Molecular Structure, Orientational Order, and Jahn−Teller Distortion of the $C_{60}{}^{4-}$ Anion in Cs_4C_{60}

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The molecular structure of the $C_{60}{}^{4-}$ anion in orientationally ordered orthorhombic Cs_4C_{60} is refined from powder neutron diffraction data at 5 and 293 K. The anion is observed to be more strongly distorted from spherical symmetry than the 3^-, 5^-, and 6^- anions previously studied in extended close-packed fulleride arrays. The orthorhombic orientationally ordered structure becomes orientationally disordered at 623 K due to jump interconversion of the $C_{60}{}^{4-}$ anions between two *mmm* symmetry anion orientations. This order−disorder transition is driven by the removal of the steric constraint which the large cesium cations exert on fulleride orientation through thermal expansion of the cation−anion distance and demonstrates that it is possible to avoid the quenched orientational disorder which characterizes the fulleride anion orientations in the A_3C_{60} cubic superconductors.

Introduction

The electronic properties of A_xC_{60} fulleride salts are strongly controlled by the electron count on the $C_{60}{}^{n-}$ anion,[1] with superconductivity being restricted to a narrow charge region around 3^-. As the C_{60} t_{1u} LUMO is triply degenerate, the changing occupancy of this orbital will render the anion unstable in principle with respect to Jahn−Teller distortions;[2] these have been observed in isolated fulleride salts, where the large interanion distances result in the C_{60} units being electronically insulated from each other. An example of this is the non-Hund's rule ground state of the $C_{60}{}^{3-}$ anion in $[PPN]_3C_{60}$ (PPN = bis(triphenylphospine) iminium).[3] In close-packed fullerides, where interanion separations of the order of 10 Å produce significant frontier orbital overlap, intermolecular interactions delocalizing the t_{1u} electrons into itinerant band states will compete with distortions driven by localized electrons. The 1^-,2^-,3^-, and 5^- anion charges have all been reported as generating metallic behavior[4,5] when the fulleride anions are close packed, whereas there are no reports of metallic behavior in A_4C_{60} phases adopting the body-centered tetragonal[6] structure. This structure is based on a body-centered packing of the fulleride anions, and the tetragonal distortion is driven by the ordering of cation vacancies introduced into the bcc A_6C_{60} structure.[7] The relative importance of both inter- and intramolecular interactions competing with band structure effects in stabilizing the insulating ground states observed in the A_4C_{60} phases is an unresolved issue. Band structure calculations which allow for the tetragonal crystal field arising from the $C_{60}{}^{4-}$ anion packing (without allowing for distortions of the anions themselves) predict metallic behavior,[8] although the possibility of metal−insulator transitions arising from the nested Fermi surface was noted. Magnetic[9] and EELS[10] measurements indicate that the materials are insulators. The charge gap has been attributed to both Jahn−Teller (single ion)[11] and Mott−Hubbard[10] instabilities. The former relies upon on-ball electron−phonon coupling to lift the degeneracy of the t_{1u} orbitals and produce a closed-shell configuration, while the latter uses the large on-site repulsion U (≈1 eV) to overcome the ≈0.5 eV bandwidth W and localize the t_{1u} electrons. Gaps can also be produced by the density waves familiar from low-dimensional organic conductors, and in such insulating ground states the t_{1u} electrons would remain predominantly itinerant and not exert a localized distorting influence on the $C_{60}{}^{4-}$ anions. To investigate the role of Jahn−Teller distortions, a detailed structure refinement of the orientationally ordered $C_{60}{}^{4-}$ phase Cs_4C_{60} from neutron powder diffraction data is presented here.

Anion orientational ordering, and particularly the relationship between the standard $m\bar{3}$ anion orientation (the highest subgroup of icosahedral $m\bar{5}m$ compatible with full translational symmetry) and possible 4-fold axes producing orientational disorder, plays a key role in fulleride structure−property relationships.[7] Superconducting K_3C_{60} adopts an $Fm\bar{3}m$ structure,[12] with 50% occupancy of two $m\bar{3}$ symmetry orientations, which is long-range disordered, though local orientational order-

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ing is predicted to be favored on energetic grounds, raising the question of why such disorder arises. The K_4C_{60} and Rb_4C_{60} phases both adopt similar orientational disorder with respect to the 4-fold axis along *c*, with 50% occupancy of two standard orientations. In contrast, Cs_4C_{60} at room temperature displays only one orientation of the anions,[13] ascribed to avoidance of overclose anion−cation contacts due to the large size of Cs^+. As an example of an orientationally ordered close-packed extended fulleride, Cs_4C_{60} presents an opportunity to investigate the factors affecting anion orientational order in fullerides. In this paper, we test the steric explanation for the anion orientational order using high-temperature X-ray diffraction, which shows a transition to a tetragonal structure in which two anion orientations are present. This is the first observation of an order−disorder transition between merohedrally related orientations of $C_{60}{}^{n-}$ anions and indicates that reorientational dynamics observed by ^{13}C MAS NMR[14] arise from jump interconversion between two discrete fulleride anion orientations, rather than rotational diffusion.

Experimental Section

The Cs_4C_{60} samples for neutron and X-ray powder diffraction were prepared by reaction between Cs and C_{60} in liquid ammonia. A portion of 366.5 mg of sublimed C_{60} (0.5086 mmol) was reacted with Cs metal (270.4 mg, 2.0345 mmol) in liquid ammonia at −78 °C for 90 min in an H-cell, followed by removal of the NH_3 under vacuum and heating of the solid at 120 °C under 10^{-5} Torr for 12 h. The product was sealed in a Pyrex tube under 10^{-5} Torr and heated to 350 °C for 5 days with two intermediate regrindings. All solid handling was performed in a helium-filled Mbraun Labmaster drybox. Neutron powder diffraction data were collected using the POLARIS diffractometer at the ISIS Spallation Neutron Source (Rutherford Appleton Laboratory, Didcot, U.K.) on a 0.5 g sample that was indium-sealed in a cylindrical vanadium can under helium, at room temperature and at 5 K in an Orange cryostat. The final structural model was derived from simultaneous refinement against all three detector banks of neutron data (35, 90, and 145° covering a range $0.5 \leq d/\text{Å} \leq 6.5$). X-ray powder diffraction data were collected at 623 K on station 9.1 of the Daresbury Synchrotron Radiation Source, with the sample sealed under helium in a 0.7 mm diameter quartz capillary tube. Rietveld refinement of the data was performed with the GSAS[15] suite of programs against the three banks of neutron data at room temperature and 5 K; correction was made for attenuation by the cryostat.

Results

The neutron powder diffraction data were refined in the *Immm* space group at both 5 and 293 K (systematic absences ruled out the alternative orientationally ordered configuration in which the anion at the body center is rotated by 90° with respect to that at the origin in space group $P4_2/mmc$). Refinements of the carbon positional parameters at both temperatures initially commenced with the C atoms strongly restrained to lie on the surface of a sphere of radius 3.550 ± 0.001 Å, with the 6:6 bonds (at the junction of the six-membered rings) and the 6:5 bonds (separating the five- and six-membered rings) restrained to be 1.40 ± 0.001 Å and 1.45 ± 0.001 Å, respectively. Refinement of the 5 K data smoothly converged to $\chi^2 = 2.63$, with an anion radius of 3.55(1) Å which, despite the heavy restraints, represents a greater extent of radial distortion than found in *unconstrained* refinements of other close-packed fullerides with anion charges of 3, 5, and 6.[16,17] The figure in brackets represents the standard deviation of observed radii from this mean rather than the mean of the absolute error on the refined radius, which is 0.002 Å. The mean 6:5 and 6:6 bond lengths at this stage are 1.45(1) and 1.404(6) Å, with the bracketed figure again representing the spread of refined bond lengths. Relaxation of the restraints led to a significant improvement in the fit quality ($\chi^2 = 2.05$) while the mean radius and 6:5 and 6:6 bond lengths became 3.55(2) Å, 1.45(2) Å, and 1.41(2) Å, respectively. Similar improvement in fit quality was observed for the 293 K data, and so at both temperatures the unconstrained refinements were adopted in the final modeling. As no improvement to the quality of fit resulted from a TL librational description of the thermal motion of the $C_{60}{}^{4-}$ anions, final refinement cycles employed a single isotropic temperature factor to describe the thermal motion of the anion, with separate isotropic parameters for each of the two crystallographically inequivalent cesium sites. Unconstrained refinement of all the carbon positions converged to yield chemically sensible bond lengths and angles. Refinement of cation site occupancies led to a composition of $Cs_{4.00(2)}C_{60}$, and so the occupancies were fixed at 1.00 in the final refinement cycles. No features in the final difference Fourier maps could be refined as atoms, and attempts to refine other anion orientations clearly indicated that the *mmm* orientation was the only one present. The final refinement at 293 K is shown in Figure 1, positional parameters at 293 K are given in Table 1, and the bond lengths in the $C_{60}{}^{4-}$ anion at 293 and 5 K are shown in Table 2 (bond angles are given in Table S1 and the 5 K fit is in Figure S2). An ORTEP representation of the refined structure is given in Figure 2.

Inspection of the diffraction pattern of Cs_4C_{60} at 623 K indicated that the higher symmetry tetragonal *I*4/*mmm* space group was adopted. Carbon positions were generated by appropriate scaling of the positions refined from neutron powder diffraction data at 293 K. Refinement of cell parameters, Cs positional, and Cs and C displacement parameters converged smoothly to $\chi^2 = 2.04$ based on the tetragonal K_4C_{60} model; in the *I*4/*mmm* space group symmetry, an alternative anion orientation in which the normals to the mirror planes cutting through the 6:6 bonds are aligned with the $\langle 110 \rangle$ rather than $\langle 100 \rangle$ directions, is allowed by symmetry. Competitive refinement indicates that there is no evidence for this orientation. The refined composition is $Cs_{3.98(2)}C_{60}$, and the structural model is similar to that derived for K_4C_{60} at ambient temperature.[18] The final refinement is shown in Figure 3.

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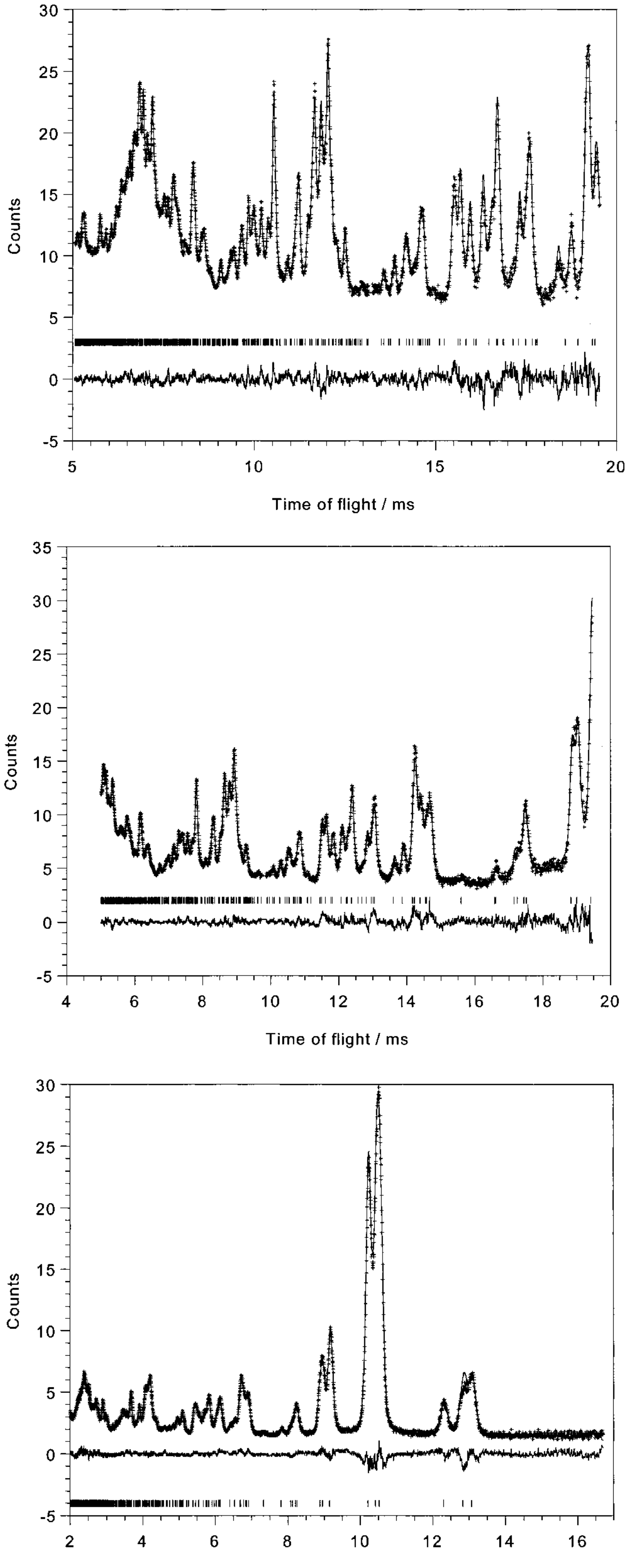

Figure 1. Rietveld refinement of powder neutron diffraction data from Cs_4C_{60} at 293 K for the (a) 145° ($0.8 \le d/\text{Å} \le 3.2$), (b) 90° ($1.1 \le d/\text{Å} \le 4.3$), and (c) 35° ($0.9 \le d/\text{Å} \le 8.0$) detector banks of the POLARIS diffractometer. The d-spacing range covered by each bank of detectors is given in brackets. The observed data are plotted as points, the calculated model is the solid line, and the difference plot is given below. Tick marks indicate the position of the Bragg peaks.

Table 1. Positional and Thermal Parameters for Cs_4C_{60} in Space Group *Immm* at 293 K Refined against Three Banks of Neutron Powder Diffraction Data[a]

name	x	y	z	100 U (Å^2)	site symmetry	multi-plicity
C(1)	0.2820(3)	0	0.0608(3)	0.66(2)	m(010)	8
C(2)	0.2499(3)	0.1006(2)	0.1243(2)	0.66(2)	1	16
C(3)	0.2126(2)	0.1936(2)	0.0624(2)	0.66(2)	1	16
C(4)	0.0562(3)	0.2921(3)	0	0.66(2)	m(001)	8
C(5)	0.1163(2)	0.2566(2)	0.1037(2)	0.66(2)	1	16
C(6)	0.0617(2)	0.2169(2)	0.2033(2)	0.66(2)	1	16
C(7)	0	0.0601(2)	0.3033(3)	0.66(2)	m(100)	8
C(8)	0.0957(2)	0.1212(2)	0.2652(2)	0.66(2)	1	16
C(9)	0.1919(2)	0.0587(2)	0.2260(2)	0.66(2)	1	16
Cs(10)	0.2403(5)	0.5	0	1.6(2)	$mm2$(100)	4
Cs(11)	0.5	0.2078(4)	0	1.0(1)	$mm2$(010)	4

[a] $a = 12.1519(4)$ Å, $b = 11.9255(4)$ Å, $c = 11.4298(4)$ Å, $V = 1656.39(10)$ Å^3. $\chi^2 = 2.45$ for 91 variables and 9627 observations. The agreement indices for the individual detector banks are as follows: 145° $R_{wp} = 1.98\%$, $R_{F^2} = 1.68\%$ for 1332 reflections; 90° $R_{wp} = 2.45\%$, $R_{F^2} = 1.32\%$ for 590 reflections; 35° $R_{wp} = 4.27\%$, $R_{F^2} = 4.67\%$ for 964 reflections (5 K: $a = 12.1195(4)$ Å, $b = 11.8677(4)$ Å, $c = 11.4314(3)$ Å, $V = 1644.17(9)$ Å^3. $\chi^2 = 2.05$; 145° $R_{wp} = 0.88\%$, $R_{F^2} = 2.67\%$; 90° $R_{wp} = 1.10\%$, $R_{F^2} = 0.97$; 35° $R_{wp} = 1.53\%$, $R_{F^2} = 3.82$).

Table 2. C−C Bond Lengths (Å) in Cs_4C_{60} at 293 and 5 K: (a) Hexagon−Hexagon 6:6 Junctions and (b) Hexagon−Pentagon 6:5 Junctions[a]

	293	5
	(a)	
C(1)−C(1) (x2)	1.389(7)	1.363(7)
C(2)−C(3) (x8)	1.392(3)	1.390(3)
C(4)−C(4) (x2)	1.365(8)	1.387(7)
C(5)−C(6) (x8)	1.401(3)	1.393(3)
C(7)−C(7) (x2)	1.433(6)	1.398(6)
C(8)−C(9) (x8)	1.457(3)	1.457(3)
mean	1.41(2)	1.41(3)
	(b)	
C(1)−C(2) (x8)	1.455(2)	1.471(2)
C(2)−C(9) (x8)	1.448(3)	1.437(3)
C(3)−C(3) (x4)	1.428(4)	1.416(4)
C(3)−C(5) (x8)	1.468(3)	1.486(3)
C(4)−C(5) (x8)	1.455(3)	1.478(3)
C(6)−C(6) (x4)	1.499(4)	1.492(4)
C(6)−C(8) (x8)	1.405(3)	1.435(3)
C(7)−C(8) (x8)	1.440(2)	1.449(3)
C(9)−C(9) (x4)	1.402(4)	1.425(3)
mean	1.44(3)	1.45(2)

Discussion

The outcome of the neutron diffraction experiments is a precise determination of the structure of the $C_{60}{}^{4-}$ anion. The t_{1u} LUMO has nodal character which renders it antibonding and bonding for the 6:6 and 6:5 bonds, respectively, and thus loss of distinction between these two sets of bonds on reduction is expected. The mean 6:6 and 6:5 bond distances show a larger second moment than in the $m\bar{3}$ local symmetry $C_{60}{}^{3-}$ and $C_{60}{}^{6-}$ anions[19] (consistent both with the lower point symmetry and the possibility of enhanced Jahn−Teller distortion) but are consistent with bond lengthening over those found in the $C_{60}{}^{3-}$ anion, without the reversal of 6:6 and 6:5 mean distances found for the 6^- anion. The distinction between single and double bonds found in C_{60} itself is thus lost only at the 6^- charge when the 6:6 antibonding t_{1u} orbital is completely full.

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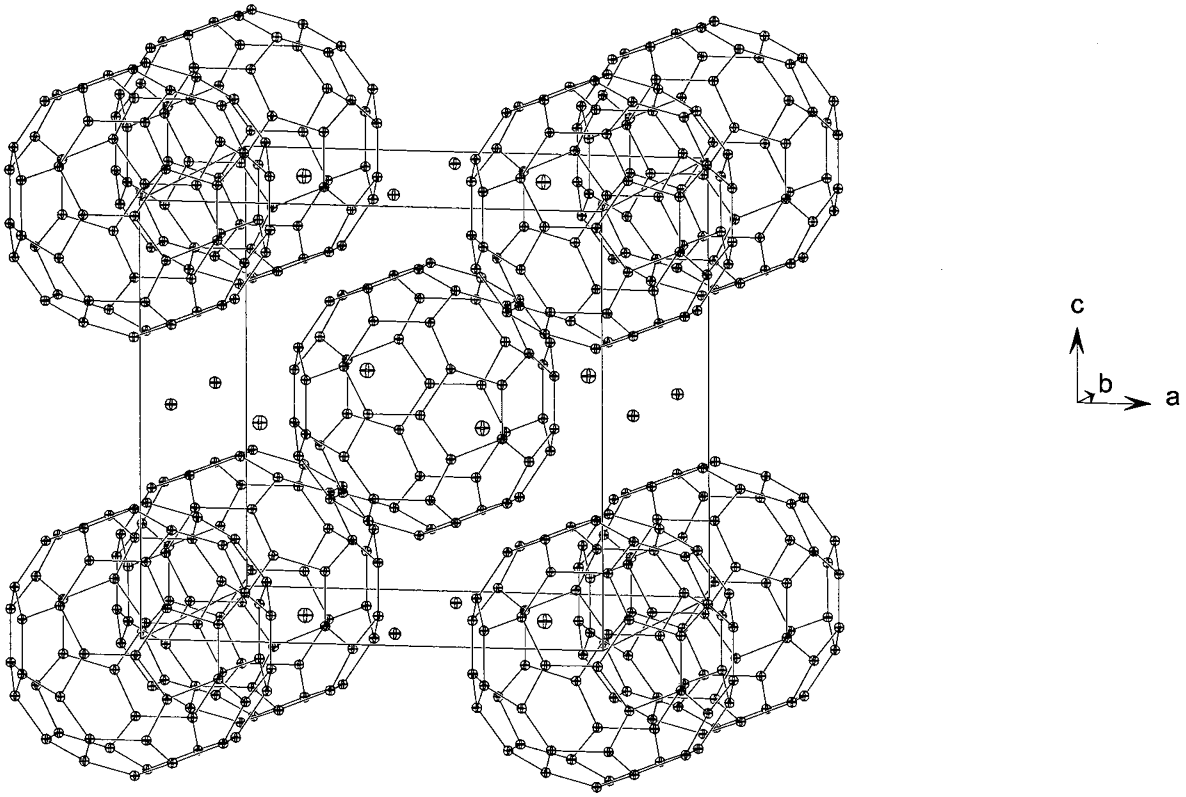

Figure 2. ORTEP thermal ellipsoid representation of the structure of Cs_4C_{60} at 5 K. Ellipsoids are represented at 50% probability.

Comparison with electronically extended fulleride structures containing the $C_{60}{}^{3-}$ (r = 3.554(6) Å) and $C_{60}{}^{6-}$ (r = 3.561(9) Å) anions indicates that the $C_{60}{}^{4-}$ anion is less spherical (r = 3.55(2) Å) with C1 displaced by 0.05 Å from the mean radius (10 times the standard deviation of its radius and five times the displacement of any C from the mean sphere radius in the $C_{60}{}^{3-}$ or $C_{60}{}^{6-}$ anions; this displacement is reduced to 0.02 Å in the most strongly restrained refinements, remaining larger than that found in the other extended fulleride structures). Figure 4a represents the distance of each C atom in the asymmetric unit from the center of the sphere, and Figure 4b shows that the largest distance from the origin is not found along the longest crystallographic axis, indicating that the relaxations seen are not simply a product of the orthorhombic crystal field in which the $C_{60}{}^{4-}$ anion resides.

It is important to note that, although bond lengths and extents of distortion change on cooling, the pattern of distortion, as defined by which C atoms are contracted or expanded with respect to the mean, remains the same at 293 and 5 K. The difference between the minimum and maximum diameters of the $C_{60}{}^{4-}$ anion is 0.152(6) Å at 293 K and 0.102(6) Å at 5 K, comparable with 0.086(10) Å and 0.098(10) Å in the Jahn–Teller distorted isolated anion $C_{60}{}^{2-}$ and $C_{60}{}^{1-}$ salts $[Ni(Cp^*)_2C_{60}]\cdot PhCN$[20] and $[PPN^+]_2C_{60}$,[21] and larger than 0.040(6) Å in K_6C_{60} (the largest distortion in the cubic symmetry of 3^-, 5^-, and 6^- salts in Figure 5). There are now sufficient data to compare the extent of distortion in $C_{60}{}^{3-}$, $C_{60}{}^{4-}$, $C_{60}{}^{5-}$, and $C_{60}{}^{6-}$ extended salts with the anions in contact (Figure 5), and the enhanced distortion in the $C_{60}{}^{4-}$ case is apparent. All the above evidence concerning anion regularity indicates that the $C_{60}{}^{4-}$ anion is the most distorted fulleride anion yet reported in a close-packed fulleride structure.

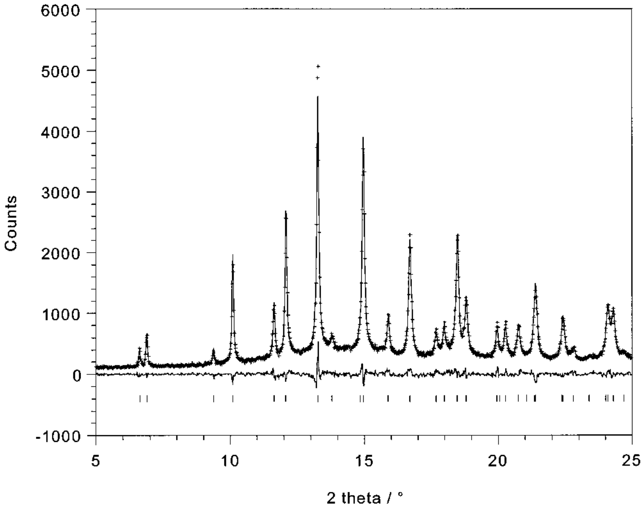

Figure 3. The X-ray diffraction pattern of Cs_4C_{60} at 623 K refined according to the $I4/mmm$ model described in the text. The Rietveld refinement is depicted as in Figure 1. λ = 0.99815 Å, R_{wp} = 6.27%, χ^2 = 2.05 for 28 variables and 999 observations, R_{F^2} = 1.57% for 39 reflections, a = 12.237(1) Å, c = 11.358(1) Å, and V = 1701.1(4) Å^3. Cs at 8j 0.2152(2), $^1/_2$, 0. The carbon positions were derived by appropriate scaling of those refined at 293 K and were not refined.

The insulating behavior of the A_4C_{60} phase has been attributed to Jahn–Teller distortion,[11] and the enhanced deviation from spherical symmetry found here is consistent with this idea. Loss of the degeneracy of

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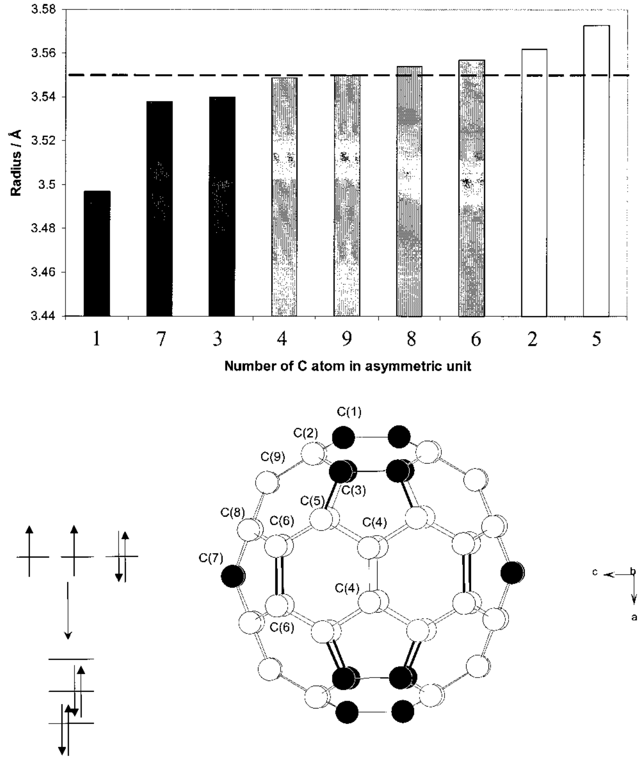

Figure 4. (a) Histogram representing the distance from the origin of the nine C atoms in the asymmetric unit of Cs_4C_{60} at 298 K. The dashed line represents the mean radius of 3.55 Å. (b) The C_{60}^{4-} anion in Cs_4C_{60}, with C atoms shaded according to their distance from the origin. The dark spheres are the C atoms that are more than three standard deviations closer to the origin than the mean radius while the light spheres are those that are more than three standard deviations farther from the origin than the mean radius. The observed distortion will lift the degeneracy of the t_{1u} orbitals and is consistent with a singlet ground state as indicated.

the t_{1u} LUMO could produce two filled and one empty LUMO-derived band. The alternative interpretation of the observed insulating behavior is that these phases are Mott–Hubbard insulators.[10] This was supported by the interfulleride distance dependence of the charge gap monitored by EELS across the A_4C_{60} series.[10] However, the singlet ground state observed in magnetic studies[11] can be understood only energetically if favored over higher spin states by a local Jahn–Teller distortion, lifting the t_{1u} orbital degeneracy (Figure 4b).

The influence of cooperative interactions in competing with distortions driven by single atom or single-molecule instabilities such as the Jahn–Teller effect is an important contributor to many cooperative phenomena in condensed matter; as an example, the suppression of Jahn–Teller distortion by the electronic bandwidth produced by interatomic wave function overlap in mixed valence $Mn^{III/IV}$ oxides is a key contributor to the colossal magnetoresistance effect. In the present case, the fulleride anions are in electronic contact in the C_{60}^{3-}, C_{60}^{4-}, C_{60}^{5-}, and C_{60}^{6-} salts considered here. As the C_{60}^{6-} anion is a closed-shell species, it is not unstable to a Jahn–Teller distortion. If the t_{1u} electrons in the frontier orbitals of the open-shell fulleride anions were to be completely delocalized, then only very small local single-molecule distortions would be expected. Electron delocalization in fullerides is critically dependent on the

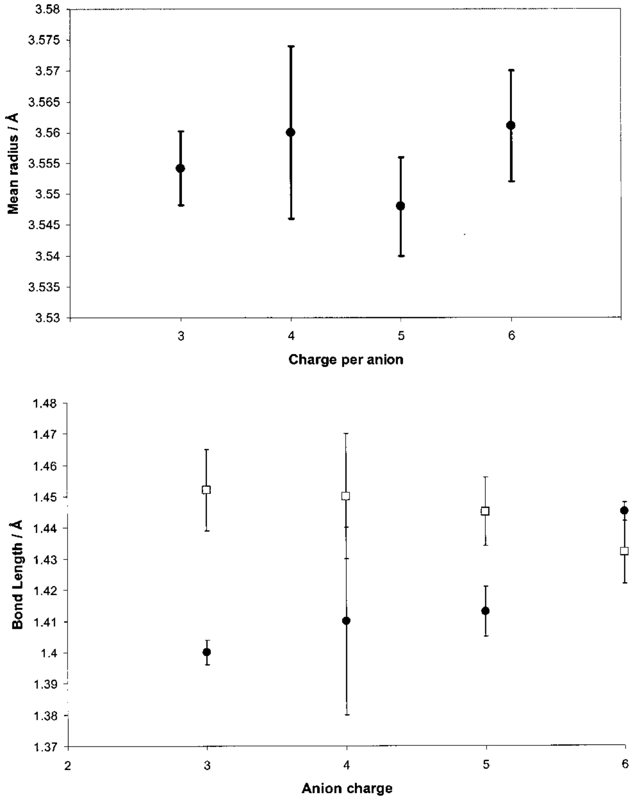

Figure 5. (a) Evolution of C_{60}^{n-} anion radius and mean deviation from it with anion charge n. The following compounds are the source of the data shown here: $n = 3$ (K_3C_{60}[19]), $n = 4$ (Cs_4C_{60}, present work), $n = 5$ (Ba_2CsC_{60}),[28] and $n = 6$ (K_6C_{60}).[19] (b) Variation with anion charge of the 6:6 (filled circles) and 6:5 (open squares) bond lengths on the C_{60}^{n-} anions. The error bars represent the standard deviation of bond lengths from the mean value, not the mean error.

competition between the t_{1u} bandwidth, favoring delocalization, and the on-site interelectron repulsion which localizes the electrons by the Mott–Hubbard mechanism. Although simple estimates of U and W indicate that K_3C_{60} should be a Mott–Hubbard insulator in the conventional singly degenerate orbital case,[22] the t_{1u} frontier orbital degeneracy favors the metallic state, reconciling theory with experiment.[23] Ba_2CsC_{60} is also metallic, and so the 3^-, 5^-, and 6^- examples are not expected to be subject to the Jahn–Teller distortion.

The C_{60}^{4-} A_4C_{60} phases, however, do appear to be Mott–Hubbard insulators with localized $(t_{1u})^4$ configurations despite the similar interanion contacts to the extended fullerides described above. Magnetic measurements indicate a singlet ground state in close-packed Rb_4C_{60}.[11] The present structural observations are consistent with a localized electron C_{60}^{4-} anion subject to a Jahn–Teller distortion which lifts the degeneracy of the t_{1u} orbitals and produces a singlet ground state. The local mmm point symmetry of the C_{60}^{4-} anion is sufficient to completely lift the degeneracy of the t_{1u} orbitals (Figure 4b). The rearrangement in relative bond lengths on cooling apparent from Table 2 is consistent with a change in the nature of the thermally populated elec-

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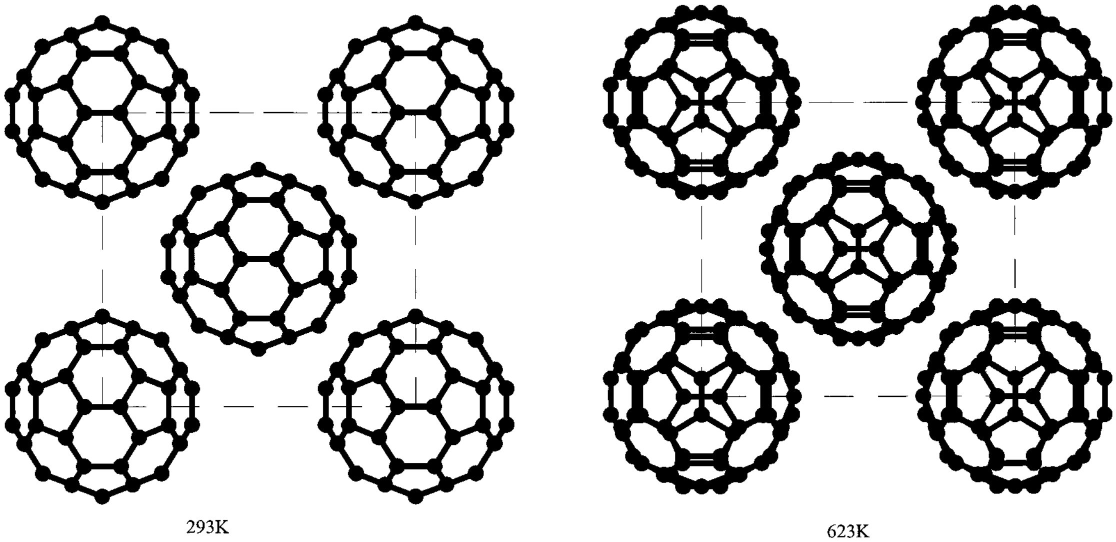

Figure 6. Transition from the orientationally ordered *Immm* structure of Cs_4C_{60} at 293 K to the orientationally disordered structure at 623 K is due to the presence of two equivalent anion orientations related by 90° rotation about the *c*-axis (the viewing direction) at high temperature.

tronic states on cooling, as found for the electronically isolated C_{60}^{4-} anion in $[Na(crypt)^+]_4$ C_{60} (crypt = cryptand 222),[24] which has equienergetic singlet and triplet states according to the ^{13}C NMR shift in solution, with EPR silence at 4 K indicating that the singlet is favored on cooling.

Although the *mmm* point symmetry itself in principle is sufficient to give a filled band C_{60}^{4-} insulator, estimates of Jahn−Teller distortion energies in fullerides suggest that they alone are insufficient (0.2−0.3 eV at most)[2] to overcome the t_{1u} bandwidth in a close-packed (rather than isolated anion) fulleride and produce insulating behavior. Considering the relative sizes of the interelectron repulsion (U) and Jahn−Teller (E_{JT}) energies opposing the metallic state favored by W, the insulating behavior and anion geometry in Cs_4C_{60} can be accounted for by localization of the $(t_{1u})^4$ configuration via the interelectron repulsion followed by local Jahn−Teller distortion at each C_{60}^{4-} anion. This model accounts for the enhanced distortions found for this 4^- anion over the C_{60}^{3-} and C_{60}^{5-} anions in metallic K_3C_{60} and Ba_2CsC_{60}.[17] The loss of the t_{1u} orbital degeneracy will restore the localized ground state expected in single-orbital treatments of the Mott−Hubbard model with values of U and W appropriate to the fullerides. Although the structural data cannot indicate whether the Jahn−Teller distortion provokes the Mott−Hubbard localization or vice versa, they do indicate that such a distortion is present.

The high-temperature form of Cs_4C_{60} is isostructural with the tetragonal K_4C_{60} and Rb_4C_{60} phases, which adopt the *I*4/*mmm* space group at all temperatures.[18] As the C_{60} molecule does not have a 4-fold axis, the space group at 623 K implies orientational disorder of the anion. The transition from the low-temperature *Immm* polymorph to the high-temperature *I*4/*mmm* tetragonal structure of Cs_4C_{60} results in the retention of the same anion orientation, with the mirror plane normals lying along the ⟨100⟩ directions, but now two such orientations related by 90° rotation about *c* are present. (Figure 6) The presence of other anion orientations in the high-temperature form is ruled out by competitive refinement of the symmetry allowed ⟨110⟩ orientation. More extensive quasi-spherical orientational disorder corresponding to rotational diffusion of the anion can be ruled out by noting that there would be over-short 3.11 Å Cs···C contacts to a spherically disordered C_{60}^{4-} anion. It is precisely to avoid Cs···C contacts of this size that Cs_4C_{60} adopts the orientationally ordered *Immm* structure at room temperature.

The orientational ordering in the *Immm* phase at 293 K was previously attributed to optimizing the Cs···C contacts in the cation vacancy-ordered structure, with the C_{60}^{4-} anions coordinating to the Cs^+ cations via five rings being at least 6.66 Å away from the cation to avoid unfavorable steric crowding.[13] Although the powder X-ray data clearly do not permit refinement of the C positions, the Cs···C_{60} separations in the high-temperature disordered *I*4/*mmm* structure are consistent with this idea; the *closest* cation−anion center approach is now 6.66 Å, allowing a given cation to be coordinated either by a hexagon or a pentagon from *any* of its four pseudo-tetrahedrally arranged C_{60}^{4-} neighbors without unfavorable Cs···C contacts arising. This permits dynamical jump reorientation of the C_{60}^{4-} anions between the two symmetry equivalent ⟨100⟩ orientations, consistent with the observation of a single ^{13}C MAS NMR resonance at high temperature.[14] The orientationally ordered and disordered phases are separated by a critical value of the closest cation−anion center distance minus the cation ionic radius, which lies between 4.51 and 4.60 Å; in orientationally disordered Rb_4C_{60} at 298 K, this parameter is 4.60 Å, compared with 4.51 and 4.64 Å in the orientationally ordered and disordered phases of Cs_4C_{60}. It is interesting to note that the *c*-axis expands only on heating in the orientationally disordered *I*4/*mmm* phase, being unchanged between 5 and 293K in the orientationally ordered *Immm* phase. Ba_4C_{60}, which adopts the *Immm* structure, also displays reduced expansivity along this direction.

The A_4C_{60} phases thus differ significantly from the metallic A_3C_{60} superconductors in the orientational

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behavior of the fulleride anions, as the merohedral disorder can be removed on cooling. In the fcc A_3C_{60} phases, the C_{60}^{3-} anions adopt two $m\bar{3}$ symmetry orientations related by 90° rotation about the ⟨001⟩ directions with equal probability in a manner that is long-range disordered at all temperatures measured thus far.[12,25] The absence of an orientational ordering transition on cooling (to $Fm\bar{3}$ if all anions adopt the same orientation or to $P4_2/mnm$ if both orientations are adopted; this latter arrangement is predicted to be favored by enhanced intermolecular t_{1u} hopping[26]) has been ascribed to kinetic effects on cooling. The energy difference between the possible pairs of near-neighbor orientations is lower than the energy barrier for interconversion between the two standard orientations, resulting in the putative mean-field ordering temperature being much less than the temperature at which interconversion between the two orientations becomes negligible, resulting in quenched orientational disorder.[27]

In the present A_4C_{60} case, orientational order of the anions requires a lowering of symmetry from tetragonal to orthorhombic, as the anion has no 4-fold axis. A critical cation−anion separation is required to allow orientational disorder in the A_4C_{60} structure because here both a six-ring and five-ring from a C_{60}^{4-} anion coordinate to the A cation at *the same* $A\cdots C_{60}$ distance. In the A_3C_{60} structure, the two disordered orientations are related by a 44° rotation about the centroid of the hexagons coordinating the cations, and thus the cation−anion distances are independent of whether the standard orientations are occupied in an ordered or disordered manner. When the A^+ cation in the A_4C_{60} structure is sufficiently large relative to its site size, the unfavorable effect of disorder on cation−anion contacts drives the transition from orientationally disordered $I4/mmm$ at high temperature to orientationally ordered $Immm$ at low temperature. The high-temperature orientational disorder is no longer quenched on cooling as the energy difference between the two standard orientations is considerable, since the coordination via a five-ring at a cation−anion separation appropriate for six-ring coordination results in over-short carbon−cesium distances.

The presence of both anion orientations at high temperature gives rise to dynamic disorder by 90° jump reorientation about the [001] direction (only a single ^{13}C MAS NMR resonance is seen above 350 K[14]). This disorder is not frozen on cooling as the reorientation rate is sufficiently rapid to allow only the favorable orientation to be adopted when the cation−anion separation becomes appropriate to the orientationally ordered phase. This indicates that the fulleride structures in which both five- and six-membered rings coordinate to a metal cation have quite different anion orientation statics and dynamics compared with those where only one type of ring is involved in coordination.

Conclusions

The molecular structure of the Cs_4C_{60} anion, in terms of the regularity of the surface described by the symmetry-independent C atoms and the distribution of the C−C bond lengths, is consistent with a Jahn−Teller distortion of the localized $(t_{1u})^4$ configuration, in contrast to metallic C_{60}^{3-} and C_{60}^{5-} and closed-shell C_{60}^{6-} salts which also have the anions in electronic contact. This is consistent with the Mott−Hubbard model for the insulating behavior of the phase, in which the t_{1u} electrons, localized by interelectron repulsion, produce a local anion distortion that results in a singlet ground state due to the loss of t_{1u} orbital degeneracy. The observation that the C_{60}^{4-} phases are Mott−Hubbard insulators suggests that the A_3C superconductors are closely related to highly correlated systems, in a manner similar to the high-T_c copper oxides, and are only prevented from electron localization by the t_{1u} orbital degeneracy which is lost in the lower symmetry orientationally ordered structures found here.

The key role of cation−anion contacts in stabilizing the orientationally ordered $Immm$ structure is demonstrated by the onset of merohedral orientational disorder when the cation−anion distances increase thermally to allow pentagon−Cs contacts at cation−anion distances where hexagon−Cs contacts are also found. This is a structural mechanism not open to the A_3C_{60} fullerides, as in both the observed disordered and putative ordered states the cation−anion contacts are the same, explaining the absence of orientationally ordered fcc A_3C_{60} phases. The cation coordination by both pentagons and hexagons in the A_4C_{60} structure removes the quenched disorder mechanism operative in the merohedrally disordered K_3C_{60} structure.

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Supporting Information Available: Figure showing Rietveld refinement of powder neutron diffraction data from Cs_4C_{60} at 5 K and table showing bond angles in the C_{60}^{4-} anion at 293 and 5 K (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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