Molecular Structure of the Fulleride Anions in Superconducting K_3C_{60} and Insulating K_6C_{60} Determined by Powder Neutron Diffraction

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The structures of K_3C_{60} and K_6C_{60} are refined by Rietveld analysis of high-resolution time-of-flight powder neutron diffraction data. Bond length and angle constraints are not necessary to produce chemically sensible molecular structures for the fulleride anions. The results suggest loss of the distinction between single and double bonds on the fullerene molecule on reduction and are consistent with recent ab initio calculations. A simple chemical interpretation of the observed trends is given.

Introduction

A detailed understanding of the electronic structure of the A_3C_{60} superconducting fullerides[1] requires knowledge of the molecular structures of the fulleride species, since the wavefunctions at the Fermi energy derive purely from overlap of the t_{1u} wave functions of the C_{60}^{3-} anions. The relatively weak intermolecular overlap results in narrow bands, and the Wannier functions occupied by the conduction electrons will closely resemble the t_{1u} molecular orbitals. The detailed composition of these orbitals (the phase and amplitude of p-orbital contributions on neighboring carbons in an LCAO picture) will strongly influence the changes in molecular geometry on reduction of the C_{60} molecules. The superconducting A_3C_{60} systems are synthesized by intercalation of alkali metal cations into the face-centered cubic (fcc) host structure of C_{60}, which is retained upon intercalation. Further reduction of the C_{60} molecule by potassium requires a change in packing motif of the C_{60} molecules from fcc to body-centered tetragonal (bct) in K_4C_{60}[2] and body-centered cubic (bcc) in K_6C_{60}.[3]

In the icosahedral (I_h or $m\bar{3}\bar{5}$ point symmetry) C_{60} molecule itself, there are two symmetry-inequivalent types of carbon–carbon bond. The shorter 6:6 bonds which connect the pentagonal rings are 1.40 Å long, while the 6:5 bonds (an edge of the truncated icosahedron shared by a hexagon and a pentagon) are 1.45 Å long, corresponding to increased double- and single-bond character, respectively. Up to this point, the details of changes in C_{60} geometry in the alkali metal fullerides with increasing reduction have been inaccessible, as the refinements of fulleride phases have necessarily been heavily constrained when variation of carbon positional parameters has been undertaken and thus prior assumptions as to relative C–C bond lengths have been imposed. Accurate bond-length information is particularly important to compare with the predictions of detailed Car–Parrinello molecular dynamics calculations for the geometries of the C_{60}^{3-} and C_{60}^{6-} anions.[4] Previous synchrotron X-ray studies of K_3C_{60}[5] and K_6C_{60}[3] did not allow definitive refinement of the carbon positional parameters, although equal bond lengths on the surface of the C_{60}^{6-} anion were favored in ref 3. A constrained refinement of the structure of Na_2CsC_{60} using powder neutron diffraction has recently been reported[6] and suggests an equalization of the lengths of the 6:5 and 6:6 bonds on reduction. In this paper, we present unconstrained refinements of the low-temperature crystal structures of K_3C_{60} and K_6C_{60} which reveal significant changes in the molecular shape as the occupancy of the t_{1u} molecular orbital is increased. In the continued absence of structurally characterized single crystals of the fullerides, powder neutron diffraction is the only means of obtaining this detailed information. The results are discussed in terms of a qualitative localized chemical model for the π electrons and compared with quantitative theoretical predictions.

Experimental Section

To produce samples of the highest quality for definitive diffraction studies, sublimed C_{60} was used in the preparation of the 0.5 g K_3C_{60} and K_6C_{60} samples used in this work. C_{60} was generated by spark erosion of graphite rods and separated from higher fullerenes by column chromatography on alumina in hexane. Sublimation was carried out at 550 °C in quartz

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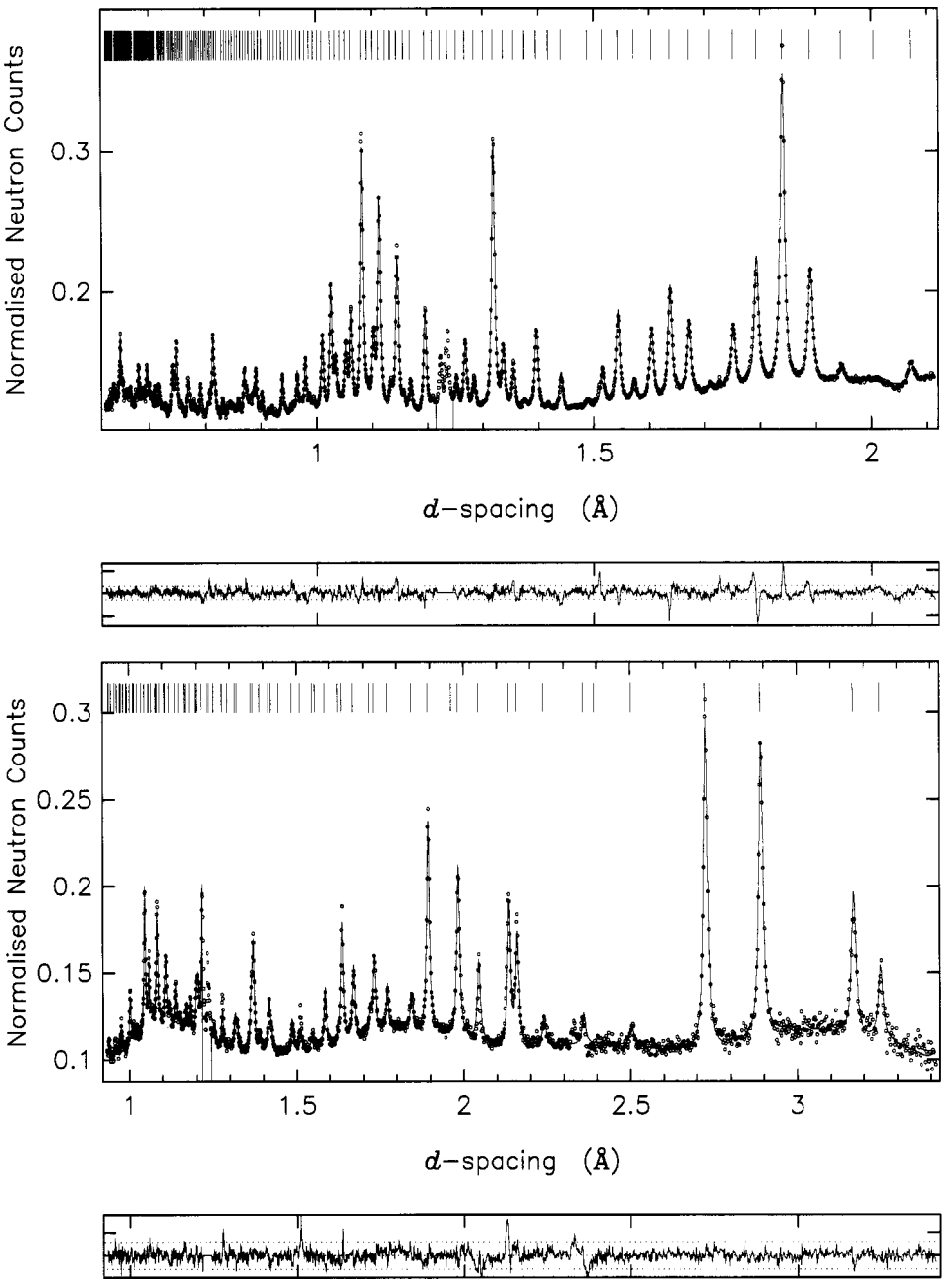

Figure 1. Rietveld refinement of time-of-flight neutron powder diffraction data for (a, top) K_6C_{60} at 5 K (b, bottom) K_3C_{60} at 1.5 K. The observed data are shown as points, the calculated model is a solid curve, and the difference divided by the estimated standard deviation of each data point is plotted at the bottom. The weak dashed lines on the difference plot represent a level of $\pm 3\sigma$. Weak vanadium reflections from the cryostat were excluded from the data sets during refinement.

tubes under a dynamic vacuum of 5×10^{-5} Torr for 12 h, with an 80% yield of C_{60} by mass. K_6C_{60} was prepared by reaction of C_{60} with excess potassium vapour for 4 days at 250 °C and 3 days at 350 °C and finally 14 days at 250 °C in a sealed Pyrex tube, with a gradient of 7 °C between the cooler potassium-containing end and the C_{60}. The progress of the reaction was monitored by ^{13}C magic angle spinning (MAS) NMR (Bruker MSL200 spectrometer) and powder X-ray diffraction (Siemens D5000 in transmission geometry with Cu $K\alpha_1$ radiation produced by a germanium incident beam monochromator and a linear position sensitive detector). The final sample had an X-ray pattern in agreement with that of Zhou et al.[3] and ^{13}C MAS NMR in accord with ref 7. K_3C_{60} was prepared according to the two-step procedure of ref 8, using sublimed C_{60} in the preparation of K_6C_{60} as outlined above followed by dilution with further sublimed C_{60} to prepare K_3C_{60}. Reaction between K_6C_{60} and C_{60} was carried out at 250 °C for 2 days then at 350 °C for 4 days in a sealed Pyrex tube, followed by regrinding, resealing, and repeating the heating cycle. The progress of the reaction was monitored by ^{13}C MAS NMR which allowed the composition of the reaction mixture to be derived by integration of the fully relaxed signals due to the $x = 3$, $x = 4$, and $x = 6$ K_xC_{60} phases. Additional C_{60} or K_6C_{60} was then added and the reaction mixture reground, resealed, and annealed until both X-ray powder diffraction and NMR indicate that a phase-pure K_3C_{60} product has been produced. This required an additional three weeks heating at 350 °C. All air-sensitive fullerides and starting materials were handled in a helium filled Mbraun Labmaster 130 drybox

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Table 1. Refined Atomic Parameters from K_6C_{60} at 5 K (Space Group $Im\bar{3}$)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
K	0	0.5	0.2815(4)	2.42(29)	0.66(19)	0.54(25)	0	0	0
C1	0.0635(1)	0	0.3074(2)	0.59(8)	0.46(9)	0.40(9)	0	−0.01(6)	0
C2	0.1278(1)	0.1030(1)	0.2689(1)	0.22(6)	0.67(5)	0.62(5)	0.06(4)	0.11(5)	−0.25(5)
C3	0.0628(1)	0.2051(1)	0.2283(1)	0.35(5)	0.33(7)	0.55(7)	0.20(5)	−0.25(4)	−0.11(4)

[a] a = 11.33648(3) Å, χ^2 = 2.62 (R_w = 1.55%, R_E = 0.96%, R_I = 3.86%). The units of B_{ij} are Å^2. The background was fitted to a fifteen term Chebyshev polynomial. The atoms were refined at the following positions in the unit cell: K at 12(e) $mm2$; C1 at 24(g) m: C2 and C3 at 48(h)1.

with total oxygen and water levels sufficiently low to allow a 25 W light bulb with a 2 cm diameter hole to burn for several days.

The fulleride samples were loaded into indium-sealed vanadium cans under helium. Neutron diffraction data were collected on the high-resolution time-of-flight powder diffractometer HRPD[9] at the spallation neutron source ISIS, Rutherford Appleton Laboratory, UK. The diffractometer was used in its lower resolution, $\Delta d/d \approx 8 \times 10^{-4}$, high-flux mode. Time-of-flight diffraction data were recorded for K_6C_{60} at 5 K and room temperature over the time-of-flight range 30−130 ms, corresponding to a d-spacing range of 0.6−2.6 Å. K_3C_{60} was measured at 1.5 K over the time-of-flight ranges 30−130 and 30−80 ms, the short window measurement being taken in order to produce better signal-to-noise at short d spacings. Data were normalized to the incident beam and corrected for attenuation by the cryostat. Rietveld and Pawley (intensity extraction) refinement were carried out using the TF12LS code based upon the Cambridge Crystallography Subroutine library.[10]

Results and Discussion

Refinement of the K_6C_{60} data at both room temperature and 5 K confirmed that the structure refined by Zhou et al. in ref 3 was correct, with the potassium cations located in distorted tetrahedral sites in a body centered cubic array of C_{60} anions. A Pawley-type refinement showed the best fit that could be attained by a standard profile refinement gave $\chi^2 = 1.74$. The peak shape used in the refinement was the standard form for the high-resolution powder diffractometer (HRPD) at ISIS consisting of the convolution of a Voigt function with a double-exponential decay (space group $Im\bar{3}m$ was used to avoid correlation problems in the $Im\bar{3}$ pattern decomposition between the reflections symmetry related by the ⟨110⟩ mirror planes in the holosymmetric point group $m\bar{3}m$). As neutron diffraction is more sensitive to the carbon than the potassium positions due to the relative scattering lengths (K 0.367 × 10^{-12} cm, C 0.6674 × 10^{-12} cm), a series of Rietveld refinements designed to investigate the geometry of the C_{60}^{6-} anion were carried out. Models in which all the carbon−carbon bond lengths were constrained to be equal, and all the angles are constrained to be either the ideal hexagonal or pentagonal values gave fits similar in quality to unconstrained refinements in which no prior knowledge is assumed about the bond lengths and angles, although the goodness of fit to the bond length constraints was relatively poor. Final refinements (Figure 1a and Table 1) were therefore carried out without any constraints on the bond lengths and angles, as these are not required in order to produce a sensible molecular geometry from the data. The constrained refinements which we consider most relevant are those in which the angles on the surface of the molecule are constrained to have the ideal hexagonal and pentagonal values. These refinements give increased confidence in the bond length trends (which are of primary chemical significance) derived from the unconstrained refinements, while the spread in bond lengths about the mean (as measured by the second moment of the distribution quoted in Table 5) is somewhat reduced. Furthermore, the data proved to be of sufficient quality to allow the refinement of anisotropic temperature factors for all the four atoms within the asymmetric unit at both temperatures. The resulting C_{60}^{6-} geometry is shown as part of the room temperature unit cell in Figure 2, which indicates that the thermal ellipsoids obtained are chemically reasonable. The shapes of the ellipsoids indicate that motion over the surface of the sphere is easier than in a radial direction, consistent with either librational motion (which we may assume to be small at 5 K) or a small degree of orientational disorder. The resulting bond lengths and angles are shown in Tables 3 and 4 and will be discussed in conjunction with those found for K_3C_{60} following the next section. We carried out a third

Table 2. Refined Atomic Positions in K_3C_{60} at 1.5 K (Space Group $Fm\bar{3}m$)[a]

atom	x	y	z	B (Å^2)	occupancy
K1	0.25	0.25	0.25	−0.98	1
K2	0.5	0.5	0.5	5.82(6)	1
C1	0.2468(3)	0	0.0492(2)	0.7(1)	0.5
C2	0.2143(2)	0.0838(4)	0.1009(3)	0.4(1)	0.5
C3	0.1829(2)	0.1634(3)	0.0510(1)	0.5(1)	0.5

[a] a = 14.1582(1) Å, χ^2 = 1.61 (R_w = 2.21%; R_e = 1.74%, R_I = 5.08%). The background was fitted to a 15-term Chebyshev polynomial. The atoms were refined at the following positions in the unit cell: K1 at 8(c) $43m$; K2 at 4(b) $m\bar{3}m$; C1 at 96(j) m; C2 and C3 at 192(l)1.

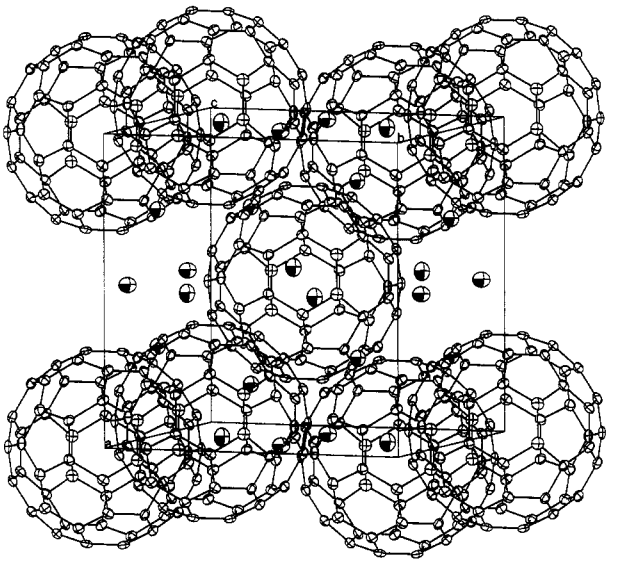

Figure 2. Unit cell of K_6C_{60} at room temperature.

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Table 3. Symmetry-Inequivalent Bond Lengths of the $m\bar{3}$ Symmetry Fulleride Anions in K_3C_{60} and K_6C_{60}

		K_3C_{60}			K_6C_{60}		
		1.5 K[a]	1.5 K[b]	theory	5 K[a]	5 K[b]	theory
6:6 bonds (Å)	C1–C1 (×6)	1.393(5)	1.393(2)	1.410	1.440(5)	1.445(3)	1.447
	C2–C3 (×24)	1.402(6)	1.396(2)	1.406	1.447(2)	1.443(2)	1.420
6:5 bonds (Å)	C1–C2 (×24)	1.469(5)	1.459(2)	1.446	1.444(3)	1.436(2)	1.443
	C2–C3 (×24)	1.442(4)	1.447(2)	1.442	1.425(3)	1.429(2)	1.442
	C3–C3 (×12)	1.442(4)	1.455(2)	1.443	1.423(3)	1.437(3)	1.436

[a] Refers to bond lengths taken from unconstrained refinements. [b] Results of refinements in which the angles were constrained to be 120 ± 0.001° and 108 ± 0.001° in the six- and five-membered rings, respectively. The theoretical values are taken from ref 4.

Table 4. Bond Angles (in degrees) in K_3C_{60} and K_6C_{60} from the Unconstrained Refinements

angle	K_3C_{60} (1.5 K)	K_6C_{60} (5 K)
C1–C1–C2	119.9(3)	120.3(2)
C2–C1–C2	107.7(4)	107.9(2)
C1–C2–C3	119.7(4)	119.1(2)
C1–C2–C3	107.3(4)	107.3(2)
C3–C2–C3	120.3(4)	120.1(2)
C2–C3–C2	119.7(4)	119.8(2)
C2–C3–C3	120.4(4)	120.6(2)
C2–C3–C3	108.8(4)	108.7(2)

refinement using a librational model for the motion of the C_{60}^{6-} anions. The thermal motion of each carbon atom in the C_{60} molecule is described by an anisotropic temperature factor in which the thermal motion is resolved into two components parallel and perpendicular to its radius vector. This yields B(perpendicular) = 1.44 Å^2 and B(parallel) = 0.388 Å^2 at 5 K (4.45 and 0.66 Å^2 at room temperature) corresponding to a root-mean-square libration angle of 3.5° at room temperature and 1.8° at 5 K. The bond lengths and angles are very similar to those derived from the other two refinements.

The structure of K_3C_{60} refined in ref 5 corresponds to the full occupancy of tetrahedral and octahedral interstitial sites in an fcc array of C_{60}^{3-} anions, as proposed in ref 11. A clear outcome of the refinement in ref 5 is that the space group is not $Fm\bar{3}$, which would allow an orientationally ordered array of C_{60} anions, but $Fm\bar{3}m$. This produces a variety of subtle structural questions when compared with other measurements. The $m\bar{3}m$ point symmetry of the refined structure requires disorder of the C_{60}^{3-} anion over the two "standard" orientations[12] (related by a 90° rotation about the ⟨001⟩ directions or 44° rotation about ⟨111⟩), each of which corresponds to alignment of six of the 6:6 bonds along the cell vectors of the fcc unit cell, such that the faces of the unit cell become mirror planes of the C_{60} molecules. The local nature of this merohedral disorder and its influence on the C_{60} dynamics is a matter of current debate. In particular, 2D ^{13}C NMR measurements by Barrett and Tycko imply that small angular jumps of the order of 5° are the dominant reorientational mechanism present in K_3C_{60} in the temperature range 195–220 K.[13] This would imply either relatively large amplitude librational motion of the C_{60}^{3-} anions about the "standard" orientations or the existence of nonzero occupancy of other orientations in the Stephens model structure. A Pawley-type refinement of the 30–130 ms data in $Fm\bar{3}m$ converged to χ^2 = 1.26. We then investigated the possibility of a disordered description of the C_{60} anions in K_3C_{60} at 1.5 K using a symmetry adapted spherical harmonic expansion of the scattering density including A_{1g} symmetry combinations of Y^l_m functions up to l = 24.[14] This model does not fit the data as well as the "Stephens model" and produces a scattering density which resembles that of the Stephens model. This model-independent analysis of the data reinforces the view that the "standard" orientations required by the Stephens model are the only ones present in K_3C_{60}. Tight-binding band structure calculations indicate that *ordering* of these two standard orientations in space group $P4_2/mnm$ is favored on energetic grounds.[15] These authors claim such an ordering would be difficult to detect using X-ray diffraction techniques. This model corresponds to a body centered tetragonal cell (which $c/a \approx \sqrt{2}$: the relationship between fcc and bct cells is outlined in ref 2) containing two C_{60} molecules, with the molecule at the origin having one of the standard orientations, and that at the body center adopting the other one, formed by 90° rotation of the origin molecule about the [001] direction. This model involves nine independent carbon atoms in the asymmetric unit, and refinement in this space group with isotropic temperature factors for all atoms converged smoothly. However the χ^2 value of 4.10 indicated a poorer fit than attained in $Fm\bar{3}m$ and bond lengths and angles around one of the carbon atoms were not chemically sensible. In particular, the orientational ordering in $P4_2/mnm$ leads to superlattice peaks that are not present in the diffraction pattern. However, relaxing the lattice symmetry from cubic to tetragonal leads to a significantly better description of the peak *shape*. (The refined lattice constants were a = 10.0006(2) Å and c = 14.1940(6) Å and should be considered in terms of a tetragonal microstrain of $(c/a\sqrt{2}) - 1 = 3.61(5) \times 10^{-3}$.) Thus while there is clearly no long-range orientational order as evidenced by the lack of superstructure reflections, the anisotropic line broadening indicates a local tetragonal microstrain that suggests, on a short length scale, that some orientational ordering, consistent with space group $P4_2/mnm$, does indeed occur. This is currently under investigation. For the purposes of detailed bond-length and -angle analysis of K_3C_{60}, all subsequent analysis was performed in space group $Fm\bar{3}m$. The potassium cations reside on the 8 c ($^1/_4$,$^1/_4$,$^1/_4$) tetrahedral sites and 4 b ($^1/_2$,0,0) octahedral sites, while there are three crystallographically distinct carbon atoms as in K_6C_{60} that represent the two disordered C_{60} orientations because of the $m\bar{3}m$ point symmetry.

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A disconcerting aspect of the original structural paper[5] was the large variation in bond lengths in the fulleride anion; the quoted positional parameters give lengths of 1.31 Å for the 6:6 bonds and 1.45–1.54 Å for the 6:5 bonds. Unconstrained refinement of the 1.5 K neutron data using the parameters of ref 5 as a starting point, with individual isotropic temperature factors for each carbon atom, converged smoothly to $\chi^2 = 1.61$ with more chemically sensible bond lengths and angles (Figure 1b and Table 2). This is very good evidence for the scattering density arising from two merohedrally related orientations of the C_{60}^{3-} anions, rather than a more locally disordered model. The question of short-range ordering of these orientations, rather than complete disorder, is not relevant to the analysis of the Bragg intensities. As for K_6C_{60}, several constrained models were also investigated, and we quote the results of the angle-only constrained refinement, allowing the bond lengths to refine under the strong shape constraint for the hexagons and pentagons. The main effect of the constraints is again to slightly reduce the spread in the observed bond lengths in comparison with the unconstrained refinement. We were unable to obtain chemically sensible refinements using anisotropic temperature factors for K_3C_{60}, even when applying constraints to all the symmetry inequivalent bond lengths and angles, due to the overlap of the scattering density from the two merohedrally related C_{60} orientations. This difficulty also prevented the use of the librational description of the thermal motion.

One disturbing feature of the final refinement is the large isotropic temperature factor of the octahedral potassium (5.8 Å^2). This corresponds to a root-mean-square displacement of 0.3 Å at 1.5 K away from the center of the octahedral site, where there are 12 3.65 Å closest contacts to the carbon atoms forming the 6:6 bonds that are directed towards the cation. We attempted to model this as static disorder by displacing the potassium along the ⟨100⟩, ⟨111⟩, and ⟨110⟩ directions. Only the displacement along ⟨111⟩ onto the 32f *xxx* positions was stable: the refinement was equivalent to that obtained from the undisplaced model, with x converging to 0.48 (this 0.5 Å displacement gives closest K···C contacts of 3 × 3.40 Å and 3 × 3.49 Å for the octahedral potassium, in comparison with 12 3.20 Å and 12 3.22 Å contacts for the tetrahedral potassium, assuming an $Fm\bar{3}$ local ordering) although both cations refined to have negative temperature factors. The data extend down to only 0.6 Å, and yet higher Q data may be required to refine a static displacement of this octahedral potassium. An alternative interpretation of the temperature factor is that it is indicative of potassium vacancies on the large octahedral site. Refinement of site occupancies indicates 100% occupancy of the tetrahedral sites whereas the octahedral site occupancy converges to 60%, with $B = 1.46$ Å^2. The large potassium isotropic temperature factor is therefore consistent with either uncorrelated displacements along the ⟨111⟩ directions or a vacancy concentration on the octahedral site. There is no evidence from our refinements for the significant concentration of tetrahedral vacancies derived from synchrotron X-ray studies on K_3C_{60} in ref 16.

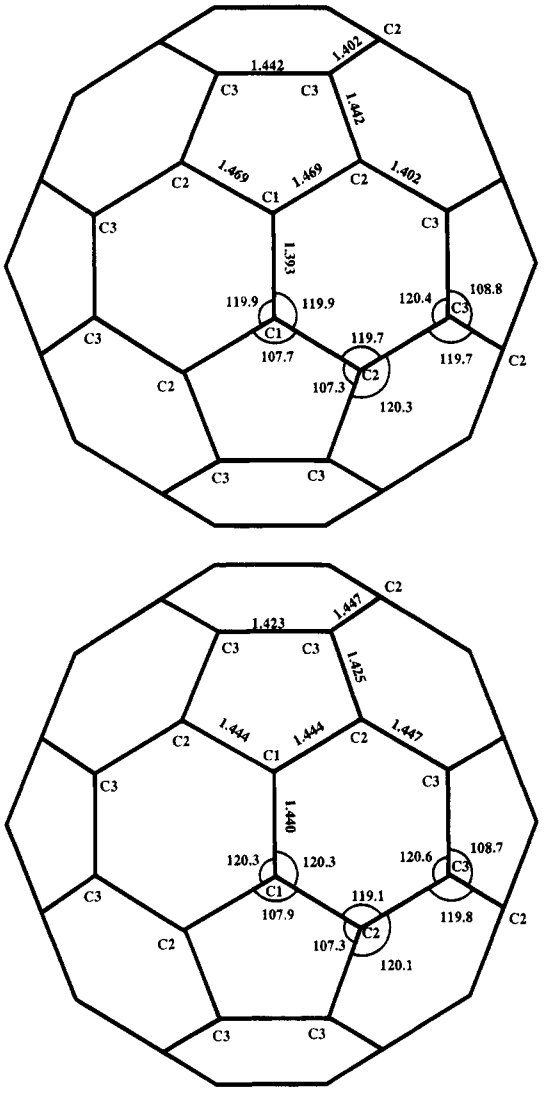

Figure 3. Bond lengths and angles in (a, top) the C_{60}^{3-} anion in K_3C_{60} at 1.5 K (b, bottom) the C_{60}^{6-} anion in K_6C_{60} at 5 K.

Vacancies on the octahedral site are consistent with the metallic, superconducting phase being the doped Mott–Hubbard insulator $K_{3-x}C_{60}$ (although they do not exclude a Fermi liquid description[17]), and further definitive research on this topic is required.

The carbon–carbon bond lengths and angles resulting from the unconstrained and angularly constrained K_6C_{60} and K_3C_{60} refinements are shown in Tables 3 and 4 and Figure 3, where they are compared with the theoretical calculations by Andreoni and co-workers. The angles in Table 4 strongly suggest that the unconstrained refinements are meaningful. Although we quote only the 5 K data for K_6C_{60} to minimize the effects of thermal motion, the trends observed in the K_6C_{60} bond lengths are the same at both room temperature and 5 K, giving increased confidence in their significance. A useful overall indicator of the trends observed is obtained by considering the variation in the mean lengths of the 60 6:5 and 30 6:6 bonds (weighted by the number of symmetry equivalent bonds of each type) as the charge state of the fullerene varies. These data are given in Table 5 in comparison with the bond lengths

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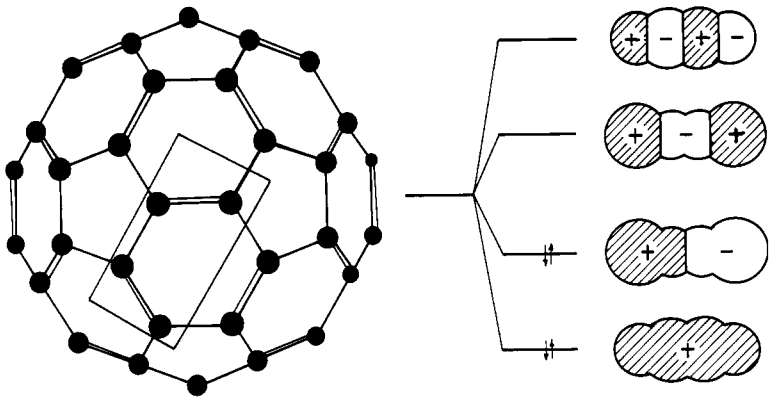

Figure 4. Molecular orbitals of a four-carbon butadiene fragment of a C_{60} molecule. Occupation of the LUMO on reduction will lengthen the 6:6 "double" bonds.

Table 5. Mean Carbon–Carbon Bond Lengths in C_{60} and Potassium Fullerides[a]

compound	C_{60}	K_3C_{60}[a]	K_3C_{60}[b]	K_6C_{60}[a]	K_6C_{60}[b]
mean 6:6 bond (Å)	1.38	1.400(4)	1.397(2)	1.445(3)	1.443(1)
mean 6:5 bond (Å)	1.46	1.452(13)	1.453(5)	1.432(10)	1.433(4)

[a] Footnotes *a* and *b* as in Table 3. The errors represent the second moment of the distribution of the observed bond lengths for each class of bond about the mean.

in C_{60} obtained by pair correlation function analysis at room temperature. Considering the mean bond lengths, to minimize the effect of particular intermolecular interactions on given symmetry inequivalent bonds, reduction lengthens the 6:6 bonds with the increase on increasing the anion charge from 3− to 6− being twice as large as on going from 0 to 3−. The effect of reduction on the 6:5 bonds is less dramatic but, surprisingly, consistent with *shortening* on reduction. This remarkable effect is apparent in both the constrained and unconstrained refinements, giving extra confidence to our conclusions. The mean bond length, averaging over both 6:5 and 6:6 bonds, is very similar (identical to two decimal places) in all three cases, indicating that the t_{1u} orbitals are essentially nonbonding; their occupancy redistributes the bonding influence of the π electrons between the 6:6 and the 6:5 bonds. The 6:6 bond in ordered $Pa\bar{3}$ C_{60} (site symmetry $\bar{3}$) has a mean length of 1.391(18) Å,[18] reflecting the increased double-bond character in this bond indicated by many electronic structure calculations. This is also consistent with a pyraclene model for the chemical reactivity of C_{60}[19] (which undergoes addition of electrophilic species primarily across the 6:6 bond) which assigns the dominant valence-bond resonance structure as one in which the 6:6 bonds have double-bond character. This mean length increases in K_3C_{60} to 1.400(4) Å and further to 1.440(4) Å in K_6C_{60}, where it is actually longer than the mean 6:5 bond length of 1.432(10) Å. It is clear that the effect of adding electrons into the t_{1u} orbitals is to lengthen the 6:6 bonds and contract the 6:5 bonds at the three standard deviation level of confidence. As noted by Haddon,[20] it appears that the C_{60}^{6-} anion is considerably more aromatic in character than C_{60} itself, in terms of both the ring-current contribution to the diamagnetic susceptibility and the distinction between the 6:6 and 6:5 bonds.

A detailed understanding of the changes in geometry on reduction requires comparison with the calculations presented in ref 4. These calculations predict that the two 6:6 bonds lengthen considerably (up to 0.05 Å) on reduction, while the 6:5 bonds actually shorten slightly. Remarkably, we observe precisely this pattern of distortion, although the details differ in some significant respects. In particular, we observe that both, rather than only one, of the 6:6 bonds lengthen to become the longest bonds in the molecule and two of the three 6:5 bonds contract to a greater extent than predicted by theory. The predicted T_h symmetry distortion, corresponding to elongation of the C_{60}^{6-} anion along the Cartesian axes, is not observed, with all three C atoms lying within 0.008 Å of the surface of a sphere of radius 3.56 Å in both constrained and unconstrained refinements (the corresponding mean radius for K_3C_{60} is 3.552(9) Å). The lengthening of the 6:6 bonds and contraction of the 6:5 bonds is also observed (to a lesser extent, corresponding to the lower degree of reduction) in the C_{60}^{3-} anion in K_3C_{60}, and agreement with theory is even better than in the K_6C_{60} case, suggesting that the calculations provide an excellent basis for understanding the electronic structure of the C_{60}^{3-} anions in the superconducting alkali metal fullerides. The calculations in ref 4 specifically exclude the possibility that the change of sphere packing rather than the different charge states is responsible for the observed distortions.

We can use an elementary model to rationalize both the general trends displayed by the mean bond lengths, and the ab initio calculations. A simple chemical analogy between the butadiene molecule and a four-carbon fragment of the C_{60} molecule helps to show why the 6:6 bonds lengthen and the 6:5 bonds shorten on reduction. In butadiene,[21] the bonds between the terminal C atoms are shorter than the central bond due to the nature of the HOMO (π bonding between the terminal carbons and antibonding between the central ones). Occupation of the LUMO will tend to lengthen the terminal bonds (as the orbital is antibonding between these carbons) while shortening the central one (6:6 and 6:5 bonds respectively in our case). The overall behaviour of the bonds in the C_{60} anions reflects this simple property of the butadiene unit. An alternative

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chemical picture is that adding π^* electrons will lengthen bonds that are short in the unreduced species due to π interactions.

We have shown that time-of-flight powder neutron diffraction allows unconstrained and definitive refinement of the molecular geometry of the fulleride anions in superconducting K_3C_{60} and insulating K_6C_{60}. The resulting bond lengths and angles suggest a simple chemical picture for the changes in molecular geometry on doping and, particularly for the superconducting system, agree relatively well with existing theoretical predictions.

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