An Orientationally-Ordered Primitive-Cubic Form of the Fulleride CsC_{60}

Alexandros Lappas,[†] Mayumi Kosaka,[‡]
Katsumi Tanigaki,[‡] and Kosmas Prassides*[,†]

School of Chemistry and Molecular Sciences
University of Sussex, Brighton, U.K.
NEC Fundamental Research Laboratories
Tsukuba 305, Japan

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The most well-known reactions of C_{60} have been with alkali metals to afford well-characterized compounds with stoichiometry A_xC_{60} ($x = 3$, A = K, Rb) that become superconducting with remarkably high transition temperatures (up to 33 K).[1] While early NMR work[2] led to the conclusion that phases with $x < 3$ were unstable with respect to disproportionation to C_{60} and A_3C_{60}, core-level and vibrational spectroscopy[3] first gave evidence for the existence of stable phases with stoichiometry AC_{60}. These have now proven to exhibit a variety of interesting properties. At high temperatures (above ~100 °C), they adopt a face-centered cubic (fcc) rocksalt structure.[4] Upon cooling, phase transitions to low-symmetry phases occur. Slow cooling leads to a conducting air-stable orthorhombic phase consisting of linear chains of C_{60}^- ions.[5] This phase undergoes a magnetic transition to a spin-density-wave (SDW)-like state in the vicinity of 50 K.[6] Rapid cooling leads to a metastable insulating orthorhombic phase which is found to consist of $(C_{60})_2$ dimeric units.[7] In this communication, we report that rapid cooling of CsC_{60} from the high-temperature fcc phase to liquid nitrogen temperatures suppresses the low-symmetry instabilities and leads instead to the formation of a cubic phase with primitive symmetry (space group $Pa\bar{3}$), resulting from the orientational ordering of the fulleride ions in the unit cell. The three-dimensional (3D) character of the structure sensitively affects the electronic and conducting properties of the material, as it no longer suffers from low-dimensional structural and magnetic instabilities. Current evidence from the temperature independence of the spin susceptibility measured by electron spin resonance (ESR) points to conducting behavior[8] for this phase and opens the way for the realization of superconducting fulleride compositions at stoichiometries other than A_3C_{60}.

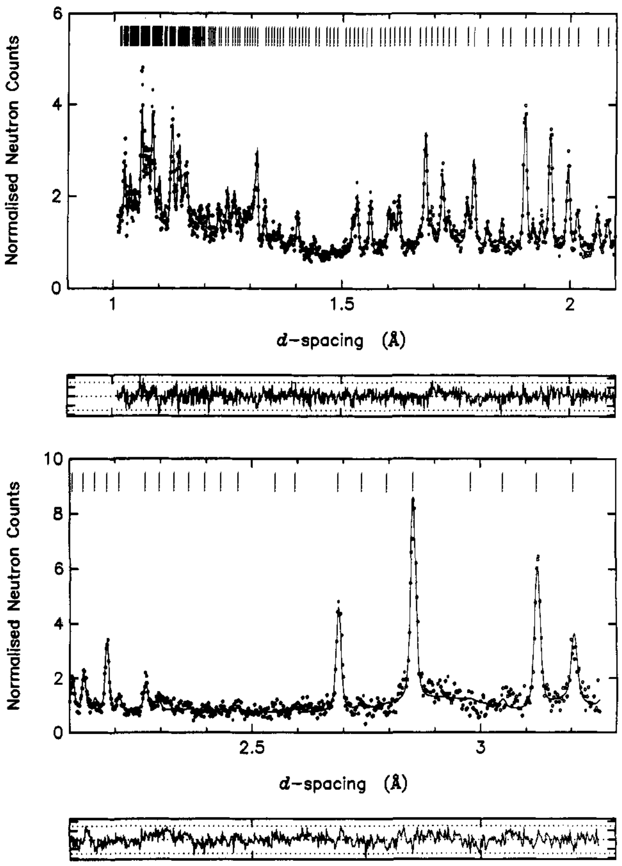

Figure 1. Observed (points), calculated (solid line), and difference (lower panel, in units of esd) plots for the final Rietveld refinement of the powder neutron diffraction data of quenched CsC_{60} at 4.5 K in the regions (a) $d = 1.0{-}2.1$ Å and (b) $d = 2.1{-}3.3$ Å. Reflection positions are shown as tick marks. The dotted lines in the lower panels indicate $\pm 3\sigma$.

The excellent quality single-phase CsC_{60} sample was prepared by reaction of stoichiometric quantities of C_{60} and Cs in sealed quartz tubes at 800 K for four weeks with intermittent shaking. Phase purity was confirmed by high-resolution synchrotron X-ray diffraction;[8] the equilibrium structure at 283 K is orthorhombic with lattice dimensions[8] $a = 9.095$ Å, $b = 10.225$ Å, and $c = 14.173$ Å. For the neutron diffraction measurements, the 300-mg sample was placed in a cylindrical 6-mm diameter vanadium sample holder and was press sealed with PTFE tape. Rapid cooling was achieved by immersing the sample, whose temperature was first raised from 300 to 450 K and held there for ~4 min, into a liquid nitrogen dewar for ~5 min. The sample was then transferred to a continuous-flow "orange" cryostat which was held at a temperature of ~30 K. Neutron powder diffraction data were collected at 4.5 K with the high-resolution powder diffractometer at the ISIS facility, Rutherford Appleton Laboratory, United Kingdom. The sample was placed at the high-flux 1-m position, and data were collected with detectors placed both at backscattering and 90° positions. The medium-resolution 90° data were preferred for the analysis in the present study because of considerably better statistics. The d-spacing range extended from 1.0 to 3.3 Å, and data analysis was performed with the ISIS powder diffraction software. The neutron scattering lengths of C and Cs are 6.648 and 5.42 fm, respectively.

Inspection of the diffraction profile at 4.5 K (Figure 1) readily reveals a number of reflections that index to primitive cubic symmetry. Systematic absences of reflections necessitated the

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[†] University of Sussex.

[‡] NEC Fundamental Research Laboratories.

(1) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600. Rosseinsky, M. J.; Ramirez, A. P.; Glarum, S. H.; Murphy, D. W.; Haddon, R. C.; Hebard, A. F.; Palstra, T. T. M.; Kortan, A. R.; Zahurak, S. M.; Makhija, A. V. *Phys. Rev. Lett.* **1991**, *66*, 12. Holczer, K.; Klein, O.; Huang, S. M.; Kaner, R. B.; Fu, K. J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154. Tanigaki, K.; Ebbesen, T. W.; Saito, S.; Mizuki, J.; Tsai, J. S.; Kubo, Y.; Kuroshima, S. *Nature* **1991**, *352*, 222.

(2) Tycko, R.; Dabbagh, G.; Rosseinsky, M. J.; Murphy, D. W.; Fleming, R. M.; Ramirez, A. P.; Tully, J. C. *Science* **1991**, *253*, 884.

(3) Winter, J.; Kuzmany, H. *Solid State Commun.* **1992**, *84*, 935. Poirier, D. M.; Ohno, T. R.; Kroll, G. H.; Benning, P. J.; Stepniak, F.; Weaver, J. H.; Chibante, L. P. F.; Smalley, R. E. *Phys. Rev. B* **1993**, *47*, 9870. Poirier, D. M.; Owens, D. W.; Weaver, J. H. *Phys. Rev. B* **1995**, *51*, 1830.

(4) Janossy, A.; Chauvet, O.; Pekker, S.; Cooper, J. R.; Forro, L. *Phys. Rev. Lett.* **1993**, *71*, 1091. Zhu, Q.; Zhou, O.; Fischer, J. E.; McGhie, A. R.; Romanow, W. J.; Strongin, R. M.; Cichy, M. A.; Smith, A. B. *Phys. Rev. B* **1993**, *47*, 13948. Tycko, R.; Dabbagh, G.; Murphy, D. W.; Zhu, Q.; Fischer, J. E. *Phys. Rev. B* **1993**, *48*, 9097. Martin, M. C.; Koller, D.; Du, X.; Stephens, P. W.; Mihaly, L. *Phys. Rev. B* **1994**, *49*, 10818.

(5) Stephens, P. W.; Bortel, G.; Faigel, G.; Tegze, M.; Janossy, A.; Pekker, S.; Oszlanyi, G.; Forro, L. *Nature* **1994**, *370*, 636. Pekker, S.; Forro, L.; Mihaly, L.; Janossy, A. *Solid State Commun.* **1994**, *90*, 349.

(6) Chauvet, O.; Oszlanyi, G.; Forro, L.; Stephens, P. W.; Tegze, M.; Faigel, G.; Janossy, A. *Phys. Rev. Lett.* **1994**, *72*, 2721.

(7) Martin, M. C.; Koller, D.; Rosenberg, A.; Kendziora, C.; Mihaly, L. *Phys. Rev. B* **1995**, *51*, 3210. Oszlanyi, G.; Bortel, G.; Faigel, G.; Tegze, M.; Granasy, L.; Pekker, S.; Stephens, P. W.; Bendele, C.; Dinnebier, R.; Mihaly, G.; Janossy, A.; Chauvet, O.; Forro, L. *Phys. Rev. B*, in press. Zhu, Q.; Cox, D. E.; Fischer, J. E. *Phys. Rev. B* **1995**, *51*, 3966.

(8) Kosaka, M.; Tanigaki, K.; Tanaka, T.; Atake, T.; Lappas, A.; Prassides, K. *Phys. Rev. B* **1995**, *51*, 12018.

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use of the primitive space group $Pa\bar{3}$, implying that the quenched phase of the CsC_{60} salt is isostructural with the low-temperature phases of pristine C_{60},[9] lightly-doped $Na_{1.3}C_{60}$,[10] and the Na_2AC_{60} (A = Cs,[11] Rb[12]) superconductors. Rietveld refinements were performed after allowing the four C_{60}^- ions in the unit cell to rotate anticlockwise in a stepwise manner by an arbitrary angle ϕ about the [111] direction and monitoring the resulting χ^2 values. A deep minimum was identified at $\phi \sim 98°$, exactly as in C_{60}; this orientation leads to optimal interball interactions, as it results in hexagon–hexagon (6:6) fusions nesting over pentagonal faces of neighboring molecules. The Cs^+ ions were placed in the octahedral holes, now coordinating[11] to hexagon–pentagon (6:5) fusions of six neighboring fulleride ions, and the C_{60} positional parameters were refined subject to restraints of ±0.010 Å on the lengths of three sets of C–C bonds (one set of 6:6 and two sets 6:5 fusions) and of ±0.10° on the pentagon and hexagon angles. Even though stable refinement was rapidly achieved with this fully ordered model, introduction of a second orientation ($\phi \sim 38°$) for the C_{60} units, involving 6:6 fusions nesting over hexagonal faces of neighboring molecules, led to significant improvement in the fit (from $\chi^2 = 2.0$ to a final value of $\chi^2 = 1.5$). The fraction of the C_{60}^- ions at ~98° converged to 84(1)%, to be compared with 88.3(8)% in Na_2CsC_{60},[11] 83.5(4)% in pristine C_{60},[13] and 80% in Na_2RbC_{60}.[12] The possibility of structural disorder for the Cs^+ ions (both within the octahedral site and between the octahedral and tetrahedral sites) was investigated, but it was found they preferred to be located at the high-symmetry (1/2,1/2,1/2) position. Table 1 summarizes the final structural parameters obtained from the Rietveld analysis. Estimates of the average C–C bond lengths can be obtained as 1.41(1) Å for the hexagon–hexagon (6:6) and 1.44(1) Å for the hexagon–pentagon (6:5) fusions. These lie between the values of the bond distances obtained before for C_{60} ($d(6{:}6) = 1.39(2)$ Å, $d(6{:}5) = 1.45(1)$ Å) and C_{60}^{3-} ($d(6{:}6) = 1.43(1)$ Å, $d(6{:}5) = 1.43(1)$ Å) from the analysis of neutron diffraction data of the isostructural pristine C_{60} and Na_2CsC_{60} solids. The observed trend is in agreement with theoretical expectations which predict a gradual smoothing out of the bond alternation upon reduction.[14]

Table 1. Atomic Coordinates (esd's in Parentheses) for Quenched CsC_{60} Obtained from Rietveld Refinement at 4.5 K[a]

atom	site	*x/a*	*y/a*	*z/a*
Cs	4b	0.5	0.5	0.5
C-1	24d	0.2273(3)	−0.0351(3)	0.1072(4)
C-2	24d	0.2467(3)	−0.0592(3)	0.0102(3)
C-3	24d	0.2068(3)	0.0627(3)	0.1330(4)
C-4	24d	0.2062(3)	−0.1449(3)	−0.0305(3)
C-5	24d	0.1672(3)	−0.0968(3)	0.1649(4)
C-6	24d	0.2459(3)	0.0138(4)	−0.0622(3)
C-7	24d	0.2060(3)	0.1347(4)	0.0618(3)
C-8	24d	0.1473(4)	−0.2048(3)	0.0259(3)
C-9	24d	0.1275(3)	−0.1802(3)	0.1247(3)
C-10	24d	0.2257(3)	0.1101(4)	−0.0369(3)

[a] The space group is $Pa\bar{3}$, the lattice constant $a = 13.9671(3)$ Å, the isotropic temperature factors $B(C) = 0.7(2)$ Å^2, $B(Cs) = 0.9(7)$ Å^2, and $\chi^2 = 1.5$. Fractional occupancies of C atoms (C-1 to C-10) in the major C_{60} orientation are 0.84(1). A minor [0.16(1)] orientation was also included in the refinement; the coordinates of the C atoms of this fraction were evaluated by anticlockwise rotation of 60° about [111] of atoms C-1 to C-10.

In conclusion, we have shown that rapid quenching of the high temperature cubic phase of CsC_{60} can lead to the stabilization of a three-dimensional orientationally-ordered primitive cubic phase at low temperatures. The properties of this phase are intriguing and merit thorough investigation, as it represents the only isotropic 3D fulleride phase isolated that does not have an A_3C_{60} stoichiometry and appears to be metallic[8] (as it is evidenced by its temperature independent spin susceptibility) despite the existence of strong electron correlation. The three-dimensional high-symmetry character of the structure is evidently responsible for the suppression of the low-dimensional instabilities (structural and/or magnetic) encountered in the orthorhombic forms of the AC_{60} salts as well as in (TDAE)-C_{60},[15] that lead to insulating behavior at low temperatures. As the $Pa\bar{3}$ structure supports superconductivity in the fullerides,[11] it is plausible that quenched CsC_{60} may show a transition to a superconducting state. Such a situation will be reminiscent of that encountered in organic charge-transfer salts (e.g., $(TMTSF)_2ClO_4$) in which differing cooling procedures can lead to the stabilization of different structural forms with varying properties[16] —from superconductivity (slow cooling, $T_c = 1.2$ K) to SDW formation (quenching, $T_{SDW} = 4$ K). If a superconducting transition is realized in the present case and extrapolation from the behavior of isostructural A_3C_{60} fullerides is valid, the small lattice constant (13.9671(3) Å) should lead to a T_c less than ~4 K.[11]

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(9) Sachidanandam, R.; Harris, A. B. *Phys. Rev. Lett.* **1991**, *67*, 1467. David, W. I. F., Ibberson, R. M.; Matthewman, J. C.; Prassides, K.; Dennis, T. J. S.; Hare, J. P.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* **1991**, *353*, 147. Liu, S.; Lu, V. J.; Kappes, M. M.; Ibers, J. A. *Science* **1991**, *254*, 408.

(10) Yildirim, T.; Fischer, J. E.; Harris, A. B.; Stephens, P. W.; Liu, D.; Brard, L.; Strongin, M.; Smith, A. B. *Phys. Rev. Lett.* **1993**, *71*, 1383.

(11) Prassides, K.; Christides, C.; Thomas, I. M.; Mizuki, J.; Tanigaki, K.; Hirosawa, I.; Ebbesen, T. W. *Science* **1994**, *263*, 950.

(12) Kniaz, K.; Fischer, J. E.; Zhu, Q.; Rosseinsky, M. J.; Zhou, O.; Murphy, D. W. *Solid State Commun.* **1993**, *88*, 47. Christides, C.; Prassides, K.; Neumann, D. A.; Copley, J. R. D.; Mizuki, J.; Tanigaki, K.; Hirosawa, I.; Ebbesen, T. W. *Europhys. Lett.* **1993**, *24*, 755.

(13) David, W. I. F.; Ibberson, R. M.; Dennis, T. J. S.; Hare, J. P.; Prassides, K. *Europhys. Lett.* **1992**, *18*, 219. Prassides, K.; Kroto, H. W.; Taylor, R.; Walton, D. R. M.; David, W. I. F.; Tomkinson, J.; Haddon, R. C.; Rosseinsky, M. J.; Murphy, D. W. *Carbon* **1992**, *30*, 1277. Burgi, H. B.; Blanc, E.; Schwarzenbach, D.; Liu, S. Z.; Lu, Y. J.; Kappes, M. M.; Ibers, J. A. *Angew. Chem.* **1992**, *31*, 640.

(14) Fowler, P. W. *Philos. Mag. Lett.* **1992**, *66*, 277. Andreoni, W.; Giannozzi, P.; Parrinello, M. *Phys. Rev. B* **1995**, *51*, 2087.

(15) Allemand, P. M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Gruner, G.; Thompson, J. D. *Science* **1991**, *253*, 301. Stephens, P. W.; Cox, D.; Lauher, J. W.; Mihaly, L.; Wiley, J. B.; Allemand, P. M.; Hirsch, A.; Holczer, K.; Li, Q.; Thompson, J. D.; Wudl, F. *Nature* **1992**, *355*, 331. Lappas, A.; Prassides, K.; Vavekis, K.; Arcon, D.; Blinc, R.; Cevc, P.; Amato, A.; Feyerherm, R.; Gygax, F. N.; Schenck, A. *Science* **1995**, *267*, 1799.

(16) Jerome, D.; Schulz, H. J. *Adv. Phys.* **1982**, *31*, 299.