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C₆₀ Intercalated Graphite: Predictions and Experiments

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We propose a new class of Graphite Intercalation Compounds (GICs) containing C₆₀ and alkali metals. The compound C₃₂K₄C₆₀ is predicted and attempts to synthesize it using a C₈K precursor and benzene-dissolved C₆₀ are reported. C₈K samples exposed to C₆₀ and benzene display a reproducible resistive transition at 19.5K indicative of superconductivity. C₈K samples exposed to benzene alone show no transition for T > 4.2K. Possible origins of the superconductivity are discussed.

A wide range of different atomic and molecular species are known to intercalate into the layers of graphite¹. These Graphite Intercalation Compounds (GICs) display many new properties not common to the host material. Superconductivity is observed in several of the GICs intercalated with alkali metals or a combination of alkali metals and Hg, Tl or Bi².

Soon after the availability of macroscopic quantities of C₆₀, it was discovered that pure C₆₀ molecules form a close-packed face-centered-cubic solid³. The large size and spherical shape of the C₆₀ molecule provides for large interstitial spaces in the lattice. A number of atomic and molecular species have been found to intercalate into the C₆₀ lattice. Of great interest are the alkali- and alkali-earth-metal-fullerides, which display metallic phases. Fullerides with stoichiometry A₃C₆₀, where A is K, Rb, or a mixture of alkalis, are found to be superconductors, with superconducting transition temperatures (T_c's) as high as 33K⁴. In addition, the alkali-earth-metal-fullerides Ca₅C₆₀, Sr₆C₆₀, and Ba₈C₆₀ are reported to be superconductors^{5,6,7}. It is notable that in the latter two materials, the C₆₀ molecules form a body-centered-cubic arrangement. In the latter three materials, the number of electrons donated per C₆₀ is expected to differ from the three electrons per C₆₀ expected in A₃C₆₀. Superconductivity is a recurring phenomenon in the fullerenes, even for differing dopant levels and structures.

We propose a new class of materials formed by the intercalation of C₆₀ into a graphite host. This new all carbon material might then be further intercalated with various species to form a wide range of new compounds. Of particular interest is the intercalation of C₆₀ and alkali metals into graphite to form single layers of doped C₆₀ in the graphite galleries. This class of materials holds possibilities for a new family of fulleride-based superconductors. It is expected these new superconductors would, unlike conventional fullerides, be inherently anisotropic. Additional structures resulting from staging, i.e. a well-ordered number of empty graphite galleries between each

intercalated gallery, might also be possible, and hence might be candidates for two-dimensional superconductivity.

As a first step toward predicting the structure of a C₆₀-intercalated graphite system, we note that the intercalant structure in alkali-metal-GICs is found to approximately resemble one atomic plane of the parent alkali metal⁸. If we extend this argument to C₆₀, we find that a plane of atoms in solid C₆₀ perpendicular to the 111 direction has an intermolecular spacing of 10.0Å². This is close to the value of four times the in-plane graphite lattice constant, 9.85Å⁹. A C₆₀ layer with intermolecular spacing of 9.85Å inserted into graphite would give a stoichiometry of C₃₂C₆₀. This structure leaves four interstitial sites per C₆₀ molecule. If we were to fill those sites with a dopant, for example potassium, we would have the stoichiometry C₃₂K₄C₆₀.

Figure 1 depicts the proposed structure and unit cell for C₃₂K₄C₆₀. Note that the interstitial sites lie one on top of another along the c-axis. Therefore in Figure 1a only half of the interstitial sites are shown. If we estimate the distance between C₆₀ molecules and the graphite sheets to be the same as the distance between C₆₀ molecules in solid C₆₀, we arrive at a distance of approximately 13 Å between the graphite sheets as shown in Figure 1b.

It is interesting to speculate on the electronic properties of the proposed compound C₃₂K₄C₆₀. In the absence of a graphite host, bulk K₄C₆₀ has a body-centered-tetragonal structure, and is electrically insulating¹⁰. Intercalated into graphite, K₄C₆₀ may have very different properties: the structure we have postulated differs from the structure of bulk K₄C₆₀, and donation of some charge to the graphite sheets could result in a different doping level for the C₆₀ molecules.

We now turn to the results of a preliminary experimental effort to realize the compound C₃₂K₄C₆₀. Attempts to synthesize the precursor C₃₂C₆₀ through exposure of graphite to C₆₀ vapor or a benzene solution of C₆₀ were unsuccessful. We therefore chose to proceed by first

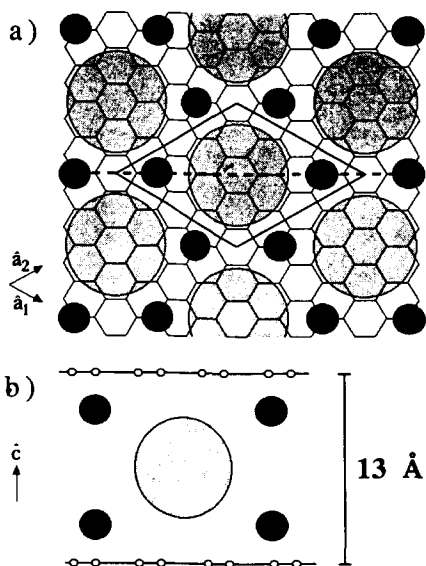


Fig. 1 The proposed arrangement of C_{60} and alkali metal atoms in $C_{32}K_4C_{60}$. C_{60} molecules are represented by the large shaded circles, and potassium atoms by the small dark circles. The unit cell is outlined in (a). Only half of the potassium sites are visible in (a), since the sites lie on top of one another in the c -direction. Fig. 1b is a cross-section of the unit cell along the dashed line in (a), showing the four potassium sites. The carbon nuclei in the graphite planes are denoted by unfilled circles in (b).

synthesizing the stage I potassium intercalated graphite compound C_8K , and then by attempting to intercalate C_{60} . It is of note that C_8K has the same ratio of potassium atoms to graphite carbon atoms as $C_{32}K_4C_{60}$. Use of a C_8K precursor could aid the synthesis in two ways: first the potassium initially spreads the graphite layers thus lowering the energy barrier for C_{60} to enter, and second, there could be charge donation from the potassium to the C_{60} and an accompanying electrostatic interaction which facilitates entry into the graphite. Because of the low vapor pressure of solid C_{60} compared to the potassium vapor pressure of C_8K , we chose to use a solution of C_{60} in benzene for intercalation.

Our starting material for this study was highly ordered pyrolytic graphite (HOPG: Union Carbide grade ZYH). This was cleaved to a thickness of approximately 0.1mm and cut into rectangular pieces. Typical sample dimensions were 5mm X 1mm X 0.1mm, with the smallest dimension corresponding to the c -axis. Contacts to the sample were made using silver paint in an in-line four-probe geometry. The samples were intercalated with potassium via a standard vapor transport method¹¹ to form the stage I intercalated compound C_8K . The stage of the sample was verified visually by its gold color, and by the temperature dependence of its electrical resistance.

Figure 2 shows a typical resistance measurement performed on a C_8K sample. The

samples show the expected quadratic form¹² of $\rho(t)$.

In an attempt to form $C_{32}K_4C_{60}$, C_8K samples were transferred under argon to new tubes containing a solution of C_{60} in dry benzene. The samples were then heated to 80°C while immersed in the solution. Samples exposed to a benzene solution containing a small amount of C_{60} caused the purple color of the C_{60} solution to disappear. The samples prepared for resistance measurements were exposed to C_{60} concentrations well in excess of the proposed stoichiometry.

After treatment with the C_{60} /benzene solution, the samples were then annealed in dynamic vacuum at 100-175°C for several hours in an attempt to drive any excess benzene out of the sample.

Figure 3 shows the resistivity behavior of a typical sample after treatment with C_{60} and annealing at 175°C. The $\rho(t)$ is approximately linear in the region 20-200K, and the resistance drops sharply at 19.5K. The resistivity is current-dependent below 19.5K, decreasing with decreasing current. Although none of the samples measured so far show zero resistance, we believe this transition is due to superconductivity in a fraction of the sample. The dependence of the resistivity on current is consistent with granular or weak-link superconductivity in the sample. A higher current will exceed the critical current of some grains or weak links, leading to a larger resistivity.

We note that C_8K samples that were treated with C_{60} but not annealed in vacuum do not show superconductivity for temperatures above 4.2K. Samples annealed at temperatures as high as 175°C show the transition at 19.5K, and a sample annealed first at 100°C and later at 175°C showed a sharper transition and increased magnitude of the resistance drop after the 175°C anneal.

It has been reported¹³ that benzene intercalates into $C_{24}K$, the stage II potassium GIC, but apparently benzene does not react with C_8K , the stage I potassium GIC, at temperatures up to 50°C¹⁴. This result would imply that the observed change in our C_8K samples on exposure to a benzene/ C_{60} solution is due to the presence of C_{60} . It is possible that benzene co-intercalates with C_{60} into C_8K . We postulate that the annealing process removes some benzene from the sample, and that this benzene removal is necessary for the formation of the superconducting phase. It has been reported that the intercalation of benzene into $C_{24}K$ is only partially reversible, with potassium catalyzing a reaction between the benzene molecules to form biphenyl and related compounds¹³.

To insure that C_{60} was necessary for formation of the superconducting phase, we tested the reaction of a C_8K sample with benzene alone. This sample was prepared in the manner described above, with the exception that no C_{60} was added to the benzene. After heating at 80°C the sample was dark in color and had increased in thickness. This reaction was not reversible on annealing. The resistivity of the sample was also changed, but there was no sign of superconductivity for temperatures greater than 4.2K.

This result suggests that benzene does react with C_8K at the elevated temperature of 80°C, although we cannot rule out the

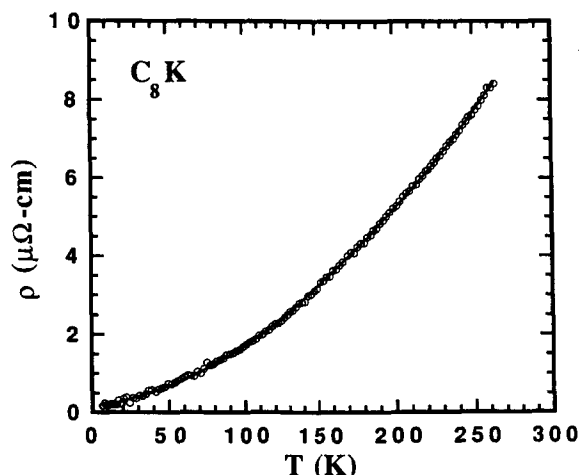


Fig. 2. Resistivity vs. Temperature for a typical C_8K sample before exposure to benzene or C_{60} . The line is a quadratic fit to the data.

possibility that the observed reaction was due to the presence of a small amount of minority phase $C_{24}K$ in our sample, or the presence of unknown impurities in the nominally pure dry, distilled benzene. In any case, the lack of superconductivity in this sample, and the presence of superconductivity in the C_{60} exposed samples only after annealing, suggests that benzene does not play a role in the superconducting phase.

The transition temperature, 19.5K, that we observe in samples of C_8K treated with C_{60} is close to that of bulk K_3C_{60} , which superconducts at 19.8K¹⁵. This raises the possibility of K_3C_{60} being present in our sample, and being responsible for the superconductivity. It is possible that C_{60} is deposited on the surface of, or between exfoliated layers in the samples. This C_{60} could then react with potassium in the sample to form K_3C_{60} . This scenario is unlikely, because C_{60} reacts with excess potassium to form K_6C_{60} , so approximately stoichiometric amounts of potassium and C_{60} would be necessary to form K_3C_{60} . It is also unlikely that this method would account for the reproducibility in the samples.

In summary, we have suggested a new class of materials formed by the intercalation of C_{60}

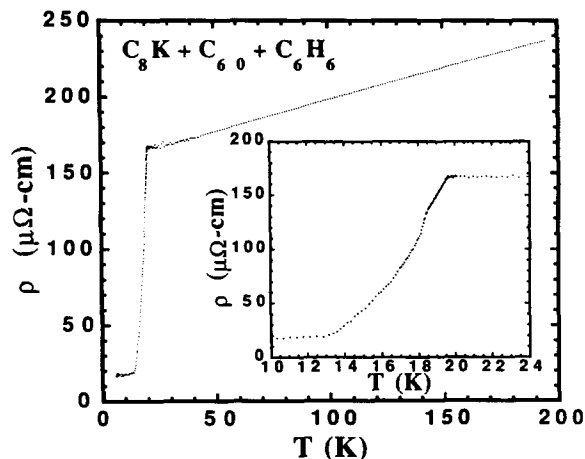


Fig. 3. Resistivity vs. Temperature for C_8K sample exposed to benzene and C_{60} , showing the resistive transition at approximately $T_c = 19.5K$. Note that the resistance is nearly linear in temperature between T_c and 200K. The inset shows the low temperature resistance behavior in detail.

into graphite. Intercalation compounds containing C_{60} and alkali metals may exhibit interesting properties such as anisotropic superconductivity at relatively high T_c 's. A likely structure for graphite intercalated with potassium and C_{60} gives a stoichiometry of $C_{32}K_4C_{60}$. We suggest that this may be achieved experimentally by exposing C_8K to a solution of benzene and C_{60} .

C_8K exposed to C_{60} shows evidence for superconductivity at 19.5K. Further characterization of this material is needed. Measurement of the pressure and magnetic field dependence of T_c could distinguish between the presence of a K_3C_{60} phase or $C_{32}K_4C_{60}$. X-ray diffraction and Raman spectroscopy may help to deduce its structure. These measurements are presently underway.

Note added in proof: After completion of this work we became aware of a recent theoretical study by S. Saito and A. Oshiyama in which the graphite intercalation compound $C_{32}K_4C_{60}$ is investigated¹⁶.

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