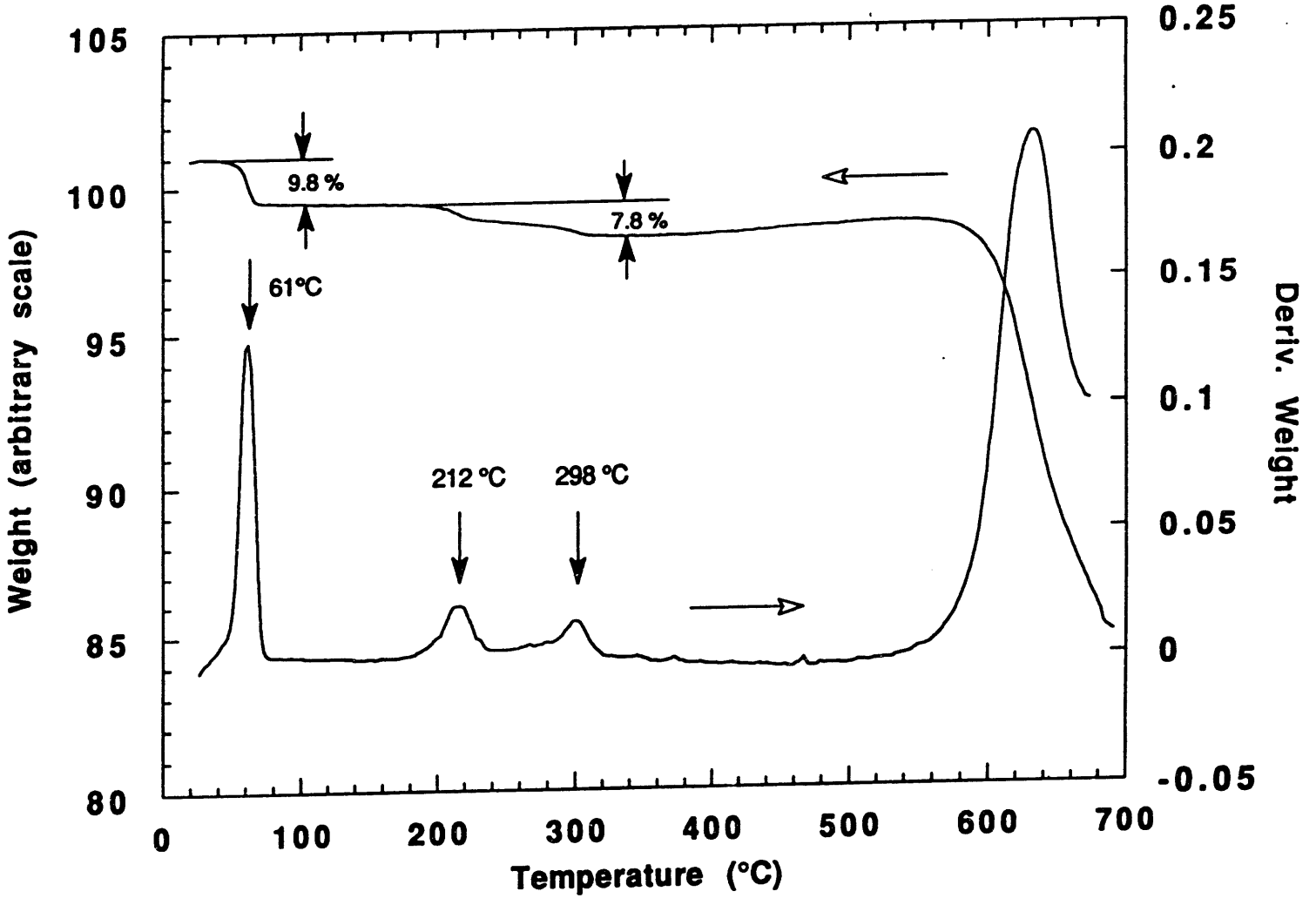
Figure 1. Temperature dependence of the normalized AC susceptibilities for sample A(cross), B(diamond), C(triangle), and D(circle), respectively. The inset shows the imaginary part ($\chi''$) of sample D.

Figure 2. Field cooled (FC) and zero-field cooled (ZFC) transitions of sample D in an applied field of 1G. The inset shows the stepwise nature of the FC transition.

Figure 3. The TGA of sample C showing the temperature dependence of the weight loss (arbitrary scale) and its derivative.


6.7 K
11.5 K
13.5 K
16.5 K
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
χ'(T)/χ'(5)
4
6
8
10
12
14
16
18
20
Temperature (K)


$Na_3(NH_3)_xC_{60}$
sample D
H = 1 G
0.10
0.00
-0.10
-0.20
-0.30
-0.40
-0.50
4π M(G)
5
10
15
20
T(K)
0.01
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
4π M(G)
5
10
15
20
T(K)


105
100
95
90
85
80
Weight (arbitrary scale)
0.25
0.2
0.15
0.1
0.05
0
-0.05
Deriv. Weight
9.8 %
7.8 %
61°C
212 °C
298 °C
0
100
200
300
400
500
600
700
Temperature (°C)

DATE
FILMED
6/10/94

END