



0025-5408(95)00149-2

**HMTTEF.C<sub>60</sub>—A 2-D CLOSE-PACKED LAYERED COMPOUND OF C<sub>60</sub>****K.K. Singh, T. Pradeep\*, A.P.B. Sinha, D.E. Morris, and J.A. Hriljac<sup>†</sup>**  
Morris Research, Inc.

1918 University Avenue, Berkeley CA 94703 USA.

<sup>†</sup> Department of Physics, Brookhaven National Laboratory,  
Upton, Long Island, New York 11973, USA.

\*Indian Institute of Technology, Madras, India.

(Received April 5, 1995; Communicated by J. B. Goodenough)

**ABSTRACT**

The analysis of high resolution synchrotron X-ray powder diffraction data of HMTTEF.C<sub>60</sub> (HMTTEF = hexamethylenetetrafulvalene) gave a triclinic unit cell with  $a = 9.9297 \text{ \AA}$ ,  $b = 9.9359 \text{ \AA}$ ,  $c = 13.1472 \text{ \AA}$ ,  $\alpha = 106.966^\circ$ ,  $\beta = 95.887^\circ$  and  $\gamma = 118.252^\circ$  in the space group  $P\bar{1}$ . Steric considerations suggest that there is a nearly close-packed layer of C<sub>60</sub> molecules in the  $ab$  plane, and HMTTEF molecules are sandwiched between layers of C<sub>60</sub>. The compound is insulating and weakly paramagnetic and the charge-transfer is small.

MATERIALS INDEX: carbonsixty, charge-transfer complex, hexamethylenetetrafulvalene, paramagnetic

**INTRODUCTION**

The rather large electron affinity of C<sub>60</sub> prompted us to react it with a powerful electron donor, hexamethylenetetrafulvalene (HMTTEF) (1), an analog of the well-known donor tetrathiafulvalene. Reactions in refluxing toluene led to solid precipitates, and X-ray diffractograms of the products with different reactant ratios established that a phase pure product was formed with a 1:1 composition. The preparation was also carried out in an inert atmosphere, and the X-ray diffraction pattern of the product was very similar to that obtained in air. Elemental analysis is consistent with a formula of C<sub>72</sub>H<sub>12</sub>Te<sub>4</sub>, that is, HMTTEF.C<sub>60</sub>. The IR spectrum of the compound is essentially a superposition of the spectra of C<sub>60</sub> and HMTTEF, suggesting that the extent of charge transfer is small. A brief account of the synthesis and characterization of this new compound has been published (2). We have now collected more precise X-ray data on this compound using synchrotron radiation, which has enabled us to get

the correct unit-cell parameters and suggests a structure built of alternating layers of  $C_{60}$  and HMTTEF. The magnetic susceptibility data reported here along with the EPR results indicate a near absence of unpaired spins in the temperature range  $20 < T < 300$  K. The related material TDAE. $C_{60}$  was reported to be ferromagnetic (3, 4), whereas the title compound is weakly paramagnetic and the charge-transfer is small.

## EXPERIMENTAL

X-ray data were collected at beamline X7A of the National Synchrotron Light Source at the Brookhaven National Laboratory on a 1 mm capillary sample at room temperature. The instrument was configured in the high-resolution mode with a channel-cut Ge(111) monochromator and a Ge(220) analyzer crystal. The wavelength was 1.19505 Å as determined by a silicon calibration standard. The position of the first 33 lines was determined by individual peak fits and auto-indexed with Visser's program (5). The initial indexing gave a monoclinic C-centered unit cell with  $a = 17.0499$  Å,  $b = 10.1930$  Å,  $c = 15.6413$  Å, and  $\beta = 129.601^\circ$ . Closer examination of the pattern, especially at high angle, revealed a small amount of peak splitting, which indicated that the true symmetry was triclinic. After lowering the symmetry and transforming to the reduced cell, an intensity extraction with Le Bail's method (6) gave the final unit-cell parameters. The fit converged to give  $R_{wp} = 11.1\%$  and  $\chi^2$  of 2.4.

The magnetic properties of HMTTEF. $C_{60}$  were investigated with a Quantum Design SQUID magnetometer. The sample was prepared as follows: A 15 cm long quartz capillary tube of 4 mm outer diameter was sealed at one end then half-filled with anhydrous toluene and degassed several times by repeated freeze-pump-thaw cycles. Into the tube was put 110 mg of the 1:1 mixture of  $C_{60}$  and HMTTEF, and the mixture in the tube was then degassed. After evacuation, the tube was sealed and then heated at one end to reflux toluene for about 1 hour. The solution became colorless as a result of the complete precipitation of HMTTEF. $C_{60}$ . The precipitate was allowed to settle, then the tube was broken and the solvent removed in vacuum, leaving a black microcrystalline solid. The tube was then resealed in vacuum at about 4 cm above the powder-fill line. The length of the sample in the sealed tube was about 6 mm.

## RESULTS AND DISCUSSION

The analysis of the high-resolution synchrotron X-ray powder diffraction data gives a triclinic unit cell with  $a = 9.9297$  Å,  $b = 9.9359$  Å,  $c = 13.1472$  Å,  $\alpha = 106.966^\circ$ ,  $\beta = 95.887^\circ$  and  $\gamma = 118.252^\circ$  in the space group PT. Steric considerations suggest that there is a nearly close-packed layer of  $C_{60}$  molecules in the  $ab$  plane. If this is correct, the inter- $C_{60}$  distances within the  $a$ - $b$  plane will be close to that found in  $K_3C_{60}$  (7), TDAE. $C_{60}$  (3, 4), (BEDT-TTF) $_2$ . $C_{60}$  (8),  $CH_2I_2$ . $C_6H_6$ . $C_{60}$  (9) and  $C_{60}I_4$  (10). However, the interplanar spacing of ca. 12.5 Å is much larger than those found in superconducting  $K_3C_{60}$  and ferromagnetic TDAE. $C_{60}$  (3, 4), but very close to that observed in the (BEDT-TTF) $_2$ . $C_{60}$ ,  $CH_2I_2$ . $C_6H_6$ . $C_{60}$  and  $C_{60}I_4$ . The crystal structure of  $C_{60}$ . $CH_2I_2$ . $C_6H_6$  contains close-packed layers of  $C_{60}$  (9) that are spaced 2 Å further apart than in the fcc lattice of pure  $C_{60}$ , thereby accommodating the methylene iodide and benzene molecules. A similar alternating guest-host layer structure is reported for  $C_{60}I_4$  (10). The increased interplanar spacing of the close-packed  $C_{60}$  planes in HMTTEF. $C_{60}$  suggests that the HMTTEF molecules are similarly accommodated between the adjacent layers of  $C_{60}$ . The details of the proposed HMTTEF layer are currently being worked out, and subsequent

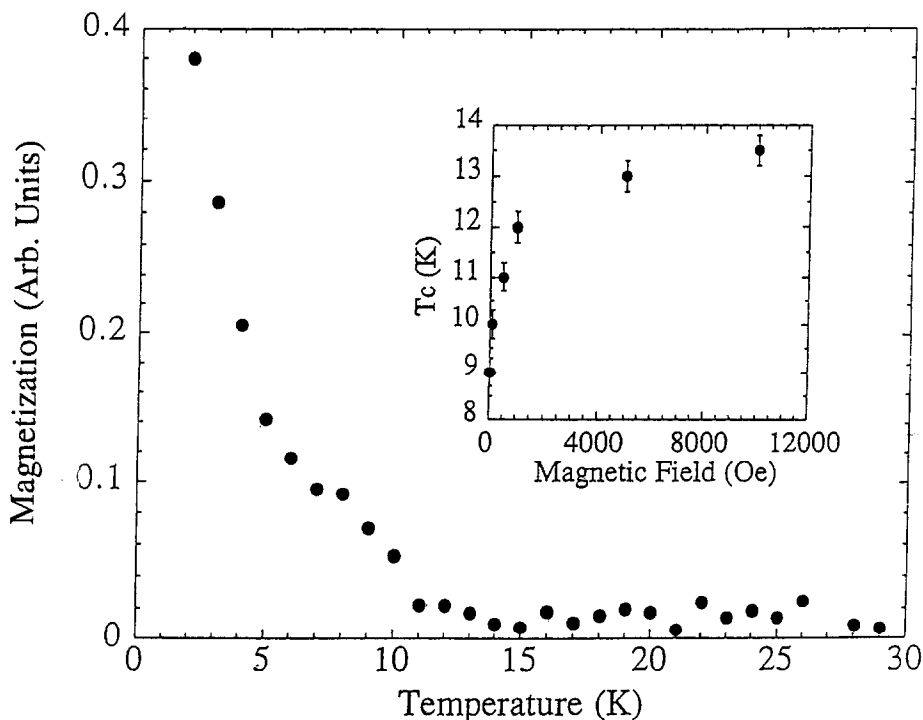


FIG. 1.

Magnetization of a 110 mg sample of HMTTEF.C<sub>60</sub> measured at an applied field of 50 Oe. Data has not been smoothed. No hysteresis was observed while cooling and subsequent warming. No correction was made for sample holder or for demagnetizing effects. Absolute value of magnetization was  $1.16 \times 10^{-5}$  emu at 30 K. Magnetization of the blank tube measured in an applied field of 5000 Oe under identical conditions showed a gradual increase from  $3.0 \times 10^{-5}$  emu at 200 K to  $4.0 \times 10^{-5}$  emu at 2 K. Inset shows the field dependence of the transition

Rietveld analysis will be performed to confirm the hypothetical crystal structure and allow calculation of the band structure.

In Fig. 1 we show the magnetization,  $M = \chi H$ , of the sample in the temperature range of 2-30 K measured at an applied field of 50 Oe. It can be seen that there is a sharp increase in magnetization (or susceptibility  $\chi$ ) below 10 K, whereas above the transition temperature the magnetization is essentially constant to room temperature. The sharp increase in magnetization was found even at a lower applied field of 10 Oe. The transition temperature, defined as the intersection of the linear extrapolations of the magnetization above and below the transition, increases with applied field (see inset of Fig. 1). The transition width was also found to increase with applied field. In Fig. 2 we show the  $M$  versus  $H$  plots of the sample at two temperatures. Whereas the 50 K plot is typical of a paramagnet, the 2 K plot shows a distinct 'S' shape. A sharp and significant increase in the susceptibility below 10 K could suggest ferromagnetism, but there are no other evidences supporting magnetic ordering. The high temperature susceptibility shows only a weak temperature dependence unlike

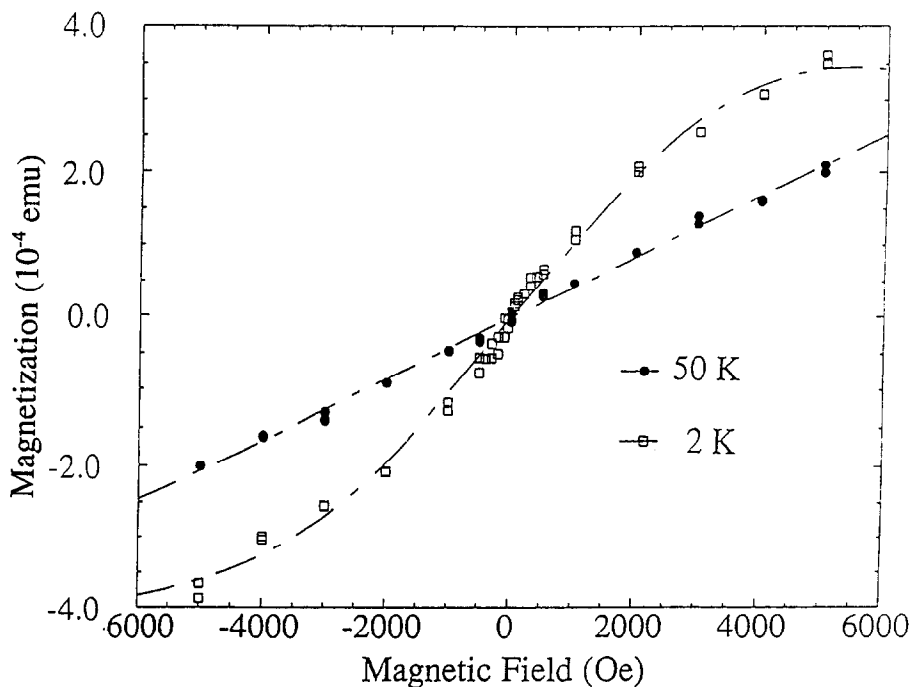


FIG. 2.

Magnetization as a function of applied field at 2 K (open squares) and 50 K (dark circles). Note the distinct 'S' shape of the 2 K curve. Lines are to guide the eye.

conventional ferromagnets and no Curie-Weiss dependence is observed. The low temperature susceptibility is field dependent; however, no hysteresis was observed.

Preliminary EPR analysis (11) of the sample also shows no evidence of magnetic ordering in the temperature range 4-300 K. Although there is a sharp increase in the signal intensity below 20 K (Fig. 3), no hyperfine splitting is observed. Above 20 K, the spectrum is essentially independent of temperature, consistent with the susceptibility data. The observed  $g$  value is 1.9975, close to the value observed for TDAE.C<sub>60</sub> (2.0008) (3) and that for electrochemically produced C<sub>60</sub><sup>-1</sup> (1.9991). Such a similarity in the  $g$  values suggests that the spins are primarily located on C<sub>60</sub>. The  $g$  value did not change significantly with temperature. The estimated number of spins per C<sub>60</sub> molecule is <0.01. This suggests that there is very small charge-transfer to C<sub>60</sub>. It appears that there are two important differences between TDAE.C<sub>60</sub> and HMTTEF.C<sub>60</sub>. Electronically, the TDAE compound shows a large degree of charge transfer, the HMTTEF compound does not.\* This must be related to the relative reducing strengths. Structurally, TDAE.C<sub>60</sub> crystallizes in a lattice that is similar to that of C<sub>60</sub> itself with the TDAE molecules occupying the voids and causing a distortion of the lattice.

\*The extent of charge-transfer (CT) is considerably smaller in HMTTEF.C<sub>60</sub> than in TDAE.C<sub>60</sub>. On adding HMTTEF to C<sub>60</sub>, a distinct band around 450 nm develops in the UV/VIS spectrum, which could have been attributed to a CT complex. However, in view of the EPR results showing very small number of free spins, alternate interpretations such as the excitation of symmetry forbidden transitions of C<sub>60</sub> as a result of complexation and concomitant symmetry change have to be considered.

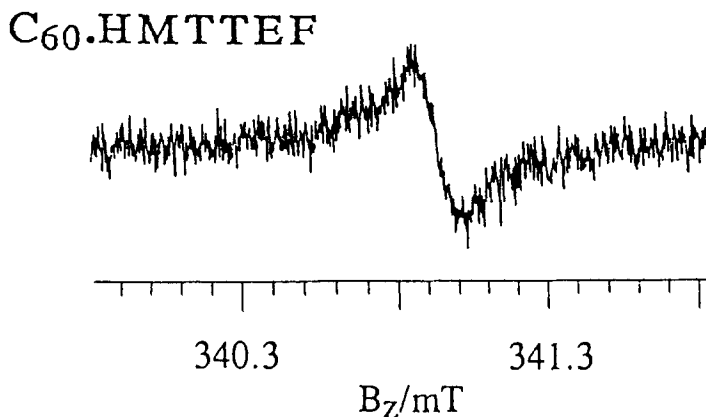


FIG. 3.  
EPR powder absorption derivatives  $dP/dB$  versus  $B_z$  of  $C_{60}\cdot HMTTEF$  at 298 K.

This leads to a quasi-2-dimensional material having an anisotropic band structure due to a small distortion from cubic symmetry.  $HMTTEF\cdot C_{60}$  is probably much more like  $(BEDT-TTF)_2\cdot C_{60}$ . It is composed of close-packed layers of  $C_{60}$  molecules alternating with layers of HMTTEF. The short inter- $C_{60}$  distance in the  $ab$ -plane should lead to significant overlap of the wave functions, but in view of the small charge transfer there are not enough carriers to give rise to overall conductivity. This material behaves like a co-crystal rather than a charge-transfer salt.  $TDAE\cdot C_{60}$  thus remains unique amongst the  $C_{60}$  charge-transfer complexes in showing ferromagnetism and metallic conductivity.

### CONCLUSION

In summary: (i)  $HMTTEF\cdot C_{60}$  appears to have a close-packed layer of  $C_{60}$  molecules with layers of HMTTEF molecules sandwiched in between; (ii) EPR results show that there are very few unpaired spins and the compound is thus weakly paramagnetic; (iii) this also indicates that the charge-transfer between  $C_{60}$  and HMTTEF is small, and (iv) the material is poorly conducting because of the small number of charge carriers. If carriers can be doped in the  $C_{60}$  layer, it can be expected to show conductivity and possibly 2-D superconductivity because the  $C_{60}\text{-}C_{60}$  distance is comparable to that in the  $K_3C_{60}$  superconductor.

### ACKNOWLEDGMENT

We thank Dr. D. E. Cox for helpful discussions and a critical reading of the manuscript. The work at Brookhaven National Laboratory was supported by the U.S. Department of Energy, Division of Materials Sciences under contract number DE-AC02-76CH00016. The National Synchrotron Light Source is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

## REFERENCES

1. P.J. Carroll, M.V. Lakshmikantham, M.P. Cava, F. Wudl, E. Aharon-Shalom and S.D. Cox, *J. Chem. Soc., Chem. Commun.*, 1316 (1982).
2. T. Pradeep, K.K. Singh, A.P.B. Sinha and D.E. Morris, *J. Chem. Soc., Chem. Commun.*, 1747 (1992).
3. P-M. Allemand, K.C. Khemani, A. Koch, F. Wudl, K. Holzner, S. Danovan, G. Gruner, J.D. Thomson, *Science*, 253, 301 (1991).
4. P.W. Stephens, D. Cox, J.W. Lauher, L. Mihaly, J.B. Wiley, P-M Allemand, A. Hirsch, K. Holzner, Q. Li, J.D. Thompson and F. Wudl, *Nature* 355, 331 (1992).
5. J. W. Visser, *J. Appl. Cryst.*, 2, 89 (1969).
6. A. Le Bail, H. Duroy, J.L. Fourquet, *Mat. Res. Bull.*, 23, 447 (1988).
7. A.F. Hebard, M.J. Rosseninsky, R.C. Haddon, D.W. Murphy, S.H. Glarum, T.T. M. Palstra, A.P. Ramirez and A.R. Korton, *Nature* 350, 600 (1991).
8. A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito and H. Shinohara, *J. Chem. Soc., Chem. Commun.*, 1472 (1992).
9. U. Geiser, S.K. Kumar, B.M. Savall, S.S. Harred, K.D. Carlson, P.R. Mobley, H.H. Wang, J.M. Williams and R.E. Botto, *Chem. Mater.*, 4, 1077 (1992).
10. Q. Zhu, D.E. Cox, J.E. Fischer, K. Kniaz, A.R. McGhie and O. Zhou, *Nature*, 355, 712 (1992).
11. K.K. Singh, T. Pradeep, D.E. Morris, C. Lei, H. Nguyen and J.A. Acrivos, *Solid State Commun.* (1994, communicated).