

SUPERCONDUCTIVITY AT 40K IN CESIUM DOPED  $C_{60}$ 

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We report superconductivity in  $Cs_3C_{60}$  at 40K using ac susceptibility measurements under hydrostatic conditions up to 15 kbar.  $Cs_3C_{60}$  was prepared by reaction of  $C_{60}$  with Cs in liquid ammonia, followed by heating at 150°C. This route circumvents formation of the energetically more stable  $Cs_1C_{60}$  and  $Cs_4C_{60}$  phases. We have studied the synthesis and phase formation by measuring the symmetric  $A_g$  pentagonal pinch mode of  $C_{60}$  using Raman spectroscopy. Whereas Raman spectroscopy indicates homogeneous charge transfer of three electrons, x-ray diffraction indicates two phases other than the commonly observed fcc structure. This superconducting transition temperature is considerably higher than for known doped  $C_{60}$  compounds and intermetallic compounds.

Superconductivity in alkali (A) doped  $C_{60}$  is a consequence of a high density of states at the Fermi surface  $N(E_F)$ , and coupling of these conduction electrons to high frequency phonons. Superconductivity was discovered<sup>[1]</sup> at 18K for  $K_3C_{60}$ , raised soon thereafter to 28K for  $Rb_3C_{60}$ .<sup>[2]</sup> Higher values of  $T_c$  were obtained on ternary alloys: single phase  $Rb_2CsC_{60}$  (31K),<sup>[3]</sup> mixed phase  $Cs_2RbC_{60}$  (33K),<sup>[4]</sup> and mixed phase  $Cs_xC_{60}$  (30K).<sup>[5]</sup> We report superconductivity in  $Cs_3C_{60}$  at 40K under hydrostatic conditions.  $Cs_3C_{60}$  was prepared by reaction of  $C_{60}$  with Cs in liquid ammonia, followed by heating at 150°C. This route circumvents formation of the energetically more stable  $Cs_1C_{60}$  and  $Cs_4C_{60}$  phases. We have studied the synthesis and phase formation by measuring the symmetric  $A_g$  pentagonal pinch mode of  $C_{60}$  using Raman spectroscopy. Whereas Raman spectroscopy indicates a homogeneous charge transfer of three electrons, x-ray diffraction indicates two non-fcc phases. This  $T_c$  is significantly higher than for all intermetallic compounds, and exceeded only by the ceramic copper-oxide superconductors.

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While in most superconductors  $T_c$  is almost impossible to predict, it turns out that for  $A_3C_{60}$  there are simple guidelines. Since the relevant high frequency phonons are intramolecular modes and almost unaffected by the alkali doping,  $T_c$  is determined by the band width. The band width can be decreased by reducing the wavefunction overlap, and a higher  $N(E_F)$  can be obtained by expanding the lattice. In fact, this results in a monotonic relation between  $T_c$  and the fcc lattice parameter. This relationship can be verified by two methods: first by plotting  $T_c$  versus lattice parameter for the various fcc  $A_3C_{60}$  compounds, and second by applying hydrostatic pressure and shrinking the lattice uniformly. It turns out that both methods yield an identical  $T_c$  for a given lattice parameter, emphasizing the passive role the alkali ions have for the electronic properties. Various attempts have been reported to synthesize  $Cs_3C_{60}$ , since it is the obvious candidate to expand the crystal lattice from the present highest  $T_c = 33K$  in  $Cs_2RbC_{60}$ . We will show that it is essential to use a low temperature synthesis route, since already at 200°C the phase segregates in the energetically favorable compounds  $Cs_1C_{60}$  and  $Cs_4C_{60}$ .  $Cs_3C_{60}$  already exists at ambient pressure albeit not in the common fcc structure. Hydrostatic pressures are required to raise

superconductivity to 40K, but without the formation of fcc  $Cs_3C_{60}$ . This increases the superconducting transition temperature by 25% from previous results on  $A_3C_{60}$ , and is almost a factor of two higher than for any intermetallic compound.

We used the following method to synthesize  $Cs_3C_{60}$ . Cs metal and  $C_{60}$  powder in a stoichiometric ratio of 3:1 were cooled in an evacuated flask by a dry-ice/isopropanol slush. Anhydrous  $NH_3$  was condensed onto the Cs/ $C_{60}$  mixture through a vacuum line. The  $C_{60}$  powder completely dissolved in the liquid  $NH_3$ , indicating charge transfer from Cs to  $C_{60}$ . (Pristine  $C_{60}$  is insoluble in liquid  $NH_3$ ). After about half an hour,  $NH_3$  was evaporated from the solution by heating up the flask to 150°C under vacuum, conditions sufficient to remove  $NH_3$  from  $NH_3K_3C_{60}$ . All the evolving gas is condensable in a liquid nitrogen trap, hence no measurable  $H_2$  is evolved during the reaction. Heating was stopped when no more  $NH_3$  evolved from the flask.

Figure 1 shows the Raman spectra of  $Cs_3C_{60}$ . Experimental procedures are described elsewhere.<sup>[6]</sup> In undoped  $C_{60}$  the pentagonal pinch mode of  $A_g$  symmetry

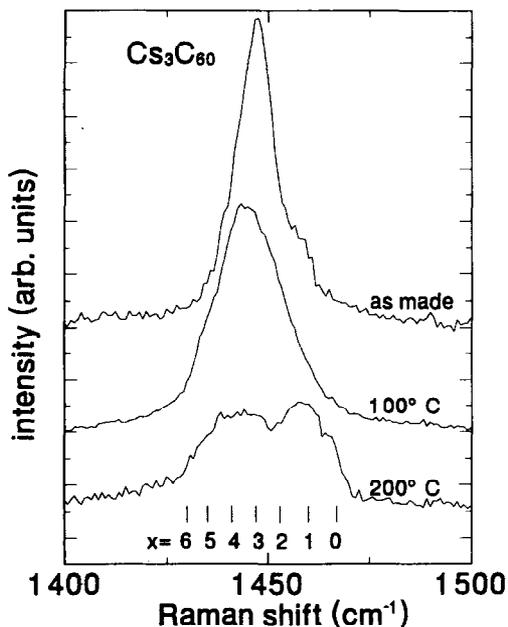
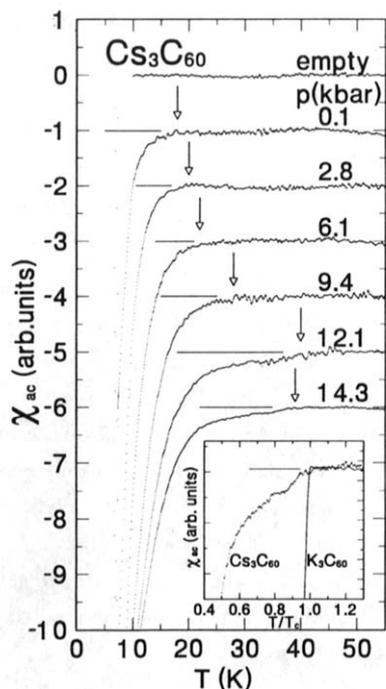


Figure 1  
Raman spectra of  $Cs_3C_{60}$  at room temperature, showing the  $A_g$  pentagonal pinch mode, for as-made samples and samples annealed at 100°C and 200°C, as indicated. The lines at the bottom indicate the position of the  $A_g$  mode for  $A_xC_{60}$  compounds.

occurs at  $1467\text{ cm}^{-1}$ . On doping, this mode softens by  $6\text{ cm}^{-1}$  per transferred electron,<sup>[7] [8]</sup> since the added electrons enter antibonding molecular orbitals. The frequency shift reflects only the electron transfer to the  $C_{60}$  independent of the alkali-metal, A, and provides a convenient diagnostic probe of the charge transfer. For example, in  $K_3C_{60}$  this  $A_g$  mode appears at  $1446\text{ cm}^{-1}$  and in  $Rb_3C_{60}$  at  $1447\text{ cm}^{-1}$ , with linewidths of  $9\text{ cm}^{-1}$  (FWHM). The observed peak position of  $1447\text{ cm}^{-1}$  and linewidth of  $10.8\text{ cm}^{-1}$  of the  $A_g$  mode for the as-made  $Cs_3C_{60}$  sample, as seen in Fig. 1, demonstrate the stability of the  $Cs_3C_{60}$  phase at room temperature. Annealing the sample overnight at 100°C results in a softening of the mode to  $1445\text{ cm}^{-1}$  and a broadening of the width to  $20\text{ cm}^{-1}$ . On further annealing the sample at 200°C the  $A_g$  mode splits into two broad lines at  $1442$  and  $1459\text{ cm}^{-1}$ . We interpret these two lines as the signature of phase separation of the  $Cs_3C_{60}$  at elevated temperatures into  $Cs_1C_{60}$  and  $Cs_4C_{60}$ . Under hydrostatic pressure of 10 kbar at room temperature the  $A_g$  mode of the unannealed material does not broaden significantly, but increases in frequency by  $3\text{ cm}^{-1}$ , similar to the value reported for pristine  $C_{60}$ .<sup>[9]</sup> Our observation of phase separation corroborates previous studies on powder and thin film samples indicating that  $Cs_1C_{60}$  and  $Cs_4C_{60}$  are readily synthesized and are the energetically more stable phases.<sup>[10] [11] [12]</sup> It is possible that reports of superconductivity near 30K at ambient pressure<sup>[4][5]</sup> have probed the same phase on which we report superconductivity under pressure at 40K.  $Cs_3C_{60}$  is a metastable compound which requires gentle synthesis.

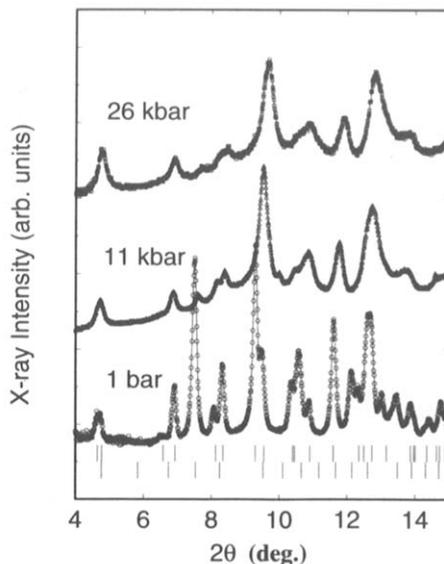
Figure 2 shows the ac susceptibility of  $Cs_3C_{60}$  at hydrostatic pressures between 0 and 15 kbar. The pressure cell is a clamp-type cell, described elsewhere, using mineral oil as pressure medium.<sup>[13]</sup> ac susceptibility was measured using a primary coil generating  $\sim 0.1\text{ Oe}$  at 88 Hz, and two counterwound secondary coils. We used a Pb chip for pressure calibration. Since the samples react with water and oxygen in air, we avoided any exposure to the ambient. The ac susceptibility measurements are non hysteretic with temperature, or pressure cycling. Figure 2 shows that hydrostatic pressures are needed to observe superconductivity at 40K. At residual pressure only a small superconducting signature is observed near 18K, which increases and shifts to 40K upon applying pressure. The susceptibility at 4K has a value of  $-8 \times 10^{-4}\text{ emu/cm}^3$ , comparable to the early results on  $K_3C_{60}$ <sup>[11]</sup> and  $Rb_3C_{60}$ <sup>[12]</sup>. For the fullerene superconductors the particle



**Figure 2**  
 Temperature dependence of the ac susceptibility of Cs<sub>3</sub>C<sub>60</sub> under hydrostatic pressures up to 14.3 kbar. The arrows indicate the onset of the superconducting transition. The inset shows a blow-up of the transition comparing the ac susceptibility versus reduced temperature of Cs<sub>3</sub>C<sub>60</sub> at 14.3 kbar with the transition of K<sub>3</sub>C<sub>60</sub> at ambient pressure.

size is often smaller than the magnetic penetration depth  $\lambda \sim 0.4 \mu\text{m}$ . For uncoupled grains with typical size  $D$ , the superconducting signal has a magnitude that depends on the ratio  $x=D/\lambda$ .<sup>[14]</sup> The Meissner state has a magnetic susceptibility  $\chi = -\frac{1}{4\pi} \frac{x^2}{60}$  for  $D < \lambda$ , and  $\chi = -\frac{1}{4\pi} (1 - \frac{2}{x})^3$  for  $D > \lambda$ . The typical particle size is usually larger than the x-ray coherence length of  $\sim 300 \text{\AA}$ , but presumably somewhat smaller than that of sintered material of  $\sim 1 \mu\text{m}$ . Using a particle size of  $0.5 \mu\text{m}$ , we obtain a superconducting volume fraction of  $\sim 25\%$ . The weak Josephson coupling between the grains may be enhanced by the two-phase nature of the material.

Whereas Raman spectroscopy indicates that we successfully synthesized Cs<sub>3</sub>C<sub>60</sub>, x-ray diffraction shows a more complicated situation. In Figure 3, we show the 300K powder x-ray diffraction patterns of the as-made Cs<sub>3</sub>C<sub>60</sub> sample at atmospheric pressure, 11 kbar and 26 kbar. The data were collected using  $0.6911 \text{\AA}$



**Figure 3**  
 X-ray diffraction pattern of Cs<sub>3</sub>C<sub>60</sub> at 1 bar, and 11 and 26 kbar. At 1 bar the structure can be indexed by a mixture of the A15 and a body centered tetragonal phase. The allowed reflections are marked below the 1 bar spectrum for the bct structure (top) and the A15 structure (bottom). At 26 kbar the structure can be indexed by a body centered cubic structure.

monochromatic synchrotron x-ray radiation and a linear detector. The atmospheric pressure data were taken on a sample in a sealed glass capillary and the 11 kbar and 26 kbar patterns were taken on a sample of the same batch in a diamond anvil cell. The 1 bar x-ray pattern cannot be indexed as from a single phase sample. The presence of fcc Cs<sub>3</sub>C<sub>60</sub> is ruled out from peak positions and intensity calculations. We have indexed the pattern as a two-phase mixture of a cubic A15 and a body-centered tetragonal (bct) structure, with lattice parameters of  $a = 11.770 \text{\AA}$  for the A15 phase and  $a = 12.057$  and  $c = 11.432 \text{\AA}$  for the bct phase. The unit cell volumes for the cubic and tetragonal phase are  $815.3$  and  $830.9 \text{\AA}^3/\text{C}_{60}$ , and are essentially the same as that of the bcc Cs<sub>6</sub>C<sub>60</sub><sup>[15]</sup> and the bct Cs<sub>4</sub>C<sub>60</sub> phase,<sup>[10]</sup> respectively. A preliminary two-phase refinement was carried out using the structural models proposed for the A15 Ba<sub>3</sub>C<sub>60</sub><sup>[16]</sup> and bct K<sub>4</sub>C<sub>60</sub> phase<sup>[10][17]</sup> with the Cs occupancy and coordinates in the bct structure and the ratio of the two phases as adjustable parameters. The result shows that the observed pattern can be qualitatively described by a two-phase mixture of A15 Cs<sub>3</sub>C<sub>60</sub> and bct Cs<sub>3</sub>C<sub>60</sub>, with partial occupancy of Cs in the bct  $(x, 1/2, 0)$

site. This is consistent with the result from Raman measurement which shows homogeneous charge transfer of 3 electrons per  $C_{60}$ . Under pressure, the distinct A15 Bragg peaks (not allowed for a bcc phase with the same lattice parameter) are diminished, suggesting structural transition from A15 to bcc or bct. For the bct component, the a-axis is found to be more compressible under pressure than the c-axis, and the structure becomes equilateral at 26 kbar. The powder pattern at 26 kbar can be qualitatively described as a single phase bcc structure with a volume of  $764\text{\AA}^3$  per  $C_{60}$ . For comparison,  $K_3C_{60}$  and  $Rb_3C_{60}$  have a unit cell volume of 722 and  $744\text{\AA}^3$  per  $C_{60}$  at 1 bar, respectively. Band structure calculations have reported a  $T_c$  of 47.4K<sup>[18]</sup> and 70K<sup>[19]</sup> for fcc  $Cs_3C_{60}$ , based on a unit cell volume of 810 and  $767\text{\AA}^3$  per  $C_{60}$ , respectively.

Our measurements show that for pressures lower than 12 kbar  $T_c$  increases with pressure. This is contrary to what one would expect, based on the broadening of the band when applying pressure. This behavior has been observed for the alkaline earth doped fullerene  $Ca_5C_{60}$ , and these authors suggested band structure effects other than the pressure-induced band broadening.<sup>[20]</sup> We would like to propose a different explanation, in view of the complicated phase formation of our material. We suggest that at ambient pressure the shielding currents are suppressed by disorder, caused by the fine grain and two phase nature of the sample. In disordered materials  $T_c$  can be reduced due

to fluctuations in the phase of the superconducting order parameter.<sup>[21]</sup> Hydrostatic pressure can, in conjunction with stabilizing the superconducting phase, improve the connectivity of the material by pressing the grains intimately together, and thus reduce the phase fluctuations. A third possibility is that  $Cs_3C_{60}$  is a Mott insulator, and that hydrostatic pressure is needed to drive it metallic.

While our present result enhances  $T_c$  to a record level of 40K for conventional electron-phonon coupling superconductors, it may be evident that the limits can be pushed further. Firstly,  $T_c$  can still be limited by phase fluctuations, which could be suppressed by other synthetic routes. Secondly, hydrostatic pressure to stabilize a phase can usually be supplanted by chemical modifications. While  $T_c$  is limited to 12K in the simple cubic  $Pa\bar{3}$  structure,<sup>[22]</sup> and to 33K in the fcc structure, higher  $T_c$ 's than the present result of 40K may be achieved in other fullerene based compounds.

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#### REFERENCES

1. A.F. Hebard et al. *Nature* **350**, 600-601 (1991).
2. M.J. Rosseinsky et al. *Phys. Rev. Lett.* **66**, 2830-2832 (1991).
3. R.M. Fleming et al. *Nature* **352**, 787-788 (1991).
4. K. Tanigaki et al. *Nature* **352**, 222-225 (1991).
5. S.P. Kelty et al. *Nature* **352**, 223-225 (1991).
6. O. Zhou et al. *Nature* (submitted).
7. P. Zhou et al. *Phys. Rev. B* **48**, 8412 (1993).
8. S.J. Duclos et al. *Science* **254**, 1625-1627 (1991).
9. D.W. Snoke et al. *Phys. Rev. B* **45**, 14419-14422 (1992).
10. R.M. Fleming et al. *Nature* **352**, 701-703 (1991).
11. Q. Zhu et al. *Phys. Rev. B* **47**, 13948-13951 (1993).
12. R.C. Haddon et al. *Chem. Phys. Lett.* **218**, 100-106 (1994).
13. J.D. Thompson, *Rev. Sci. Instrum.* **55**, 231-234 (1984).
14. D. Shoenberg, *Proc. Roy. Soc. (London)* **A175**, 49 (1940).
15. O. Zhou et al. *Nature* **351**, 462-464 (1991).
16. A.R. Kortan et al. *Nature* **360**, 566-568 (1992).
17. O. Zhou, and D.E. Cox, *J. Phys. Chem. Solids* **53**, 1373-1390 (1992).
18. D.L. Novikov et al. *Physica C* **191**, 399-408 (1992).
19. M.-Z. Huang et al. *Phys. Rev. B* **46**, 6572-6577 (1992).
20. J.E. Schirber et al. *Physica C* **213**, 190-192 (1993).
21. T.T.M. Palstra et al. *Phys. Rev. Lett.* **68**, 1054-1057 (1992).
22. K. Prassides et al. *Science* **263**, 950-954 (1994).