

Excess Lithium Intercalation in the Fulleride Superconductor $\text{Li}_3\text{CsC}_{60}$

Serena Margadonna,[†] Kosmas Prassides,^{*,‡} Andrew N. Fitch,[‡] Mayumi Kosaka,[§] and Katsumi Tanigaki^{||}

School of Chemistry, Physics and Environmental Science
University of Sussex, Brighton BN1 9QJ, U.K.
European Synchrotron Radiation Facility
F-38043 Grenoble, France
NEC Fundamental Research Laboratories
Tsukuba 305, Japan
Faculty of Science, Osaka City University
PREST, JST, 3-3-138 Sugimoto, Sumiyoshi-ku
Osaka 558-8585, Japan

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Alkali fullerides $\text{A}_2\text{A}'\text{C}_{60}$ (A, A' = alkali metals) are superconducting with T_c at ambient pressure ranging from 3.5 K for $\text{Na}_2\text{RbC}_{60}$ ¹ to 33 K for $\text{RbCs}_2\text{C}_{60}$.² The only exception is provided by $\text{Li}_2\text{CsC}_{60}$ and $\text{Li}_2\text{RbC}_{60}$ which do not show superconductivity down to 50 mK.³ Otherwise, T_c increases monotonically with increasing interfullerene separation, d , as the density of states at the Fermi level, $N(\epsilon_F)$ increases. The absence of superconductivity in the Li fulleride family has been associated with the presence of strong bonding Li^+-C interactions.⁴ These lead to a reduced formal charge of the C_{60}^{n-} ions in $\text{Li}_2\text{A}'\text{C}_{60}$, found experimentally as ~ 2.5 by Raman measurements.⁵ In an attempt to overcome the Li^+-C interactions and achieve half filling ($n = 3$) of the t_{1u} band, we synthesized the $\text{Li}_x\text{CsC}_{60}$ ($x = 1.5-6$) fullerides.⁵ By adjusting x , we can control the electron transfer from Li to C_{60} and tune the filling level of the conduction band continuously. Half filling is achieved for $\text{Li}_3\text{CsC}_{60}$ which is a bulk superconductor with $T_c = 10.5$ K.⁵ In this paper, we discuss the structural properties of the $\text{Li}_3\text{CsC}_{60}$ superconductor. At low temperatures, it is primitive cubic (space group $Pa\bar{3}$), isostructural with the metastable $\text{Na}_2\text{A}'\text{C}_{60}$ phases⁶ with orientationally ordered C_{60}^{3-} ions in the unit cell. The tetrahedral and octahedral interstices are occupied by Li and Cs, respectively, while the excess Li (one per C_{60} unit) is disordered at the corners of a cube with an edge length of ~ 3.4 Å, centered at the octahedral sites. On heating to room temperature, a phase transition occurs to a face centered cubic structure (space group $Fm\bar{3}m$) which contains orientationally disordered C_{60}^{3-} ions. These results provide clear evidence of the importance of the Li^+-C interactions in sensitively controlling the structural, conducting and electronic properties of the family of lithium intercalated fullerides.

The synchrotron X-ray powder diffraction profile (Figure 1a) of $\text{Li}_3\text{CsC}_{60}$ ⁷ at 295 K shows no reflections present which violate

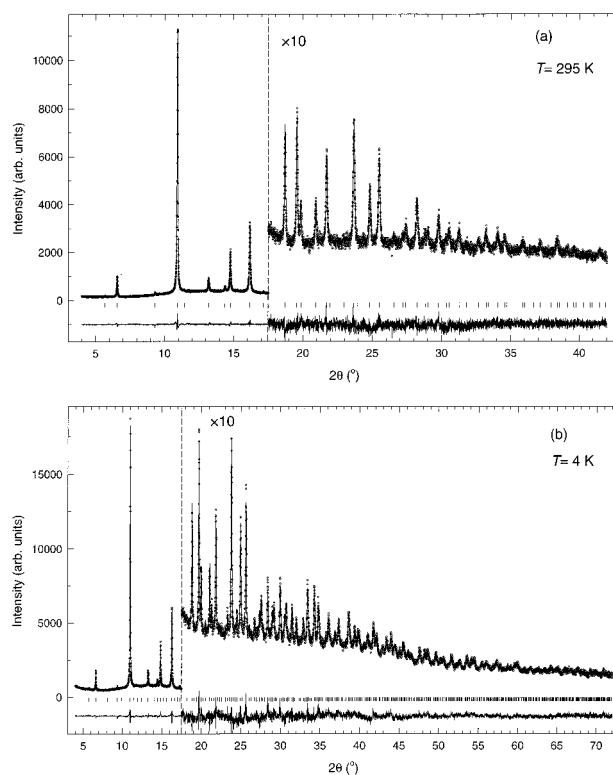


Figure 1. Final observed (○) and calculated (—) synchrotron X-ray diffraction profiles for $\text{Li}_3\text{CsC}_{60}$ at (a) 295 and (b) 4 K. In each case, the lower solid line shows the difference profile and the tick marks show the reflection positions. The profiles have been expanded for clarity by a factor of 10 at Bragg angles larger than 17.5° .

fcc rules. Rietveld profile refinements were initiated using the structural model of $\text{Li}_2\text{CsC}_{60}$ (space group $Fm\bar{3}m$).^{4,9} The fullerene units were modeled as quasi-spherical orientationally disordered units of radius, R , placed at the $4a$ (0,0,0) sites, and their scattering density was described in terms of symmetry-adapted spherical-harmonic (SASH) functions.^{4,9,10} Refinements proceeded smoothly with the Li^+ and Cs^+ ions placed in the $8c$ ($1/4, 1/4, 1/4$) and $4b$ ($1/2, 1/2, 1/2$) sites of the unit cell, respectively, resulting in a lattice constant, $a = 14.1089(4)$ Å. The radius, R of the spherical shell is $3.560(2)$ Å, and the fitted coefficients of the SASH functions are $C_{6,1} = 0.024(4)$ and $C_{10,1} = -0.12(1)$. These imply an orientational distribution function for $\text{Li}_3\text{CsC}_{60}$, comparable to that for $\text{Li}_2\text{CsC}_{60}$ with an accumulation of electronic density along the cubic $\langle 111 \rangle$ direction, but with a considerably weakened Li^+-C interaction. Refinement of the Li^+ occupation number of the tetrahedral sites necessitated a value, n_{Li} , substantially larger

[†] University of Sussex.

[‡] European Synchrotron Radiation Facility.

[§] NEC Fundamental Research Laboratories.

^{||} Osaka City University.

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(7) The $\text{Li}_3\text{CsC}_{60}$ sample (600 mg) used in the present work was prepared by reaction of stoichiometric quantities of C_{60} , Li, and Cs contained in a tantalum cell inside a sealed glass tube at 703 K for 2 days; after an intermediate regrinding, the sample was annealed at 703 K for more than 2 months, employing the same experimental setup. Phase purity was confirmed by X-ray diffraction using a Siemens D5000 diffractometer. High-resolution synchrotron X-ray diffraction data on the sample (4 mg) sealed in a 0.5-mm glass capillary were collected on the BM16 beamline at the European Synchrotron Radiation Facility (ESRF), Grenoble, France at 4 and 295 K ($\lambda = 0.81073$ Å) and at 150 K ($\lambda = 0.83502$ Å). Data were rebinned in the 2θ ranges $4-72^\circ$ to a step of 0.01° (4 K), $4-55^\circ$ to a step of 0.01° (150 K) and $4-42^\circ$ to a step of 0.005° (295 K). Data analysis was performed with the PROFIL suite of powder diffraction programs,⁸ incorporating form factors for spherically disordered molecules.

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than that required for full occupancy, consistent with the expected stoichiometry of the material. A search for the location of the excess intercalated Li^+ proved a formidable task, given the weak X-ray scattering power of this light element. A difference Fourier analysis of the diffraction data revealed the existence of scattered intensity in the vicinity of the $32f$ ($0.375, 0.375, 0.375$) sites of the unit cell that define a cube, centered at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ position. Thus the Rietveld refinements were repeated after introducing a Li^+ ion in the $(0.375, 0.375, 0.375)$ sites and allowing for its occupation number to vary. This converged to 1.00(1) per C_{60} , implying that the Li^+ defect is disordered over the corners of a cube of size 3.527 \AA with an $\sim 1/8$ occupancy. The refinement results at 295 K are shown in Figure 1a (agreement factors, $R_{\text{wp}} = 7.8\%$, $R_{\text{exp}} = 5.2\%$).

However, in contrast to the situation encountered for $\text{Li}_2\text{CsC}_{60}$, which showed no structural phase transitions to liquid helium temperatures,^{4,9} the diffraction profiles of $\text{Li}_3\text{CsC}_{60}$ measured at 150 and 4 K readily revealed the presence of a number of reflections which index to primitive cubic symmetry (lattice constants: $a = 14.0545(7) \text{ \AA}$ at 150 K, $a = 14.0261(3) \text{ \AA}$ at 4 K; space group $Pa\bar{3}$). Rietveld refinements of the diffraction data were performed with orientationally ordered C_{60}^{3-} units in analogy with the structural model developed for $\text{Na}_2\text{CsC}_{60}$.⁶ The C_{60}^{3-} ions with an average C–C bond length of $\sim 1.43 \text{ \AA}$ were rotated anticlockwise about the $[111]$ direction by either 98° or 38° , and the Li^+ and Cs^+ ions were originally placed at the unit cell positions identified by the data analysis at 295 K. While the Cs^+ ions are kept at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ position, the $Pa\bar{3}$ space group allows the displacement of the Li^+ ions (local symmetry C_3) from the ideal tetrahedral positions along the $[111]$ cube diagonals. At the same time, the reduction in symmetry necessitates the splitting of the Li^+ defect at $(0.375, 0.375, 0.375)$ into two symmetry-inequivalent positions, those at (x, x, x) ; $x \approx 0.375$ and (x, y, z) ; $x \approx y$, $x \approx z + \frac{1}{2}$, $z \approx 0.375$. Stable Rietveld refinements of both datasets were achieved with this structural model with the results shown in Figure 1b (150 K: $R_{\text{wp}} = 11.7\%$, $R_{\text{exp}} = 8.4\%$; 4 K: $R_{\text{wp}} = 10.7\%$, $R_{\text{exp}} = 6.7\%$). The fraction of the C_{60}^{3-} ions at 98° converged to 86(2) and 82(1)% at 150 and 4 K, respectively, comparable to the values of 88(1)% in $\text{Na}_2\text{CsC}_{60}$ ⁶ and 84(1)% in CsC_{60} .¹¹ The geometry of the Li^+ defect whose position and occupation number were allowed to vary¹² is also defined well at low temperatures. Its positional parameter converged to $x = 0.381(9)$ at 150 K and $0.378(5)$ at 4 K and its occupancy to 0.97(2) per C_{60} at 150 K and 0.99(1) per C_{60} at 4 K, implying disorder over the corners of a cube with edge size $3.35(19) \text{ \AA}$ at 150 K and $3.41(9) \text{ \AA}$ at 4 K and an $\sim 1/8$ occupancy. The positional parameters of the Li^+ ions in the tetrahedral interstices, (x, x, x) , $x \approx \frac{1}{4}$ were also varied, converging to $x = 0.244(3)$ at 150 K and $0.243(2)$ at 4 K. The projection of the primitive cubic structure of $\text{Li}_3\text{CsC}_{60}$ on the basal plane of the unit cell is shown in Figure 2a.

Figure 2b shows an expanded view of the alkali metal coordination along the $[111]$ cube diagonal. While the tetrahedral and octahedral interstices are fully occupied by Li^+ and Cs^+ ions, respectively, the excess Li^+ is disordered over the corners of a cubic $(\text{Li}_{1/8})_8$ cluster. Such metal clusters, incorporated into fullerene structures, have been encountered before¹³ in the sodium fullerenes Na_6C_{60} and $\text{Na}_{11}\text{C}_{60}$. The small size of Li^+ ($r_{\text{Li}} = 0.60 \text{ \AA}$) is of paramount importance in minimizing steric crowding

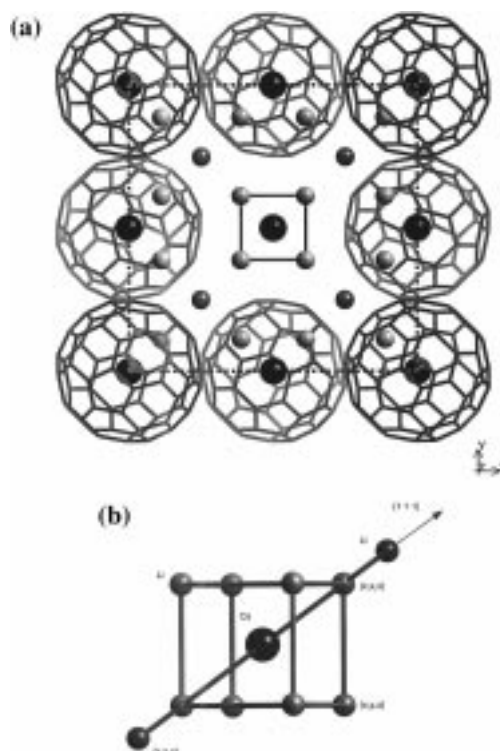


Figure 2. (a) Unit-cell basal plane projection of the primitive cubic $\text{Li}_3\text{CsC}_{60}$ structure at low temperatures. The C_{60} units at the center of the (110) face have been removed for clarity. (b) Schematic diagram of the alkali metal coordination in $\text{Li}_3\text{CsC}_{60}$ along one of the body diagonals. The Cs^+ and Li^+ ions are depicted as large dark and small light spheres, respectively. The defect Li^+ ions are shaded to a lighter tone than the tetrahedral ones.

and thus allowing the incorporation of excess Li in the space surrounding the octahedral interstice. The closest distances at 4 K between the Li^+ defects and the Li^+ ions in the tetrahedral interstices vary between $3.07(6)$ and $3.28(6) \text{ \AA}$, while those between the Li^+ defects and Cs^+ ($r_{\text{Cs}} = 1.69 \text{ \AA}$) are $2.95(6) \text{ \AA}$. In both cases, no unfavorable steric influence is evident. Moreover, the edge size of the $(\text{Li}_{1/8})_8$ cluster is $\sim 3.40 \text{ \AA}$, larger than the Li–Li distance of 3.04 \AA in Li metal. Finally, examination of all Li^+ – C_{60} contacts reveals shortest distances of $\sim 2.7 \text{ \AA}$ for the Li^+ in the tetrahedral site and $\sim 2.5 \text{ \AA}$ for the Li^+ defect. These are comparable to those in sodium fullerenes⁶ and larger than the sum of the ionic radius of Li^+ and the van der Waals radius of C.

In conclusion, we have shown that superconducting $\text{Li}_3\text{CsC}_{60}$ ($T_c = 10.5 \text{ K}$) adopts a primitive cubic structure in which the C_{60} units are orientationally ordered. While the tetrahedral and octahedral interstices are fully occupied, the excess Li (one per C_{60} unit) is disordered over the corners of a cube of size $\sim 3.4 \text{ \AA}$, centered at the octahedral Cs^+ site. No anomalous close contacts between either the alkali metal ions or between Li^+ and the C_{60} units are encountered. The observed geometry of the Li defect is consistent with the existence of additional overdoped $\text{Li}_x\text{CsC}_{60}$ phases⁵ with x between 4 and 6. On heating to room temperature, a phase transition to fcc , with orientationally disordered C_{60}^{3-} ions occurs. The geometry of the Li^+ defect is unaffected by this phase change.

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