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KC_{60} fulleride phase formation: An x-ray photoemission study

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A reversible transformation has been observed in the K_xC_{60} system, for $0<x<3$, which is characterized by a redistribution of K ions within the fcc C_{60} lattice. Below ~ 150 °C the tetrahedral and octahedral sites are occupied in the ratio found for K_3C_{60}, 2 to 1, and C 1*s* photoemission spectra indicate phase separation into α-C_{60} and K_3C_{60}. Above ~ 150 °C, only octahedral sites are occupied for $x<1$, which results in KC_{60} in the NaCl structure. Tetrahedral sites are then successively filled for $x>1$, reflecting K_3C_{60} formation and coexistence with KC_{60}. These results suggest a eutectoid reaction with KC_{60} transforming into α-C_{60} plus K_3C_{60}.

Incorporation of alkali metals, denoted *A*, into solid C_{60} has been found to proceed, in general, by the formation of discrete A_xC_{60} phases with integer values of x.[1–7] At room temperature, line phases with compositions $x=3$ and 4 are now well established, as are terminal compounds of nominal composition $x=0$ and 6 that show a small compositional range. For K_xC_{60}, synthesis can be performed at room temperature due to the facile diffusion of K into the C_{60} host.[4] However, incorporation is generally performed at elevated temperatures, especially for bulk samples, to speed reaction times and to improve homogeneity and crystallinity. Knowledge of the K_xC_{60} phase diagram at higher temperatures is therefore desirable. Recent Raman-scattering[7] and x-ray diffraction[8] results have identified a KC_{60} phase at elevated temperatures. With x-ray photoelectron spectroscopy (XPS), we are able to characterize KC_{60} and observe its transformation into α-C_{60} plus K_3C_{60} upon cooling through ~ 150 °C, thereby identifying an invariant eutectoid reaction and refining the phase diagram for $x\leq 3$. (α-C_{60} denotes the dilute solid solution of K in C_{60}.)

The XPS studies were performed using monochromatized Al $K\alpha$ radiation ($h\nu=1486.6$ eV, Surface Science Instruments SSX-100-03). The resolution was 0.7 eV and binding energies were referenced to the Fermi level. Chromatographically purified C_{60} powder[9] was evaporated from a Ta boat and condensed onto cleaved GaAs(110) in ultrahigh vacuum. A tungsten filament was used to heat the sample. The temperature was measured with an optical pyrometer that was calibrated against a Chromel-Alumel thermocouple attached to the sample face. An estimate of the uncertainty is ±10 °C. During C_{60} deposition, the sample was held at 180 °C. Scanning-tunneling-microscopy studies[10] have shown epitaxial growth under these conditions with $C_{60}(111)$ domains spanning step-free regions of the substrate and commonly attaining ~ 1000 Å lateral dimensions. The C_{60} film thickness, ranging from 150 to 500 Å, was determined based on the attenuation of electrons photoemitted from the GaAs substrate. C_{60} was doped with K at 180 °C using a SAES getter source while maintaining a chamber pressure in the low 10^{-10}-Torr range. The stoichiometry was also varied by adding C_{60} to the K_xC_{60} film at 180 °C. Frequent contamination checks showed that the O 1*s* photoemission intensity was below our detection limit, indicating less than ~ 0.01 at. % O.

In earlier work with A_xC_{60} we showed that the surface concentration was the same as the bulk.[6] Here, the samples were held at 180 °C for ~ 10 h at each stoichiometry and polar-angle-dependent XPS measurements indicated a slight deficiency of K at the surface. This high-temperature loss of K from the surface layer may indicate a thermodynamic preference for K-deficient fulleride surfaces (thermally activated surface vacancy creation). The corrected stoichiometries given herein are derived from K and C photoemission intensities (uncertainty in x of ±0.2).[11]

Previous XPS studies of K_xC_{60} have identified K 2*p* features associated with ions in the octahedral and tetrahedral sites of the fcc K_3C_{60} lattice.[4,6,12] The lower spectrum of Fig. 1 shows the K 2*p* signature at 25 °C acquired for a sample with $x=0.7$. At 25 °C, the relevant portion of the K_xC_{60} phase diagram indicates that the sample is composed of regions of K_3C_{60} and α-C_{60}.[1,3–6] Since the solubility of K in α-C_{60} is small ($x_{max}\sim 0.1$, Ref. 6), this spectrum represents the K 2*p* signature of K_3C_{60}. Stoichiometry-dependent results show that the K 2*p* line shape at 25 °C is nearly unchanged for x between 0 and 3 with account taken of the background from the C 1*s* satellites. The K 2*p* doublets labeled *T* and *O* are due to ions in tetrahedral and octahedral sites, respectively. The binding energy difference, 1.17 eV, is determined largely by a difference in the local Madelung potentials. In K_3C_{60}, all tetrahedral and octahedral sites are occupied and the intensity ratio of the corresponding features is 2:1.

The top spectrum of Fig. 1, obtained from the same sample at 180 °C, shows a single doublet corresponding to K in octahedral sites. The depopulation of tetrahedral sites begins as the temperature is increased above ~ 150 °C. This change in site occupancy is completely reversible over multiple heating and cooling cycles and is also reflected in the K 3*s* and K 3*p* core-level spectra. X-ray diffraction results[8] show a transformation to a KC_{60} phase (NaCl structure) that is completed by ~ 180 °C, in agreement with the exclusive occupancy of octahedral

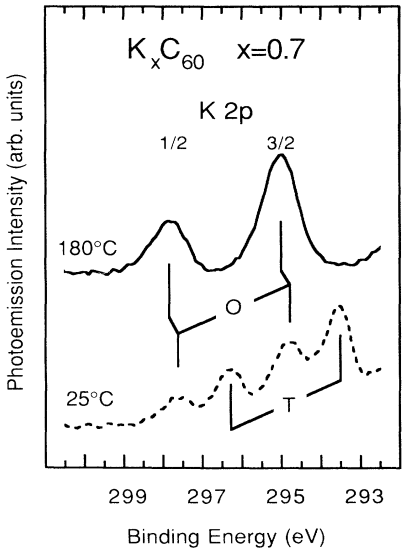

FIG. 1. K $2p$ photoemission spectra ($h\nu = 1486.6$ eV) for $K_{0.7}C_{60}$. The sample is a mixture of α-C_{60} and K_3C_{60} at 25 °C characterized by tetrahedrally and octahedrally coordinated K^+ ions in a 2:1 ratio, as identified for the inequivalent features labeled T and O. For $T > 150$ °C, K ions vacate the tetrahedral sites, occupying only the larger octahedral sites and forming KC_{60} with the NaCl structure.

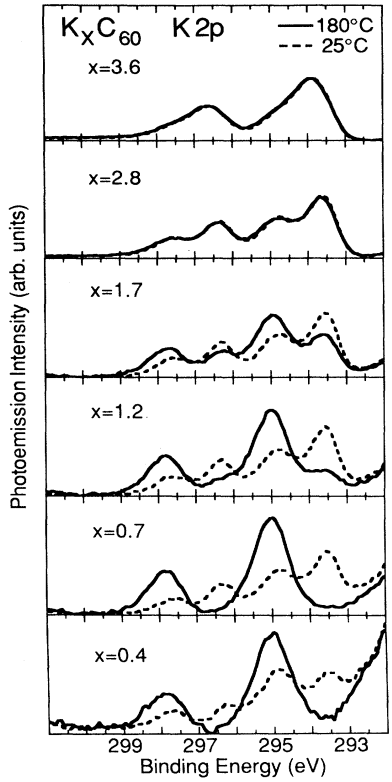

FIG. 2. K $2p$ spectra, as in Fig. 1, for representative stoichiometries. The solid lines show only octahedral site occupancy for $x < 1$ at 180 °C. The dashed spectra show the K_3C_{60} signature for $x < 3$ at 25 °C. The rising background at low binding energy is due to overlapping C $1s$ satellite structure. The spectra are dominated by the K_3C_{60} signature at $x = 2.8$, independent of temperature, and the signature of K_4C_{60} emerges beyond $x = 3$.

sites. Raman-scattering experiments[7] have also indicated a phase characterized by unity negative charge on the C_{60} molecules, although at a somewhat lower temperature.

Figure 2 shows how the K $2p$ spectra evolve with increasing K content at 180 °C (solid lines) and 25 °C (dashed lines). The spectra are normalized to give approximately constant K $2p$ intensities. The room-temperature results show a K_3C_{60} signature that grows on the sloping background of the C $1s$ satellite structure for $x < 3$, as demonstrated by Poirier *et al.*,[6] with minimal change in K $2p$ line shape. Only when there is a significant fraction of α-C_{60} is this trend violated, e.g., $x = 0.4$, but this is expected since the dilute phase is characterized by preferential octahedral site occupancy.[6] Analysis of the spectra for $x > 3$ shows that a new K $2p$ doublet emerges between the O and T features as K_4C_{60} is produced.

The spectra in Fig. 2 show a very different evolution at 180 °C (solid lines) since they demonstrate only octahedral site occupation until $x \sim 1$. Beyond $x \sim 1$, the tetrahedral holes begin to fill. The tetrahedral contribution grows and, finally, the K_3C_{60} signature is obtained. At the final K_3C_{60} state, the spectra are unchanged from 25 °C to 180 °C. Hence, interstitial sites are occupied in the ratio found for K_3C_{60} at 25 °C for $x \leq 3$ while K ions avoid tetrahedral sites at 180 °C until the octahedral sites have been completely filled.

Examination of the C $1s$ spectra at 25 °C shows that the signatures of both α-C_{60} and K_3C_{60} are present for any value of x less than 3, reflecting the two-phase character of the sample.[6] Figure 3 shows the spectrum for $K_{1.2}C_{60}$. The narrow peak at 285.1 eV represents α-C_{60}. The K_3C_{60} signature first emerges as a low binding energy shoulder for $x = 0.4$ but eventually dominates the C $1s$ emission for $x = 2.8$. Spectra at intermediate compositions, as in Fig. 3, represent superpositions of these signatures. A partial decomposition is shown in Fig. 3 where the C $1s$ feature obtained for $x = 2.8$ has been scaled appropriately and is shown by unconnected data points. The center of mass of the C $1s$ feature moves to lower binding energy as K is added, consistent with an increase in average negative charge on the C_{60} molecules. KC_{60} continues this trend since the spectra obtained upon heating to 180 °C show a shift in spectral weight to an energy intermediate to those found for α-C_{60} ($x \cong 0$) and K_3C_{60}. Thermal broadening was found to be negligible between 25 °C and ~140 °C and could not account for the large temperature-dependent changes in line shape. As for the K $2p$ results, there is little temperature dependence for $x > 3$.

The original fulleride phase diagram proposed by Zhu *et al.*[1] suggested a miscibility gap between α-C_{60} and A_3C_{60} based on results for Rb_xC_{60}. In this scheme the solubility limits of A in α-C_{60} and of A vacancies in A_3C_{60} would increase with temperature until the phase boundaries met, producing a single-phase region for $0 < x < 3$. Subsequent work[3,6,13] showed that a generic

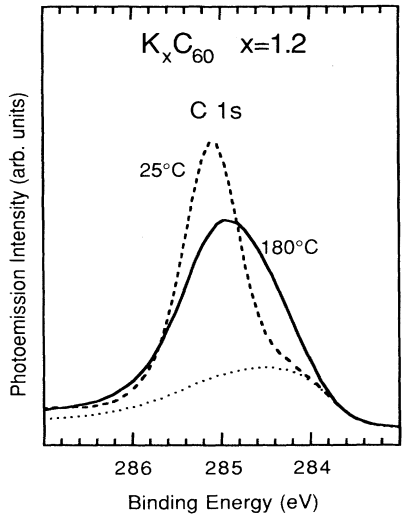

FIG. 3. C 1*s* spectra for $K_{1.2}C_{60}$. At 25 °C, the α-C_{60} signature (peak at 285.1 eV) and the K_3C_{60} signature are present. The unconnected data points show the C 1*s* spectrum for $x = 2.8$ appropriately scaled to show the K_3C_{60} contribution at 25 °C. At 180 °C, the C 1*s* peak is dominated by a KC_{60} contribution and is centered between the α-C_{60} and K_3C_{60} features.

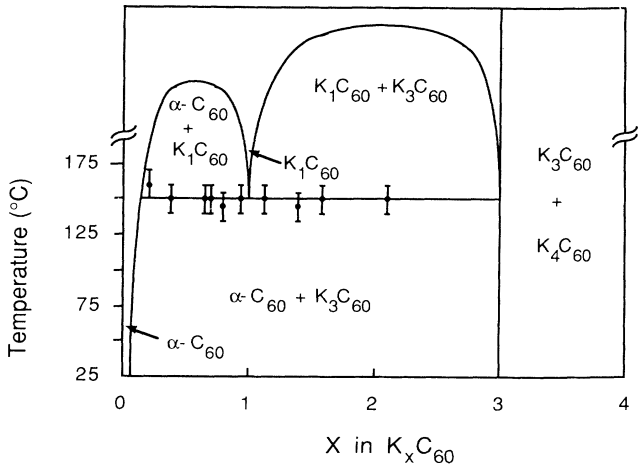

FIG. 4. Proposed binary phase diagram for K_xC_{60} showing a eutectoid transformation $KC_{60} \rightleftharpoons \alpha$-$C_{60}$ plus K_3C_{60} at 150 °C. The measured transition temperatures are indicated by data points. The upper limit of our experimental data is indicated by a break in the temperature axis beyond which no firm temperature scale is implied. We speculate that the two phase regions above the eutectoid are defined by miscibility gaps.

phase diagram does not exist for the alkali-metal fullerides. From the XPS results for K_xC_{60}, we propose an alternate phase diagram which includes an invariant eutectoid reaction $KC_{60} \rightleftharpoons \alpha$-$C_{60} + K_3C_{60}$.

The eutectoid phase diagram of Fig. 4 identifies the transformation of KC_{60} into α-C_{60} plus K_3C_{60} upon cooling below ~150 °C. This transition temperature is independent of stoichiometry between the phase boundaries and the relative amounts of the constituents follow the lever rule. Figure 4 shows that the transition temperatures measured upon heating are constant within experimental uncertainty.[14] The observed reactions were completed over a ~20 °C range of temperature on a time scale of ~30 min. There was hysteresis over a cooling and warming cycle, as expected since the reaction temperature defines the start of the forward and reverse transformations and some degree of undercooling may be necessary for the forward (cooling) transformation to proceed at an observable rate.

The eutectoid phase diagram stipulates coexistence of α-C_{60} and KC_{60} above ~150 °C for $\sim 0.2 < x < 1$. The binding energy of the K 2*p* octahedral feature is invariant with x and this supports the phase separation picture. This insensitivity to x suggests a well-defined octahedral site Madelung potential of the sort found for phase-separated regions of KC_{60} but not for K ions randomly distributed in a solid solution. While the XPS results clearly show the absence of tetrahedral site occupation in this region for either α-C_{60} or KC_{60}, the broad C 1*s* features are less informative.

The eutectoid phase diagram shows coexistence of K_3C_{60} and KC_{60} between $x = 1$ and 3 for $T > 150$ °C. In this region, the binding energy of the tetrahedral component appears in the position expected for K_3C_{60} and does not change with stoichiometry. Line-shape analysis shows the evolution that would be expected if the octahedral feature of K_3C_{60} replaced that of KC_{60} with increasing x. For the C 1*s* feature, decomposition into KC_{60} and K_3C_{60} components can be done, though less convincingly than for the sharply contrasting α-C_{60} and K_3C_{60} signatures at room temperature.[6] We note that the Raman-scattering results support this picture of a two-phase region for $1 < x < 3$ although the apparent transition temperature is lower.[7] We speculate that the two-phase regions above ~150 °C may represent dual miscibility gaps, as drawn, but a firm temperature scale must await measurements at higher temperature than could be achieved with thin films *in vacuo*.

The redistribution of K ions associated with the eutectoid transformation reflects a destabilization of K_3C_{60} relative to KC_{60}. This is probably the result of increased C_{60} motion and the consequent change in size of the tetrahedral holes of the lattice. The radii of C_{60} and K^+ suggest a tight fit for K in the tetrahedral sites, leading Stephens *et al.*[15] to suggest that the C_{60} molecules are locked in place with hexagons facing tetrahedral sites in order to accommodate the cations. Nuclear magnetic resonance (NMR) studies indicate that the speed of C_{60} rotational diffusion is decreased in K_3C_{60} with respect to the pure fullerene solid[5] and this is presumably the result of steric interaction with the K ions. With increased temperature, the C_{60} molecules reorient more rapidly[16] and the hexagonal "dimples" will not face the tetrahedral K ions simultaneously. This effect, coupled with increased intermolecular vibrational amplitudes, reduces the effective size of the tetrahedral site and forces a compensating expansion of the lattice. This reduces the stabilizing Madelung energy and the free energy of K_3C_{60} increases relative to KC_{60}. The transformation is accomplished as tetrahedrally coordinated K ions migrate to vacant octahedral sites of neighboring α-C_{60} domains,

converting the α phase to KC_{60} around the nucleus of the old K_3C_{60} grain. This would proceed until all vacant octahedral sites were occupied or until all the K_3C_{60} had "dissolved," depending on the global stoichiometry. While the KC_{60} phase should be less favorable in terms of the Madelung energy,[3] it is probably preferred on steric grounds. X-ray diffraction results indicate that the lattice constant of KC_{60} is smaller than that of K_3C_{60} and, in fact, smaller than that of pure C_{60}, thereby supporting the hypothesis that the K_3C_{60} lattice is sterically limited.

In addition to KC_{60} in the NaCl structure, x-ray diffraction experiments[8] suggest a disordered fcc "lattice gas" at $x=1$, with K ions occupying tetrahedral and octahedral sites between $\sim 150\,^{\circ}C$ and $\sim 70\,^{\circ}C$ in a 2:1 ratio. Below $\sim 70\,^{\circ}C$ they suggest a third KC_{60} structure, with rhombohedral symmetry, that persists to zero degrees Kelvin. Evidence of a second transition of some type is corroborated by differential scanning calorimetry.[8] Careful inspection of the XPS spectra yields no evidence for these additional structures. We find that the high-resolution C 1*s* spectra are identical between 25 °C and $\sim 140\,^{\circ}C$ and are derived from two features, thereby indicating at least two inequivalent chemical environments for C. Significantly, the two C 1*s* signatures are those found for $x \sim 0$ and 3 and the spectra can be decomposed into appropriate amounts of the K_3C_{60} and α-C_{60} signatures for $0 \leq x \leq 3$ (Ref. 6).

The mixed-site occupation of KC_{60} is in stark contrast to results for RbC_{60} and CsC_{60} where the spectroscopic results showed exclusively octahedral site occupancy and a single C 1*s* feature at 25 °C.[6] NMR results[17] also indicate a similar distinction between KC_{60} and the AC_{60} phases of the heavier alkali metals. XPS investigations of RbC_{60} showed no spectral change between 25 °C and 175 °C, bridging the regime around 60 °C where x-ray diffraction results indicate that the high-temperature NaCl structure distorts to rhombohedral symmetry.[8] While XPS is not expected to be sensitive to a slight change in symmetry, there remains a fundamental discrepancy in the case of K_xC_{60} because the x-ray diffraction results indicate a single phase at room temperature while the XPS, Raman,[7] and NMR (Ref. 5) results indicate a two-phase region for $0 < x < 3$.

The presence of a eutectoid transformation has important implications for synthesis of K_xC_{60} samples with $x < 3$. Specifically, if the sample is heated above $\sim 150\,^{\circ}C$, it will transform partially to KC_{60} and rapid cooling will quench in this high-temperature structure. In our case, we were able to quench in a large portion of KC_{60} by cooling with a thermal time constant of ~ 10 min. In contrast, holding the sample just below the eutectoid temperature for long periods of time should result in large grains in the mixed-phase samples. Variations in the cooling schedule may produce a variety of microstructures.[18]

In summary, we have observed a reversible transformation from KC_{60} into α-C_{60} plus K_3C_{60}. The eutectoid temperature is $(150 \pm 10)\,^{\circ}C$. Coexistence of KC_{60} and K_3C_{60} is found above $\sim 150\,^{\circ}C$ for $1 < x < 3$. For $0 < x < 1$, we show evidence for a mixture of KC_{60} and α-C_{60} above $\sim 150\,^{\circ}C$ although the possibility of an interstitial solid solution in which K ions randomly occupy the octahedral sites of the C_{60} host lattice cannot be completely ruled out. At room temperature, K_xC_{60} consists of phase separated α-C_{60} and K_3C_{60} for $0 < x < 3$.

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