

Na₄C₆₀: An Alkali Intercalated Two-Dimensional Polymer

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The long-missing stoichiometric phase of Na₄C₆₀ has been identified by Rietveld analysis of synchrotron powder diffraction data. Its monoclinic structure is based on polymer planes of C₆₀ where each molecule forms four “single” bonds within the plane. This compound is not only the first fulleride polymer with such bonds, but also the first two-dimensional polymer which is naturally intercalated with alkali ions and can be synthesized at ambient pressure. Na₄C₆₀ is a metal and is expected to be a prototype structure where electronic overlap between the planes can be tuned by the alkali cation size. [S0031-9007(97)03291-2]

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A remarkable feature of C₆₀ molecules is that they may form bonds with each other leading to a variety of crystal structures and physical properties. Possible polymerization was first suggested for phototransformed pure C₆₀ [1]. The convincing evidence for bonding was observed in AC₆₀ alkali fulleride polymers [2–4]. The quality of structural [4] and NMR data [5,6] rendered the bonding unquestionable, and suggested this scenario for systems where experimental data were less convincing. High-pressure high-temperature synthesis of pure C₆₀ also leads to polymerized structures [7–10], some of which are two dimensional. In all these cases the mechanism for bond formation is the Diels-Alder type [2 + 2] cycloaddition leading to a characteristic four-membered ring of carbon atoms. Recently a different type of interfullerene bond was detected [11] in a metastable phase [12,13] of AC₆₀ where (C₆₀)₂²⁻ dimer anions are formed by joining single carbon atoms (one “single” bond). Up to now there have been no reports on fulleride-polymer formation based on this type of bond.

Alkali intercalation into the C₆₀ host lattice is a successful technique [14] for synthesizing new fullerenes, among which superconducting A₃C₆₀ compounds have received extended attention [15]. The Na_xC₆₀ system was studied during the search for higher *T_c*'s but neither superconductivity nor bond formation was found in this system. Compositions with *x* = 2, 3, 6, and 10 were identified [16,17], all with a face-centered cubic (fcc) structure. In contrast to all the larger alkali cations, sodium preferentially occupies the tetrahedral sites and multiple occupation of the octahedral site is reported for *x* = 6 and 10 [16–18]. This remarkable structural variance was appreciated but as dc conductivity [19] and photoelectron spectroscopy [20] reported insulating behavior for the entire composition range, interest for this system has drooped. Recent experimental and theoretical efforts focused on the incomplete charge transfer for *x* > 6, while around *x* = 4 solid solution behavior was reported [21].

We started a search for a yet unreported stoichiometric phase in the Na_xC₆₀ system after realizing that in samples with nominal composition of *x* = 3 a minority noncubic phase existed. The amount of the new phase did not depend on the synthetic method, reacting stoichiometric amounts of C₆₀ and sodium metal or NaN₃ at 200–400 °C gave the same result. This was in contrast to all previous reports, so we performed a systematic study in the 2 ≤ *x* ≤ 6 composition range. Samples were prepared by the usual solid state reaction of C₆₀ and Na metal, using copper reaction tubes which were cleaned with HF beforehand. After two weeks of reaction at 200 °C and an additional grinding process, the powder samples were sealed in quartz capillaries for x-ray diffraction. Parallel beam x-ray diffraction data were collected at beam line X3B1 of the National Synchrotron Light Source, Brookhaven National Laboratory. This synthesis led to a new phase at the nominal composition *x* = 4.2, and reproduced the known phases at *x* = 2 and 6. The rest of the samples were two-phase mixtures, so neither solid solution behavior nor the previously reported stoichiometric *x* = 3 phase was detected.

Figure 1 shows the x-ray diffractogram of the nominal *x* = 4.2 sample at 300 K. All reflections are indexed [22] with a body-centered monoclinic unit cell with lattice parameters *a* = 11.24 Å, *b* = 11.72 Å, *c* = 10.28 Å, β = 96.2°. This unconventional monoclinic unit cell choice (body center) was chosen to have β close to 90° making it easier to visualize the structure.

The monoclinic unit cell and the skeleton structure of C₆₀ balls are shown in Fig. 2. It is immediately obvious that a special two-dimensional net is generated by the $\frac{1}{2}(\mathbf{a} + \mathbf{b} + \mathbf{c})$ and $\frac{1}{2}(\mathbf{a} - \mathbf{b} + \mathbf{c})$ nearest neighbor directions. The nearest interfullerene distance within the plane is 9.28 Å while it is 9.93 Å out of the plane. The 9.28 Å distance is nearly identical to the center-to-center separation of singly bonded (C₆₀)₂²⁻ [11] and (C₅₉N)₂ dimers [23] as it was shown by experiments [11,24] and quantum chemical calculations [25]. It is plausible that

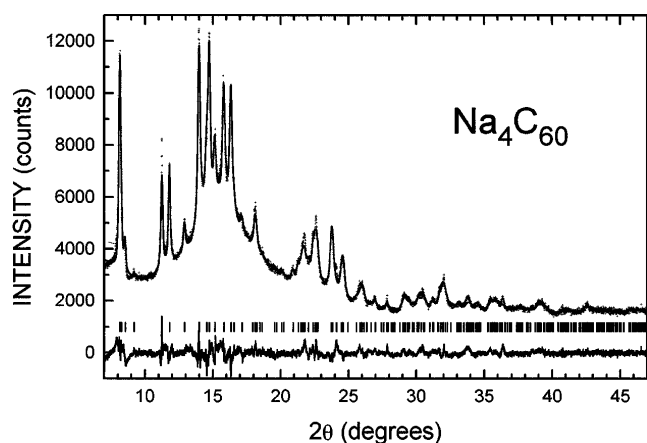


FIG. 1. X-ray diffraction pattern of Na_4C_{60} . X rays of wavelength 1.14893 \AA were selected by a double Si(111) monochromator, and the diffracted beam was analyzed by a reflection from a Ge(111) crystal before the NaI scintillation detector. Observed data are denoted by the data points (+ symbols), calculated and difference plots by solid lines, and allowed reflection positions by ticks. Parameters of the Rietveld fit are given in Table I.

bond formation occurs at an orientation when carbon atoms simultaneously face each other in four directions within the plane (see Fig. 2). If so, the 78.3° intraplanar angle must be close to the central angle between two atoms of the undistorted C_{60} molecule.

The determination of space group and molecular orientations is linked intimately. The trivial space group $I2/m$ gives a fully ordered molecular structure only if the generating C_{60} molecule at $(0, 0, 0)$ is aligned with one of its two-fold axes towards the monoclinic \mathbf{b} direction. Otherwise binary disorder is introduced and there is no symmetry constraint on the fullerene orientation. Simple geometry considerations show that the latter case is more favorable. If bonding atoms along $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$ are chosen so that they are at ends of a zigzag line of

three hexagon-pentagon and one hexagon-hexagon bonds (see Fig. 3), then their 78.8° central angle is within 0.5° of the required intraplanar angle. This arrangement can have four possible orientations relative to the lattice and there is a second competing arrangement with a central angle of 81.1° . General fullerene orientation and absence of disorder can be simultaneously realized in the pseudocentered space group $P2_1/n$. It is for Rietveld refinement to discriminate these possibilities.

There are two symmetrically inequivalent sodium positions in the structure, which are located at centers of distorted tetrahedra. One of the tetrahedral sites [denoted as Na(2) in Table I] can also be viewed as a distorted octahedral site split into two. The size of the alkali sites is a good match for the sodium ion. The multiplicity of both Na positions is four, so the ideal composition for the structure is Na_4C_{60} .

The best Rietveld fit [26] is shown in Fig. 1 and structural parameters are summarized in Table I. The fit is sufficiently sensitive to the orientation of the molecule as a whole but the powder diffraction technique cannot reliably locate each of the 60 carbon atoms. To find the best orientation of undistorted C_{60} we performed extensive R_{wp} mapping with Rietveld fits similar to that described in Ref. [11]. We have taken an unbiased approach and searched the space of fullerene orientations in space group $I2/m$ for the best agreement between the calculated and observed diffraction patterns (definition of Eulerian angles is given in Table I). Two orientations are clearly favored: $(\psi, \theta, \phi) = (-55.3^\circ, 25.8^\circ, 49.1^\circ)$ and $(-124.7^\circ, 154.2^\circ, -130.9^\circ)$ corresponding to bonding configurations depicted in Fig. 2 and are connected by point symmetries 2 and m . Both orientations correspond to the 78.8° central angle of bonding atoms. There is only a 0.03 \AA tangential misfit between bond directions determined by the crystal lattice and corresponding atoms on the surface of the C_{60} molecule. The tangential

TABLE I. Na_4C_{60} structural data derived from the Rietveld fit. Remaining differences between the observed and calculated patterns can be accounted for by the exact molecular geometry.

Lattice parameters	$a = 11.235(5) \text{ \AA}, b = 11.719(5) \text{ \AA}, c = 10.276(5) \text{ \AA}, \beta = 96.16(5)^\circ$	
Space group	$I2/m$ (cell choice 3 of #12)	
$^a\text{C}_{60}$ center	(a) $2/m$ at $(0, 0, 0)$	
b Orientation	$\psi = -55.3^\circ, \theta = 25.8^\circ, \phi = 49.1^\circ$	
$\text{Na}^+(1)$	Occupancy = 1.00	$B = 2 \text{ \AA}^2$
	(h) 2 at $(\frac{1}{2}, y, 0)$	$y = 0.214(3)$
	Occupancy = 0.93(2)	$B = 5 \text{ \AA}^2$
$\text{Na}^+(2)$	(i) m at $(x, 0, z)$	$x = 0.698(3), z = 0.476(3)$
	Occupancy = 0.93(2)	$B = 5 \text{ \AA}^2$
Reliability factors	$R_{wp} = 4.02\%, R_p = 3.12\%, S = 2.2$	

^aThe Cartesian coordinates of the 60 carbon atoms at the reference position are generated by $m3$ point group symmetry from the seed (expressed in angstroms): $C1(0.700, 0.000, 3.479)$, $C2(3.031, 1.425, 1.173)$, $C3(2.598, 0.725, 2.306)$.

^bThe C_{60} orientation is defined by the usual Eulerian angles: $\text{Rot}_z(\psi)\text{Rot}_y(\theta)\text{Rot}_x(\phi)$ in a Cartesian coordinate system where \mathbf{x} , \mathbf{y} , and \mathbf{z} are along \mathbf{a} , \mathbf{b} , and $\mathbf{a} \times \mathbf{b}$, respectively.

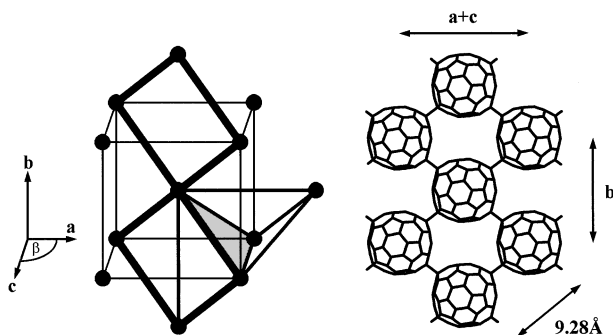


FIG. 2. Left: Body-centered monoclinic unit cell of Na_4C_{60} . Fullerene molecules are denoted by balls; polymer planes are emphasized by bold connections. The two types of face-sharing tetrahedra which enclose sodium cations are also shown. Right: Polymer plane of C_{60} showing the correct orientation and approximate distortion of the molecule. Orientational disorder in $I2/m$ is described by a two-fold rotation around \mathbf{b} .

misfit would be 0.17 \AA for the 81.1° choice of central angle described above and is clearly rejected by our analysis. This indicates the C_{60} molecule's limited flexibility to form polymer structures. The fit degrades only slightly ($\Delta R_{\text{wp}} = 0.2\%$) if one of the orientations is taken in space group $P2_1/n$ corresponding to complete orientational order. However, the symmetries of $I2/m$ constrain alkali positions to be at centers of fullerene tetrahedra, while $P2_1/n$ leaves them at general positions. Atomic coordinates of the C_{60} molecule were not refined, and a comparison with the results of quantum chemical calculations will be necessary to resolve remaining discrepancies between observed and calculated intensities. The distortion of the molecular shape is expected to be less dramatic than for a cycloadduct polymer. It might affect low- q intensities but not the molecular orientation determined in the present analysis.

The temperature dependent spin susceptibility of the sample measured by ESR is shown in Fig. 4. Its magnitude $1.7 \times 10^{-4} \text{ emu/mole}$ at 300 K is to be compared with $8 \times 10^{-4} \text{ emu/mole}$ of metallic RbC_{60} suggesting a larger bandwidth for Na_4C_{60} . The spin susceptibility has a weak temperature dependence; it cannot be fitted simply with a Curie plus Pauli contribution. It rather resembles a strongly correlated metal, like RbC_{60} and CsC_{60} polymers. Here we note that although Na_xC_{60} is generally assumed to be nonmetallic, the gap is small and there is one report in the literature [27] on the metallic behavior for Na_2C_{60} .

The two-dimensional polymerized structure of stoichiometric Na_4C_{60} is unique in several respects. This is the first fulleride polymer with singly bonded monomers. It is the only two-dimensional polymer which is synthesized at ambient pressure in contrast to $[2 + 2]$ cycloadduct polymers of pure C_{60} for which high-pressure, high-temperature synthesis is inevitable. Metallic Na_4C_{60} is naturally intercalated with alkali ions while successful doping of insulating C_{60} polymers has not been achieved. The present result prompts a reinvestigation of $\text{Na}_2\text{AC}_{60}$ ($A = \text{Rb}, \text{Cs}$) high-pressure linear polymers [28]. Their

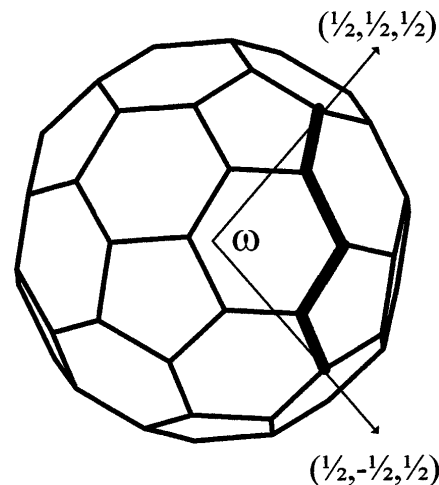


FIG. 3. Bonding atoms of the undistorted C_{60} molecule lying at ends of a zigzag line of three 56 and one 66 bonds. The atoms close an $\omega = 78.8^\circ$ central angle which is within 0.5° the intraplanar angle determined by the lattice.

structure was analyzed on the basis of $[2 + 2]$ cycloaddition bonds while considering the reported lattice parameters single bonds are more likely [29].

The existence of stoichiometric Na_4C_{60} raises new questions. Is the bond purely of σ -type or is there conjugation in the plane? What is the role of off-stoichiometry, does it affect magnetic and transport properties? On the technical side, reports on stoichiometric Na_3C_{60} and on solid solution behavior of Na_xC_{60} thin films are at odds with the present result and this inconsistency must be resolved.

It is important to check if partial substitution of sodium at the two inequivalent cation sites is possible while preserving the structure. If yes, a family of compounds may emerge where the distance between polymeric planes and thus electronic properties can be tuned by the alkali cation size. We foresee a competition between body-centered tetragonal and monoclinic phases governed by

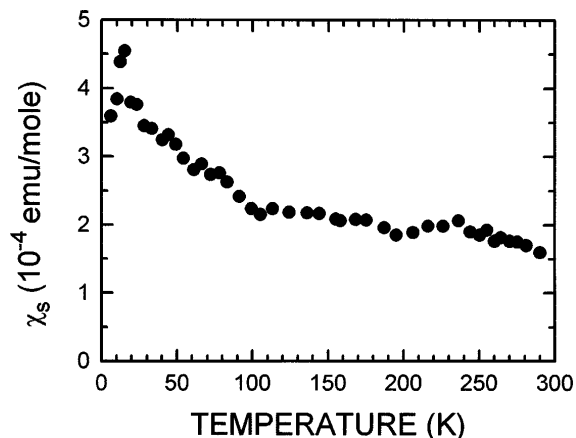


FIG. 4. Temperature dependent spin susceptibility of Na_4C_{60} measured by ESR at 9.4 GHz.

Coulomb attraction and repulsive core overlap. More generally, our result shows that fullerene polymerization as a function of charge state is not yet understood. If bond formation of this type is favored by charge transfer and requires less stringent stereochemical constraints than $[2 + 2]$ cycloaddition, then linear or three-dimensional polymers can also be expected.

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- [1] A. M. Rao, *Science* **259**, 955 (1993).
[2] O. Chauvet *et al.*, *Phys. Rev. Lett.* **72**, 2721 (1994).
[3] S. Pekker *et al.*, *Solid State Commun.* **90**, 349 (1994).
[4] P. W. Stephens, *Nature (London)* **370**, 636 (1994).
[5] K.-F. Thier *et al.*, *Phys. Rev. B* **53**, R496 (1996).
[6] H. Alloul *et al.*, *Phys. Rev. Lett.* **76**, 2922 (1996).
[7] Y. Iwasa *et al.*, *Science* **264**, 1570 (1994).
[8] G. Oszlányi and L. Forró, *Solid State Commun.* **93**, 265 (1995).
[9] M. Nunez-Regueiro *et al.*, *Phys. Rev. Lett.* **74**, 278 (1995).
[10] C. H. Xu and G. E. Scuseria, *Phys. Rev. Lett.* **74**, 274 (1995).
[11] G. Oszlányi *et al.*, *Phys. Rev. B* **54**, 11 849 (1996).
[12] Q. Zhu *et al.*, *Phys. Rev. B* **51**, 3966 (1995).
[13] G. Oszlányi *et al.*, *Phys. Rev. B* **51**, 12 228 (1995).
[14] R. C. Haddon *et al.*, *Nature (London)* **350**, 320 (1991).
[15] For a review, see M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, New York, 1996).
[16] M. J. Rossinsky *et al.*, *Nature (London)* **356**, 416 (1992).
[17] T. Yildirim *et al.*, *Nature (London)* **360**, 568 (1992).
[18] W. Andreoni *et al.*, *Phys. Rev. Lett.* **72**, 848 (1994).
[19] F. Stepniak *et al.*, *Phys. Rev. B* **48**, 1899 (1993).
[20] C. Gu *et al.*, *Phys. Rev. B* **45**, 6348 (1992).
[21] W. Andreoni *et al.*, *Europhys. Lett.* **34**, 699 (1996); J. F. Armbruster *et al.*, *Z. Phys. B* **102**, 55 (1997).
[22] A. Boulitif and D. Louer, *J. Appl. Cryst.* **24**, 987 (1991).
[23] J. C. Hummelen *et al.*, *Science* **269**, 1554 (1995).
[24] C. M. Brown *et al.*, *Chem. Mater.* **8**, 2548 (1996).
[25] J. Kürti and K. Németh, *Chem. Phys. Lett.* **256**, 119 (1996); G. E. Scuseria, *Chem. Phys. Lett.* **257**, 583 (1996); G. Bortel *et al.*, *J. Phys. Chem. Solids* (to be published); W. Andreoni *et al.*, *J. Am. Chem. Soc.* **118**, 11 335 (1996).
[26] Program FULLPROF by J. Rodriguez-Carvajal, ILL, Grenoble, France.
[27] G. K. Wertheim *et al.*, *Chem. Phys. Lett.* **202**, 320 (1993).
[28] Q. Zhu, *Phys. Rev. B* **52**, R723 (1995).
[29] K. Prassides *et al.*, *J. Am. Chem. Soc.* **119**, 834 (1997).