SYNTHESIS AND CHARACTERIZATION OF ALKALI METAL FULLERIDES: $A_xC_{60}$


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Abstract—Alkali metal fullerides ($A_xC_{60}$) are a subject of considerable current interest because of the occurrence of superconductivity for $A_xC_{60}$ at temperatures surpassed only by the high $T_c$ copper oxides. The preparation and characterization of $A_xC_{60}$ ($A =$ alkali metal, $x = 2, 3, 4, 6$) by powder X-ray diffraction, NMR ($^{13}C$, $^{23}Na$ and $^{87}Rb$), and d.c. magnetization are reported. The structures are described as intercalation compounds of the FCC structure of pristine $C_{60}$ or of hypothetical BCC or BCT structures. The structures and phase diagrams can be rationalized on the basis of ion size and electrostatic considerations. Only the $A_xC_{60}$ compounds are metallic (and superconducting). The superconducting $T_c$ increases nearly linearly with unit cell size. EHT (Extended Hückel Theory) calculations and $^{13}C$ NMR relaxation measurements indicate higher densities of states for the higher $T_c$ compositions.

Keywords: Superconductivity, Fullerenes, carbon, structures.

INTRODUCTION

Since the discovery of [1] of $C_{60}$ and higher fullerenes there has been considerable interest in the chemistry and physical properties of these molecular forms of carbon. The isolation of macroscopic quantities of $C_{60}$ by the spark erosion technique [2] added the possibility of investigating solid state properties. The molecular fullerene solids are held together by relatively weak van der Waal's forces similar to those between layers in graphite. A rich variety of physical properties have already been identified for solid $C_{60}$ and its compounds [3]. The discovery of superconductivity in $K_xC_{60}$ [4] and identification of $K_xC_{60}$ as the superconducting phase [5,6] has led to a broad class of superconductors [4–11] of composition $A_xC_{60}$ ($A =$ alkali metals) with superconducting critical temperatures, $T_c$, surpassed only by the copper oxides. The occurrence of superconductivity has focused considerable interest on $A_xC_{60}$ and a rich variety of $A_xC_{60}$ have already been reported with compositions at $x = 2$ [11, 12], 3 [6, 8, 11], 4 [13] and 6 [11, 14] depending on $A$. Alkali metal intercalation in the fullerenes already appears to be more diverse than the widely investigated graphite analogs [15]. In this paper we expand on our previous reports on bulk, polycrystalline $A_xC_{60}$ and integrate these with the results of others to present an overall picture of the $A_xC_{60}$ compounds.

EXPERIMENTAL

The $C_{60}$ used in this work was purified by standard extraction and chromatography of soot prepared in-house by the spark erosion technique [2] or purchased from Texas Fullerenes. Extract was also purchased from MER. We have observed no differences in the materials prepared from any of these sources. A variety of techniques have been employed to synthesize $A_xC_{60}$ with the choice of technique dependent on both $A$ and $x$. $A_xC_{60}$ ($A =$ K, Rb, Cs), is best prepared by direct reaction with excess alkali metal vapor at 250–350°C for 10–15 days in sealed Pyrex tubes [14], and $A = Na$ at 350–400°C for 6 days in stainless steel tubes [11]. The $A_xC_{60}$ and $A_xC_{60}$ ($A =$ K, Rb, Cs) phases can be prepared by several methods, but the most reliable way to control stoichiometry is reaction of appropriate amounts of $A_xC_{60}$ and $C_{60}$ at 200–250°C for 10–15 days [16]. For $A = Na$, $Na_xC_{60}$ is best prepared by reaction of $NaH$ or $Na_xHg$ with $C_{60}$ at 350°C for nine days with two intermediate regrindings [11]. $Na_xC_{60}$ is best synthesized by reaction of $Na_xHg$ with $C_{60}$ at 330°C for 10–15 days followed by distillation of $Hg$ away from the product [11]. $A_xC_{60}$ with mixed alkalins are prepared either by reaction of appropriate quantities of the different $A_xC_{60}$, or by reaction of $A_xC_{60}$, $C_{60}$ and $NaH$ for $Na$ containing compositions. In each of these methods the reaction times.
are dependent on amount and crystallite size of the C\textsubscript{so} and the size and ambient pressure in the reaction tube. Reactions in this study used from 10 to 500 mg C\textsubscript{so}. Appropriate physical properties (e.g. X-ray diffraction, NMR, magnetization) must be monitored to insure phase purity. Even brief exposure to air results in serious degradation of the superconducting properties of A\textsubscript{2}C\textsubscript{so}. They should be maintained in an inert atmosphere at all times.

Powder X-ray diffraction patterns were taken using CuK\textsubscript{α} radiation from a high intensity rotating anode source with a singly bent pyrolytic graphite (PG) focusing monochromator and a flat PG analyser. The resolution was enhanced over that provided by the 0.5° acceptance of PG by placing slits before the monochromator and the analyser. This gives an instrument with a moderate angular resolution (∼0.25° 2θ) but a high dynamic range (> 10⁵ for powder diffraction). Samples for X-ray diffraction were sealed in Debye-Scherrer capillaries to protect them from air. The capillaries were then mounted in a vacuum chamber with a beryllium window to eliminate scattering from air at low angles.

LAZY/PULVERIX [17] and the NRCVAX [18] package were used in refinement and modeling of intensity data after modification of the source code to allow a form factor for C\textsubscript{so}, \(\propto \sin \theta R / R^2\), which models C\textsubscript{so} as a hollow spherical shell of radius \(R\) containing 360 electrons. \(R\) was fixed at 3.55 Å as determined from our previous single crystal analysis [19]. The value of \(R\) was manually varied for various A\textsubscript{2}C\textsubscript{so} and found to be constant for each. The NMR spectra were obtained at 9.39T (100.5 MHz for 13C). Samples for NMR were sealed in Pyrex under a He atmosphere, except for 23Na which were sealed in quartz to minimize background signals. Superconducting shielding measurements were taken on a Quantum Design SQUID at fields of 5–10 Oe. DSC data were taken on a DuPont 1090 Thermal Analyser. Electronic structure calculations were carried out with the EHT (Extended Hückel Theory) band structure programs.

**STRUCTURES**

The room temperature solid state structure of C\textsubscript{so} may be described as FCC packing of identical, spherical C\textsubscript{so} molecules. The observed X-ray powder data are modeled well by using uniform shells of electron density (radius 3.55 Å) for the C\textsubscript{so} molecules at the 4\(a\) positions of a FCC cubic cell of symmetry \(Fm\text{3}m\) [19, 20]. A van der Waal's radius of 5.01 Å is calculated from the crystallographic unit cell. Motional narrowing of the 13C NMR spectra shows that the molecules rotate rapidly compared to the NMR timescale (∼100 μs) [21, 22]. At 260 K there is a first order phase transition to a simple cubic cell [20] of symmetry \(P\text{a}3\), corresponding to rotational ordering of the molecules. The \(P\text{a}3\) structure has been refined by X-ray [20] and neutron diffraction [23] on powders and X-ray diffraction on twinned single crystals [24]. Continued motional narrowing of the 13C NMR spectra below 260 K leads to the conclusion that C\textsubscript{so} molecules continue to rapidly 'ratchet' between symmetry equivalent orientations above about 140 K [25].

The structures of all the alkali metal fullerides characterized to date may be regarded as intercalation compounds of the pristine FCC structure or of hypothetical C\textsubscript{so} structures with BCC (body centered cubic) or BCT (body centered tetragonal) ball packing. The ideal sizes and coordination numbers of interstitial sites for FCC and BCC packings of rigid spheres of radii 5.01 Å are summarized in Table 1 along with the ionic radii of the alkali metal ions. The octahedral and tetrahedral interstices of FCC are fixed on special positions. The octahedral site is larger than any alkali metal ion, and the tetrahedral site is closest in size to Na\textsuperscript{+}. (Ions can generally occupy sites smaller than their hard sphere sizes would indicate.) These are the only interstitial sites generally considered for FCC packing, but the large size of the C\textsubscript{so} molecules makes consideration of other sites reasonable. The most likely of these is \((x,x,x)\) which for \(x = 1/3\) gives a trigonal site of appropriate size for small cations (e.g. Li\textsuperscript{+}). For FCC packing, the

<table>
<thead>
<tr>
<th>Structure type</th>
<th>Unit cell ((\text{Å}))</th>
<th>Interstitial sites</th>
<th>No. per C\textsubscript{so}</th>
<th>CN</th>
<th>Radius ((\text{Å}))</th>
<th>Alkali metals</th>
<th>(A^+)</th>
<th>Radius ((\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC ((s.g. \text{Fm}3))</td>
<td>14.17 ((\text{Å}))</td>
<td>((l, \frac{1}{2}, \frac{1}{2}))</td>
<td>2</td>
<td>4</td>
<td>1.12 ((\text{Å}))</td>
<td>Cs</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>BCC ((s.g. \text{Im}3))</td>
<td>11.57(\dagger) ((\text{Å}))</td>
<td>((0, \frac{1}{2}, z) z = \frac{1}{2})</td>
<td>6</td>
<td>4</td>
<td>1.46 ((\text{Å}))</td>
<td>Rb</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>((x, y, z) x = y = 1/8, z = \frac{1}{2})</td>
<td>6</td>
<td>3</td>
<td>1.13 ((\text{Å}))</td>
<td>K</td>
<td>1.38</td>
<td></td>
</tr>
</tbody>
</table>

\(\dagger\)Calculated lattice parameter for spheres of radius 5.01 Å.
interstitial sites located at \((0,1/2,z)\) are tabulated for 
\(z = 0.25\), which is equidistant from four \(C_{60}\)s. The
sites for BCT packing are more complex, depending both on \(x\) and \(c/a\), but are approximately the size of those for BCC.

Schematic representations of the known \(A_xC_{60}\)
structures are illustrated in Fig. 1. Tables 2 and 3 list
unit cell data for the various observed phases. The
\(A_xC_{60}\) structure was first refined by Stephens et al. [6]
for \(K_xC_{60}\). For the \(C_{60}\) to be completely ordered and

### Table 2. Unit cell and \(T_s\) for FCC \(A_xC_{60}\)

<table>
<thead>
<tr>
<th>(A_xC_{60})</th>
<th>Lattice parameter(s) (Å)</th>
<th>(T_s) (K) (%)(^\dagger)</th>
<th>(^{13})C shift (ppm vs TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Na_xC_{60})</td>
<td>14.189 (1)</td>
<td>—</td>
<td>173 (2)</td>
</tr>
<tr>
<td>(Na_xC_{60})</td>
<td>14.183 (3)</td>
<td>—</td>
<td>175 (2)</td>
</tr>
<tr>
<td>(Na_xC_{60})</td>
<td>14.380 (8)</td>
<td>—</td>
<td>167 (2)</td>
</tr>
<tr>
<td>(Na_xC_{60})</td>
<td>14.120 (4)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(Na_xRbC_{60})</td>
<td>14.148 (3)</td>
<td>8.0 (3)</td>
<td>—</td>
</tr>
<tr>
<td>(Na_xCsC_{60}) No. 1^|$</td>
<td>14.132 (2)</td>
<td>10.5 (8)</td>
<td>182 (2)</td>
</tr>
<tr>
<td>(Na_xCsC_{60}) No. 2^|$</td>
<td>14.176 (9)</td>
<td>14.0 (9)</td>
<td>—</td>
</tr>
<tr>
<td>(K_xC_{60})</td>
<td>14.253 (3)</td>
<td>19.3 (30)</td>
<td>183 (2)</td>
</tr>
<tr>
<td>(K_xRbC_{60})</td>
<td>14.209 (2)</td>
<td>21.8 (32)</td>
<td>—</td>
</tr>
<tr>
<td>(Rb_xKC_{60}) No. 1^|$</td>
<td>14.336 (1)</td>
<td>24.4 (34)</td>
<td>—</td>
</tr>
<tr>
<td>(Rb_xKC_{60}) No. 2^|$</td>
<td>14.364 (5)</td>
<td>26.4 (32)</td>
<td>—</td>
</tr>
<tr>
<td>(Rb_xCsC_{60})</td>
<td>14.436 (7)</td>
<td>79.4 (35)</td>
<td>171 (5)</td>
</tr>
<tr>
<td>(Rb_xCsC_{60})</td>
<td>14.493 (2)</td>
<td>31.3 (48)</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^\dagger\)\(T_s\) and shielding fractions (%) were measured by d.c. magnetization.

^\$Sample is simple cubic.

^\$Samples labeled No. 1 and No. 2 have the same nominal composition.
Table 3. Unit cell and alkali sites for A₆C_{60} and A₆C_{80}

<table>
<thead>
<tr>
<th>Phase</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>c/a</th>
<th>rₐÅ⁺ (avg)</th>
<th>rᵢCÅ⁻ (avg)</th>
<th>¹³C shift (ppm vs TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₆C_{60}</td>
<td>BCT</td>
<td>11.886 (7)</td>
<td>10.774 (6)</td>
<td>0.906</td>
<td>1.48 (1.40)</td>
<td>1.39 (1.53)</td>
</tr>
<tr>
<td>Rb₆C_{60}</td>
<td>BCT</td>
<td>11.962 (2)</td>
<td>11.022 (2)</td>
<td>0.921</td>
<td>1.52 (1.48)</td>
<td>1.44 (1.72)</td>
</tr>
<tr>
<td>Cs₂C_{60}</td>
<td>BCT</td>
<td>12.057 (18)</td>
<td>11.443 (18)</td>
<td>0.949</td>
<td>1.58 (1.60)</td>
<td>1.52 (1.67)</td>
</tr>
<tr>
<td>K₆C_{80}</td>
<td>BCC</td>
<td>11.390</td>
<td>1.00</td>
<td>1.52</td>
<td>1.36</td>
<td>1.48</td>
</tr>
<tr>
<td>Rb₆C_{80}</td>
<td>BCC</td>
<td>11.548</td>
<td>1.00</td>
<td>1.61</td>
<td>1.50</td>
<td>1.58</td>
</tr>
<tr>
<td>Cs₂C_{80}</td>
<td>BCC</td>
<td>11.790</td>
<td>1.00</td>
<td>1.75</td>
<td>1.43</td>
<td>1.59</td>
</tr>
</tbody>
</table>

rᵢDistance from center of A ion site to center of C₆₀ minus the van der Waals radius of C₆₀ (5.01 Å).  
†The 0 denotes a vacancy.  
§Data from Ref. 14.

Na on the tetrahedral sites and 50% occupancy of a cubic cluster of sites at 32f positions (0.43, 0.43, 0.43) centered on the octahedral site. An arrangement of Na atoms consistent with half occupancy of these sites is the presence of Na₆ tetrahedra formed by Na atoms at opposite corners of the cube. These tetrahedra would then be disordered between parent octahedral sites. This structure has also been proposed for Ca₆C₆₀ [26]. The diffraction pattern of Na₆C₆₀ at room temperature fits the normal FCC A₆C₆₀ structure. Although Na₆C₆₀ refines well for Na on both octahedral and tetrahedral sites, the possibility of Na displacement to a more general position (e.g. 32f) is likely. Below 260 K there is a structural transition in Na₆C₆₀, resulting in an X-ray pattern (Fig. 2) that appears to be a two-phase mixture arising from disproportionation into compositions with lattice parameters close to those of Na₆C₆₀ and Na₆C₈₀. Remarkably this transition is reversible with temperature. Since it is hard to imagine facile Na motion over large distances to produce a macroscopic two phase material, we envisage a shorter range diffusion of Na from the tetrahedral site to form clusters about the octahedral site. Preferred compositions (still to be determined) such as Na₆C₆₀ with all Na clustered about the octahedral site could account for formation of two phases.

The BCC A₆C₆₀ (A = K, Rb, Cs) structure, first reported by Zhou et al. [14], is based on BCC packing of C₆₀ molecules with A ions occupying four coordinate interstices between rotationally ordered C₆₀ molecules. For A = Cs, refinement located A at (0,1/2,0.28), which may be described as a distorted tetrahedron with A closer to two C₆₀. Assuming the same fractional coordinate for other A, the radii of the sites are given in Table 3. The average of the four distances to C₆₀ is close to the A⁺ ionic radii. The
A\textsubscript{2}C\textsubscript{60} structure, described by Fleming et al. [13], has a BCT structure and was refined in the I\textsubscript{4}mm space group with C\textsubscript{60} as a shell of electron density. The true symmetry must be lower if the C\textsubscript{60}s are completely ordered due to the absence of a four-fold axis in the C\textsubscript{60} molecule. The sizes of the A\textsuperscript{+} sites in A\textsubscript{2}C\textsubscript{60} are given in Table 3. The sizes of the A\textsuperscript{+} ion sites in both A\textsubscript{2}C\textsubscript{60} and A\textsubscript{2}C\textsubscript{60} closely match the ionic radii of the A\textsuperscript{+} ions. The A\textsubscript{2}C\textsubscript{60} structure may be viewed as a defect A\textsubscript{2}C\textsubscript{60} structure. The six identical sites in the BCC structure disproportionate into four slightly smaller sites and two larger ones for BCT structures with c/a < 1.0. The A ions occupy the smaller sites.

The observed structures can all be rationalized on the basis of alkali ion size and electrostatic considerations. A plot of the unit cell volumes of the A\textsubscript{2}C\textsubscript{60} normalized per C\textsubscript{60} molecule versus the total cation volume calculated from the ionic radii, shown in Fig. 3, makes a useful comparison both within and between structure types based on alkali ion sizes. For the FCC series, compositions exist with both larger and smaller cell volumes than for the pristine host. This is also true for the BCC series, based on the estimated volume of a hypothetical 'pristine BCC host' with spheres of the same radius as C\textsubscript{60}. For A\textsubscript{2}C\textsubscript{60} the cell is contracted for A = K (r\textsubscript{K+} = 1.38 Å) which is smaller than the hard sphere site size (r = 1.49 Å), whereas Rb (r\textsubscript{Rb+} = 1.49 Å) is nearly a perfect match and Cs (r\textsubscript{Cs+} = 1.70 Å) causes a lattice expansion. The A\textsubscript{2}C\textsubscript{60} data are more complicated because there are two different types of sites. The smaller tetrahedral site is 'lattice expanding' for ions larger than Na, and the octahedral site is 'lattice contracting' for all A ions, giving rise to a minimum in the lattice parameter as a function of cation size. Refinements of X-ray powder intensity data for mixed alkali A\textsubscript{2}C\textsubscript{60} show distinct site ordering only between ions with the largest size differences, i.e. Na\textsubscript{2}CsC\textsubscript{60} and Na\textsubscript{2}RbC\textsubscript{60} [11]. It should be noted that the large size of the octahedral site compared to that of the A\textsuperscript{+} ions is reflected in large thermal factors in the structure refinements of A\textsubscript{2}C\textsubscript{60}. The larger unit cells of Na\textsubscript{2}CsC\textsubscript{60} and Na\textsubscript{2}KCC\textsubscript{60} compared to Na\textsubscript{2}RbC\textsubscript{60} are attributed to Na\textsuperscript{+} occupation of sites displaced from the centers of the octahedral sites. The larger volume of A\textsubscript{2}C\textsubscript{60} compared to the A\textsubscript{2}C\textsubscript{60} of the same A reflects the disproportionate of site sizes in the former with the vacant sites being larger as shown in Table 3. The difference is most pronounced for the smallest ion, K\textsuperscript{+}.

Electrostatic calculations shed light on the existence of the observed phases and their detailed structures [13, 27]. The calculations assume point charges for A\textsuperscript{+} and C\textsubscript{60}, experimental lattice parameters for known phases, and an electrostatic energy of putting x electrons on C\textsubscript{60} of $E_x = -E_A + CJR$, where the electron affinity, $E_A$, is taken as 2.6 eV. For C\textsubscript{60} with radius R = 3.5 Å, CJR is the minimum Coulomb repulsion of x point charges on the sphere. For Rb\textsubscript{2}C\textsubscript{60} the known phases (x = 3, 4 and 6) are the ones found to be most stable with these simple assumptions and have electrostatic energies within 0.1 eV of each other. Two other structures, Rb\textsubscript{2}C\textsubscript{60} (Rb in tetrahedral sites) and Rb\textsubscript{2}C\textsubscript{60} with the Al\textsubscript{5} structure (Fig. 4) are less stable by only about 0.2 eV. Other calculations suggest that the Al\textsubscript{5} structure is energetically comparable [28]. The A\textsubscript{2}C\textsubscript{60} phase is experimentally observed for A = Na, but the Al\textsubscript{5} structure has yet to be observed. The most likely place to find an Al\textsubscript{5} structure would be for A = Cs.
where there would be a good size match and the FCC structure would be destabilized by the size mismatch between Cs and the tetrahedral sites. The report by Kelty et al. [10], of superconductivity in CsCsO could be due to an A15 phase. We have also observed small amounts of superconductivity in CsCsO but have only observed CsCsO and CsCsO by X-ray diffraction.

The octahedral and tetrahedral sites in FCC lattices are electrostatic saddle points rather than minima, and the total energy can be lowered by displacement of the cations to positions of lower symmetry. Uncorrelated cation displacements would preserve FCC symmetry, but correlated displacements would be symmetry lowering. Both Na,KCsO and Na,KCsO exhibit symmetry lowering transitions below room temperature [11]. Displacement of Na from the octahedral site becomes massive for Na,KCsO, resulting in a new phase. The minimum electrostatic energy for the A,KCsO structures, employing experimental lattice parameters, occurs for cation position about (0.21,0,1/2), in good agreement with the refined value of (0.22,0,1/2) for Rb,CsO [13]. The electrostatic calculations similarly predict the optimal position (0,1/2,z) to be z = 0.29 site for the BCC A,KCsO structure in agreement with the refined Cs position (z = 0.28) of Cs,CsO [14]. The success of the simple electrostatic model for most A,KCsO supports the description of these compounds as fulleride salts. The Na,KCsO phase and its Cs analog, are notable in being the only A,KCsO structures observed so far that do not correspond to electrostatically favorable structures, leading to the conclusion that they are stabilized by covalent interactions either within the A, cluster or between A and CsO. Tetrahedral Na, clusters are also found in (CH,Na), [29] and an Na,⁺ cluster has been implicated in zeolite Y [30].

One might expect extensive solid solutions in the A,KCsO based on partial filling of interstitial sites. However, the bulk of the data reported to date indicate that most of the observed phases for A = K, Rb and Cs are line phases or nearly so. This was first shown in connection with superconductivity by Holzer et al. [5], who realized that different nominal compositions of K,CsO with the same T and volume fractions peaked at x = 3 indicated a line phase superconductor at that composition. From X-ray powder diffraction Zhu et al. [31] have reported that for A = Rb, the x = 0 and x = 6 phases show variations in lattice parameters indicative of a broader region of homogeneity. They suggest that Rb,CsO forms a solid solution (BCC) for 5 < x < 6 and that a dilute FCC phase is present for 0 ≤ x < 1. ¹³C NMR supports a two phase description of K,RbCsO as CsO + K,CsO [27], but DSC of the same sample shows no evidence of the Fm3m to Pa3 transition at 260 K. Thus, there must be a K,RbCsO phase with x being sufficiently small that the ¹³C NMR chemical shift is unaffected. Our experience with these materials has been that there is no single technique capable of demonstrating phase purity for all A,KCsO, but rather a combination of techniques is essential. Thus, we expect the exact determination of phase limits in these materials will be the subject of considerable future work. Our current view of the phase diagrams for the A,KCsO is illustrated in Fig. 5. We use gradually shaded regions around CsO and A,KCsO to reflect our uncertainty about the exact location of the phase boundaries and our prejudices about which ions might exhibit larger solid solution regions.

### CHEMICAL PROPERTIES OF A,KCsO

Knowledge of the chemical properties of CsO and its compounds with alkali metals is crucial to the synthesis of single phase materials, their handling in the measurement of physical properties, and the eventual synthesis of new materials or crystals. In addition to the reactions outlined above that we consider the best current methods of synthesis for A,KCsO, we have explored several other reactions that may prove useful in the preparation of new materials or the growth of crystals.

All of the alkali metals react directly with CsO, but the reactions are most facile for the heavier alkali, presumably due to higher alkali metal vapor pressure, higher diffusivity of A in the solid A,KCsO, and lower reactivity with glass. Direct reaction is the most convenient route to the highest stoichiometry fullerides, A,KCsO (A = Na, K, Rb, Cs). For K, Rb and Cs...
the \( \text{A}_3\text{C}_{40} \) and \( \text{A}_4\text{C}_{40} \) phases are more conveniently prepared by reaction of \( \text{C}_{60} \) with \( \text{A}_x\text{C}_{60} \) as first described by McCauley et al. [16]. This is especially true for small quantities because the difficulty of accurately weighing small quantities of \( \text{A} \) is circumvented. McCauley et al. [16] noted that the actual stoichiometry by weight uptake was \( \text{A}_x\text{C}_{60} \) rather than the crystallographically limiting composition \( \text{A}_4\text{C}_{40} \). We have also found this to be the case and attribute the difference to alkali adsorbed on the surface of crystallites or associated with defects. Because of the heterogeneous nature of the reactions, the conditions necessary for equilibration vary considerably and monitoring of several physical properties is necessary to assure complete reaction. For direct reaction with 20–50 mg of \( \text{C}_{60} \) powder in tubes with a volume of \( \sim 1 \text{cc} \), measurements of X-ray powder patterns, NMR and superconducting flux exclusion indicate that 7–14 days at \( 250-350^\circ \text{C} \) may be needed for completion. In one experiment, the superconducting shielding fraction increased with increasing reaction time and temperature before leveling off at 35% shielding after 21 days [32]. The thermal stability in the absence of oxygen or moisture is not known with any precision. Superconducting shielding fractions of \( \text{K}_3\text{C}_{60} \) begin to decrease on annealing above \( 450^\circ \text{C} \), but this is likely dependent on annealing time and may be different for other alkalis. \( \text{K}_3\text{C}_{60} \) decomposes by 550°C to give \( \text{K}_x\text{C}_{60} \) [13] with the liberated \( \text{K} \) reacting with the glass. For molecular compounds, all of the \( \text{A}_x\text{C}_{60} \)s are remarkably stable thermally.

The molecular nature of \( \text{C}_{60} \) and its solubility in organic solvents makes solution chemistry routes to \( \text{A}_x\text{C}_{60} \) tempting. In addition, solution electrochemistry shows that \( \text{C}_{60} \) is reduced in a series of one electron reductions [33] (so far five 1e reductions have been reported) differing by \( \sim 0.5 \text{ V} \) with the first reduction near \( -0.25 \text{ V} \) vs SCE. Bausch et al. [34] obtained solutions of \( \text{C}_{60} \) anions by sonication of \( \text{C}_{60} \) and \( \text{Li} \) in THF that had a \( ^{13} \text{C} \) NMR of 157 ppm. Wang et al. obtained superconducting \( \text{K}_3\text{C}_{60} \) [35] and \( \text{Rb}_3\text{C}_{60} \) [36] by reaction of toluene solutions of \( \text{C}_{60} \) with the alkali metal followed by filtration of the resulting precipitate. We have obtained \( \text{A}_x\text{C}_{60} \) by reaction of \( \text{C}_{60} \) with alkali metals in liquid ammonia or THF, followed by heating to \( \sim 300^\circ \text{C} \) (eqns (1)-(2))

\[
\text{C}_{60(\text{ins})} + 3\text{K}(\text{ins}) \rightarrow 3\text{K}_3\text{C}_{60} \quad \text{[K}_{3}\text{C}_{60}] \quad (1)
\]

\[
\text{C}_{60(\text{ins})} + 3\text{K} + \text{NH}_3 \rightarrow 3\text{K}_3\text{C}_{60} \quad \text{[K}_3\text{C}_{60}] \quad (2)
\]

The first point of note concerning these reactions is that \( \text{A}_3\text{C}_{60} \) (at least for \( \text{K} \) and \( \text{Rb} \)) is soluble in \( \text{NH}_3 \) and in THF (the pure phases prepared by the standard routes are also soluble in THF). The solubility in THF is further evidence that these compounds behave as fulleride salts. However, heating to \( \sim 300^\circ \text{C} \) was necessary to remove solvated solvent from the reaction products. Nominal compositions \( \text{K}_3\text{C}_{60} \) and \( \text{Rb}_3\text{C}_{60} \) prepared in this way showed only small amounts of superconductivity and were non-crystalline, but showed \( ^{13} \text{C} \) NMR spectra similar to those of material prepared by solid state routes. Reaction with excess alkali metal in either \( \text{NH}_3 \) or THF gave insoluble products, presumably a solvated \( \text{A}_x\text{C}_{60} \).

Wudl et al. [37] have reported that \( \text{C}_{60} \) reacts with amines in a nucleophilic addition and we cannot exclude the possibility that \( \text{NH}_3 \) is added to the \( \text{C}_{60} \) and is then eliminated on heating. Since the \( \text{A}^+ \) ions coordinate strongly to THF and \( \text{NH}_3 \), we attempted a modification of the McCauley prep. using \( \text{C}_{60} \) in a toluene solution (eqn (3))

\[
\text{A}_x\text{C}_{60(\text{ins})} + \text{C}_{60(\text{sol})} \rightarrow \text{A}_x\text{C}_{60(\text{ins})} \quad (3)
\]

The characteristic color of \( \text{C}_{60} \) in toluene disappears after approximately 30 min and all the \( \text{C}_{60} \) precipitates. The as-precipitated material does not show superconductivity. \( ^1 \text{H} \) NMR and weight gain measurements indicate a composition \( \text{Rb}_3\text{C}_{60} \cdot (\text{C}_6\text{H}_5\text{CH}_3)_x \), for the reaction with \( \text{A} = \text{Rb} \). It is presumably the \( \text{C}_{60} \) anions that are solvated rather than the cations in this case. Powder X-ray diffraction shows that this material is crystalline. The powder pattern has not been indexed, but shows a prominent 10.0 Å peak previously associated with solvated \( \text{C}_{60} \) phases [38]. DSC measurements show an endotherm at \( 350^\circ \text{C} \), presumably associated with solvent loss. The strong tendency for solvation of both anions and cations in this system makes finding a true solution route challenging.

We have prepared \( \text{A}_x\text{C}_{60} \) (\( \text{A} = \text{Na}, x = 2,3; \text{A} = \text{K}, x = 3 \)) by reaction of solid \( \text{C}_{60} \) with solid \( \text{AH} \) or \( \text{ABH}_4 \) as shown in eqns (4) and (5)

\[
x\text{AH} + \text{C}_{60} \rightarrow \text{A}_x\text{C}_{60} + \frac{x}{2} \text{H}_2 \quad (4)
\]

\[
x\text{ABH}_4 + \text{C}_{60} \rightarrow \text{A}_x\text{C}_{60} + \frac{x}{2} \text{H}_2 + \frac{x}{2} (\text{B}_2\text{H}_6) \quad (5)
\]

These reactions are convenient because it is much easier to handle small quantities of \( \text{AH} \) or \( \text{ABH}_4 \) than the alkali metal. The reactions were run in sealed Pyrex ampoules after grinding the reagents together in a mortar and pestle. \( \text{K}_3\text{C}_{60} \) prepared by eqn (5) (200°C for 12 h, 275°C for 4 h, 350°C for 72 h) gave as sharp a superconducting transition as we have seen from any reaction. These reactions are closely related since the reaction temperature is near the temperature that borohydrides decompose to give hydrides. It is
noteworthy that graphite reacts with KII to form the ternaries KH$_{0.8}$C$_6$ and KH$_{0.8}$C$_6$. No tendency to form ternary hydrides was observed for C$_{60}$ under our conditions, but Wudl et al. [37] have shown that alkyl borohydrides add H to C$_{60}$. These routes are particularly attractive for Na since its low vapor pressure and reactivity with pyrex present problems for the direct reaction of Na and C$_{60}$. Kelty et al. [10] used Hg amalgams to prepare A,C$_{60}$ with K, Rb, Cs and mixed alkalis. We have also used the amalgam Na,Hg to prepare Na,C$_{60}$. Analogous reactions with graphite again lead to ternary phases [39] which we have not observed for C$_{60}$.

NMR

$^{13}$C NMR has proven a useful spectroscopy for fullerenes, affording information on the structure, dynamics and electron structure [21, 22, 25, 27, 40]. For pristine C$_{60}$, the room temperature $^{13}$C spectrum consists of only one motionally narrowed line at 143 ppm corresponding to freely rotating molecules [21, 22, 25]. Transition to the ordered Pa$_{3}$ structure at 260 K is accompanied by a sudden increase in the spin–lattice relaxation rate, (1/T$_1$) [25], but continued motional narrowing indicates that molecular rotation remains fast on the NMR timescale down to ~140 K. Analysis of the temperature dependence of the relaxation rate indicates energy barriers to molecular reorientation of 42 meV above 260 K and 250 meV below 260 K [25].

Room temperature $^{13}$C NMR spectra of a variety of A,C$_{60}$ compounds are shown in Fig. 6. The positions of the centers of gravity (isotropic shifts) of the NMR lines are listed in Tables 2 and 3. The $^{13}$C resonances of the A,C$_{60}$ are shifted downfield from that of pure C$_{60}$. The overall shifts are the sum of chemical shifts and (for the conducting phases) Knight shifts. The magnitudes and signs of the Knight shifts are currently under study. It is apparent from the $^{13}$C shifts that there is no simple monotonic correlation of the shifts with the formal charge on C$_{60}$. At room temperature, the $^{13}$C spectra of Na$_2$C$_{60}$, Na$_3$C$_{60}$, K$_3$C$_{60}$, Na$_4$CsC$_{60}$, Rb$_2$C$_{60}$ and Na$_5$C$_{60}$ show significant motional narrowing, indicating that C$_{60}$ anions reorient on a timescale less than ~100 μs. At low temperatures, where molecular rotation is very slow, crystallographically inequivalent carbons generally have different $^{13}$C chemical and Knight shift tensors. The NMR spectra are therefore superpositions of powder patterns from the inequivalent sites. Differences in the shift tensors for different sites lead to a residual line broadening in A,C$_{60}$ (e.g. compared with pure C$_{60}$) even when molecular reorientation is rapid. The various chemical shifts and lineshapes of the A,C$_{60}$ make NMR a useful tool for evaluating phase purity.

In addition to $^{13}$C, we have used $^{23}$Na and $^{87}$Rb spectra to gain information about the alkali sites. The resonances for both $^{23}$Na and $^{87}$Rb are very close to the values for the ions in aqueous solution in agreement with the description of these compounds as A$^+$ C$_{60}^-$. For Rb,C$_{60}$ there are two resonances at room temperature with an approximately 2:1 ratio at ~5 and ~130 ppm, which we assign to the tetrahedral and octahedral sites, respectively. Powder X-ray refinements indicate that K and Rb are disordered in K$_{1.5}$Rb$_{1.5}$C$_{60}$, but $^{87}$Rb NMR finds approximately equal amounts of Rb on both sides, indicating that there is substantially more than a statistical occupation of the octahedral site by Rb as expected based on the larger size of Rb$^+$ than K$^+$. 

**ELECTRONIC PROPERTIES**

The overriding interest in A$_x$C$_{60}$ is the occurrence of superconductivity for compounds with $x = 3$. Superconducting transitions in A$_3$C$_{60}$ are readily measured by d.c. magnetization. The susceptibility measured on warming, after cooling in zero field, gives a diamagnetic shielding. Representative shielding curves for superconducting A$_3$C$_{60}$ are shown in Fig. 7 and the $T_c$'s are tabulated in Table 2. The fraction of observed diamagnetism to that expected
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Fig. 7. Shielding measurements for $A_1C_{60}$ normalized to the shielding at 5K.

for the same volume of perfect diamagnetism is the shielding fraction, or volume fraction. The shielding fraction is a quantitative determination of the phase purity of a superconductor only if the sample morphology is known. For example, anomalously large shielding fractions can be obtained if a closed shell of superconductor surrounds a non-superconductor. For $C_{60}$ there is another effect, related to the finite size of the crystallites. Low values for the shielding fraction are obtained unless the grain size of the superconductor is >10 times the London penetration depth. For these materials the particle size is of the order of 1 μ and the penetration depth of $K_2C_{60}$ is $\approx 4800$ Å [41]. A two fluid model suggests the maximum shielding for a loose powder to be near 35% for these parameters [42]. The superconducting $T_c$ of $A_1C_{60}$ are plotted against lattice parameter in Fig. 8 along with $T_c$ [43-45] and lattice constants [46] for $K_2C_{60}$ and $Rb_2C_{60}$ determined under pressure. For $a > 14.2$ Å the 1 atm and pressure data are in excellent agreement, with substantial differences only for the smallest cations where structural anomalies have been noted above. A plot of the $T_c$ against the intercalated cation volume (Fig. 9) extrapolates to $T_c = 0$ near 20–22 Å [3] corresponding to the compositions $Na_2KC_{60}$–$Na_2RbC_{60}$. $T_c$ extrapolates to zero for about the same cation size for which the $A_1C_{60}$ unit cell reaches a minimum (Fig. 3). Furthermore, compositions on the low cation volume branch of Fig. 3 are also apparently non-metallic (based on $^3C$ $T_c$ measurements). Disordered displacements of Na+ ions on octahedral sites could contribute to electron localization for the low cation volume compositions. In addition, the $Na_2C_{60}$ structure suggests covalent interactions and the possibility of only partial charge transfer. If partial charge transfer does play a role it appears to be more significant for Na on the octahedral site, since the $T_c$ of $Na_2CsC_{60}$ is as expected based on extrapolated values. It is interesting to note that the cell volumes of the $A_1C_{60}$ has a very similar dependence on intercalant volume to the $A_2C_{60}$, leading to the possibility of higher $T_c$s for this series if the electron count could be manipulated to half-fill the $t_2u$ band (three electrons per $C_{60}$).

In order to understand the origin of the superconductivity in $A_1C_{60}$ and the magnitude of the $T_c$s, a more complete picture of the electronic properties is needed both above and below $T_c$. In addition, properties of the other $A_2C_{60}$ are of intrinsic interest and may add insight into superconductivity. The unavailability of single crystals, or even dense pellets, combined with the air sensitivity of the compounds have limited the number and variety of experiments relevant to the elucidation of electronic properties. Conductivity measurements have been reported only for thin films [47-51]. These measurements show small increases in the resistivity with decreasing temperature for $K_2C_{60}$ and $Rb_2C_{60}$, with depressed $T_c$ attributed to granularity [50]. It has further been

Fig. 8. The relationship of the superconducting $T_c$ to the unit cell size of $A_1C_{60}$. □ is data from Table 2. ● and △ are data from $K_2C_{60}$ and $Rb_2C_{60}$, respectively, under pressure as given in Ref. 46.

Fig. 9. Superconducting $T_c$s plotted against calculated cation volume for $A_1C_{60}$.
suggested that the conductivity is near the Mott minimum metallic limit [49]. These studies also show that the A$_x$C$_{60+x}$ phases are insulating. A number of other techniques such as $^{13}$C NMR [27, 40], bulk magnetic susceptibility [51], EPR spin susceptibility [51, 52] and photoemission [12, 53–56] have been used to address the question of metallic conductivity and density of states. There is a general consensus from all of these techniques that the A$_x$C$_{60+x}$ (with the exception of those with Na on octahedral sites) are metallic with the other structures being non-metallic. Calculation of densities of states for A$_x$C$_{60}$ from each of these techniques, however, involve approximations and vary considerably from each other.

The EHT band structures [57] calculated for FCC C$_{60}$, Pa$_3$ C$_{60}$ and A$_x$C$_{60}$ (x = 3, 4, 6) are shown in Fig. 10. As discussed previously [47], the EHT calculations provide a qualitatively correct description of the conduction bands of C$_{60}$. The band structure calculations indicate that the DOS distributions of the $t_{2g}$- and $t_{2g}$-derived bands are relatively constant across the different phases. The band widths and energy spectra remain qualitatively unchanged, and thus the molecular features of C$_{60}$ dominate the electronic structure of the doped phases. It is clear from Fig. 10 that the A$_x$C$_{60}$ phases will be insulators (filled conduction band), and that phases with x = 3, 4 and (presumably) 2 are all predicted to have partially filled bands. Of significance to the density of states, the band width for A$_x$C$_{60}$ decreases with increasing unit cell parameter resulting in an increase in the density of states at E$_F$ of approximately 15% for Rb$_3$C$_6$ over K$_3$C$_{60}$ [8].

Information on metallic conductivity and density of states may be obtained from NMR using the Korringa relationship. The Korringa relaxation mechanism predicts that $T_1 T$ should be constant for a metal [58]. Both K$_3$C$_{60}$ and Rb$_3$C$_{60}$ exhibit $^{13}$C $T_1 T$ values that are only weakly dependent on temperature [27, 40]. Just above $T_c$, $T_1 T = 100$K-s for Rb$_3$C$_{60}$ and 165K-s for K$_3$C$_{60}$. Assuming relaxation by a contact hyperfine interaction between nuclei and non-interacting electrons, with a magnitude of 0.6 Gauss, the $T_1 T$ values imply densities of states at the Fermi energy of roughly 22 eV$^{-1}$ and 17 eV$^{-1}$ for Rb$_3$C$_{60}$ and K$_3$C$_{60}$ (per C$_{60}$ per spin state). For Na$_2$C$_{60}$, $T_1 T$ increases by a factor of six with decreasing temperature from 373 K to 93 K and that of Na$_2$Rb$_2$C$_{60}$ increases by more than a factor of two over this temperature range, suggesting loss of metallic conductivity for the A$_x$C$_{60}$ with the smallest cations. For the A$_x$C$_{60}$, A$_x$C$_{60}$ and A$_x$C$_{60}$ phases examined to date, $T_1 T$ is strongly dependent on temperature, indicating that they are not metallic. For x = 6 the insulating behavior is expected from filling of the $t_{2g}$ band. The origin of insulating behavior for x = 2, 4 is not known, but could arise from a localized Jahn–Teller distortion on C$_{60}^{-}$, a collective charge density wave, a Mott–Hubbard insulator or carrier concentrations below the Mott limit.

A useful basis for discussion of the magnitude and range of $T_c$ in the A$_x$C$_{60}$ and of possible pair mediating excitations is the McMillan equation [59]

$$T_c = \frac{k_B}{\gamma} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right],$$

where $\lambda = N(E_F)V$, $V$ is the strength of the coupling of the conduction electrons to the mediating excitation of frequency $\omega$ and $\mu^*$ is the renormalized Coulomb repulsion between conduction electrons. The relationship is valid for weak or intermediate coupling ($\lambda \leq 1.5$). Supercconductivity in the A$_x$C$_{60}$ has been attributed to phonon mediated pairing either via purely intramolecular C$_{60}$ modes [60–62] ($\approx 1000$–$2000$ K) or low energy A-C$_{60}$ optic modes [63] ($\approx 200$ K). Purely electronic coupling has also been proposed [64–66]. The modes calculated to have strong coupling to the conduction electrons are Raman active. In thin film samples, these modes [67] (predominantly $H_4$ symmetry) become unobservable on formation of A$_x$C$_{60}$ then reappear on formation of A$_x$C$_{60}$. Inelastic neutron scattering on bulk samples is consistent with this observation [68]. The fact that both K$_3$C$_{60}$ and Rb$_3$C$_{60}$ have virtually the same $T_c$ when they have the same lattice constant (under pressure) is strong evidence against involvement of modes containing the A ions. $^{13}$C isotope effect
experiments, on the other hand, show the involvement of C-based modes. Three experiments have been reported with $a$ ($T_c \propto M^{-1}$) of $1.4 \pm 0.5$ [69] and $0.37 \pm 0.05$ [70] for Rb$_2$C$_6$O and $0.30 \pm 0.06$ [71] for K$_2$C$_6$O. In our experiment [70] a decrease of $T_c$ by 0.65 K for Rb$_2$C$_6$O ($x = 0.37 \pm 0.05$) was found for a sample with 75% enrichment with $^{33}$C. Measurements of the superconducting gap are similarly divergent: values of 5.3 have been suggested from STM point contact tunneling [72, 73] although optical data [74] suggest a gap of $3-5kT_c$ and NMR data suggest $3-4kT_c$ [40]. Definitive and reproducible measurements of physical properties critical to a complete understanding of superconductivity in A$_2$C$_6$O are still needed.

SUMMARY

In this paper we have described the synthesis, structures and physical properties of A$_2$C$_6$O. Most of the compounds can be synthesized by direct reaction of C$_6$O with alkali metals at 200–300°C, although a wider variety of chemistry is available with the exception of the FCC A$_2$C$_6$O structure. The compounds are best described as salts of C$_6^-$ and have structures consistent with those predicted on the basis of ion size and electrostatic considerations. The A$_2$C$_6$O$_x$ form a class of isostructural superconductors with $T_c$ scaling with unit cell size. The important parameters needed to understand superconductivity in the A$_2$C$_6$O$_x$ are emerging, but there is considerable diversity in data from different sources and experiments that is typical of materials at this stage of development.

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