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Phase transitions in KC_{60}: Dimer formation via rapid quenching

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A metastable orthorhombic form of KC_{60} is identified from synchrotron x-ray powder-diffraction measurements. Structure analysis reveals C_{60} dimers with a 9.34 Å center-to-center separation. This structure competes with equilibrium phase separation (α-C_{60} plus K_3C_{60}) and with polymer formation; it is obtained by quenching from above 420 K to 298 K and *immediately* cooling below 270 K. If the polymer is indeed a one-dimensional metal, the dimer structure should be a Peierls insulator.

Intercalation of alkali metals M into the C_{60} lattice is accompanied by essentially complete valence electron transfer from alkali to carbon, resulting in ionic salt structures with excess pseudo-π charge delocalized on the carbons. Band theory predicts that these compounds should be metallic for essentially any alkali concentration; experimentally, the only firmly established metallic phases are the cubic M_3C_{60} binary compounds and pseudobinary solid solutions.[1] Two explanations have been proposed to explain the absence of metallic behavior in other fullerene salts: Fermi surface instabilities in phases with anisotropy, e.g., the tetragonal M_4C_{60};[2] and strong electron correlation effects which lead to finite band gaps in all phases with precisely integral charge[3] (in which case the metallic behavior of "M_3C_{60}" must be attributed to accidental errors in stoichiometry). It is in this context that the monovalent compounds MC_{60} (M= K, Rb, or Cs) have attracted considerable attention.[4–11] These are cubic at high temperatures, so the absence of metallic behavior cannot be attributed to anisotropy. At lower temperatures a metastable orthorhombic structure is found; NMR and EPR results suggest metallic behavior[7,8] consistent with a local-density approximation band structure[11] although the anisotropy should be sufficient to drive a Fermi surface instability.[11] X-ray structure refinement reveals an unusually short intermolecular distance of 9.11 Å which in turn suggests a quasi-one-dimensional polymer[8,9] ("orthopolymer").

Here we report the existence of a second metastable form of KC_{60} which evolves from the high-temperature cubic structure under different cooling conditions than used for the orthopolymer. Its structure is pseudo-orthorhombic, but with a unit cell doubled along **a** and **c**, which we attribute to the formation of C_{60} dimer pairs rather than polymer chains. The obvious inference is that if the orthopolymer is indeed a metal, the dimer phase should be insulating by a Peierls mechanism.

Samples of K_xC_{60} were prepared by direct mixing of K metal and C_{60} powder in an Ar/He atmosphere, sealing in evacuated glass tubes and annealing (the final heat treatment consisting of a week at 720 K). The nominal stoichiometry was $x=1.05 \pm 0.05$. X-ray powder-diffraction data sets were collected between 15–900 K using both a laboratory diffractometer and the X7A beamline at the Brookhaven National Synchrotron Light Source using a double-crystal Ge(111) monochromator and a Ge (220) analyzer. A sample from the same batch was also investigated by NMR.[7]

We have reported previously that the equilibrium structure of KC_{60} above 423 K is a cubic rocksalt-type phase with orientationally disordered C_{60} molecules, K ions in octahedral sites, and an unusually small lattice constant ($\mathbf{a}_0$ = 14.07 Å at 473 K) associated with Coulomb attraction and empty tetrahedral sites.[4] RbC_{60} and CsC_{60} behave similarly. The present samples exhibited a small fraction of K_3C_{60} at 443 K; two-phase Rietveld refinement yielded a global composition x = 1.055(6) consistent with the nominal value. The sample was heated to 573 K, annealed at 400 K (23 K below the rocksalt formation temperature) for 4 h and then cooled to ambient temperature. The 298 K x-ray profile unambiguously revealed two fcc phases, with peak intensities and lattice parameters [14.185(6) Å and 14.246(7) Å] consistent with phase separation into α-C_{60} ($0<x<0.1$) and K_3C_{60}, in agreement with other measurements which indicate that this represents thermodynamic equilibrium.[5–7] More rapid fur-

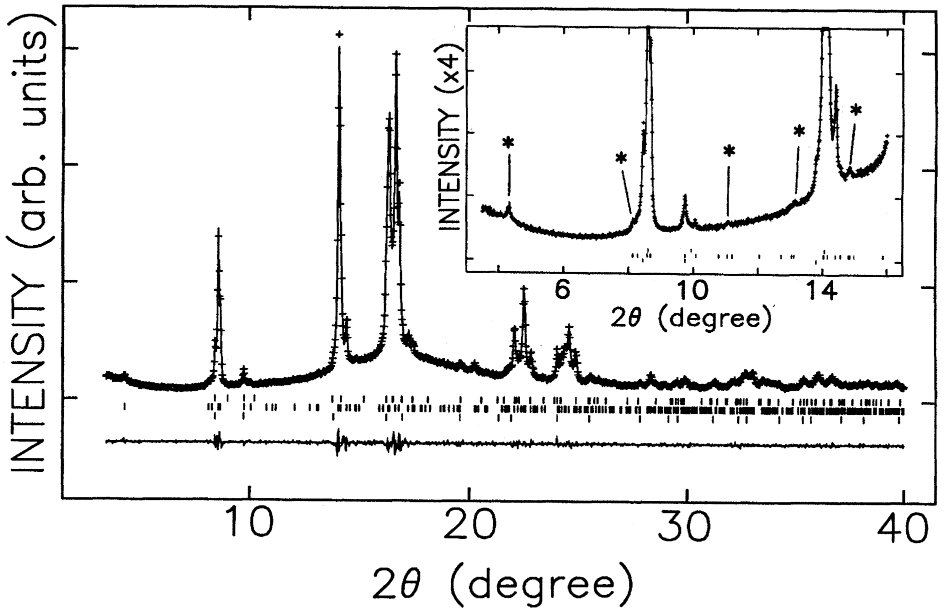

FIG. 1. Synchrotron x-ray powder-diffraction pattern from $K_{1.055}C_{60}$ at 19 K (λ = 1.2054 Å). (+)'s are experimental data and the solid curve is a Lebail fit based on monoclinic symmetry $C2/m$. Minority phase reflections from fcc KC_{60} and K_3C_{60} [$\mathbf{a}$=13.910(5) Å and 14.169(4) Å, respectively] are indicated by the upper and lower markers. Weak superlattice peaks resulting from doubling of the fundamental orthorhombic cell along the $\mathbf{a}$ and $\mathbf{c}$ axes are denoted by (*)'s in the inset.

nace cooling from 573 K to 298 K ($\sim$10 K/min) yielded mainly ($>$70%) the orthorhombic phase[4,9] identified as a polymeric structure with $\mathbf{a}$ = 9.11 Å, $\mathbf{b}$ = 9.95 Å, and $\mathbf{c}$ = 14.32 Å,[9] with minor amounts of α-C_{60} and K_3C_{60}. The lattice constants of the orthopolymer are related to those of the rocksalt cell ($\mathbf{a}_0$) approximately as follows: $\mathbf{a}\approx\mathbf{a}_0/\sqrt{2}$, $\mathbf{b}\approx\mathbf{a}_0/\sqrt{2}$, and $\mathbf{c}\approx\mathbf{a}_0$, $\mathbf{a}$ being considerably shortened relative to $\mathbf{a}_0/\sqrt{2}$ due to the formation of intermolecular bonds. Similar experiments on RbC_{60} suggest that the time scale for the large-scale diffusion necessary for phase separation exceeds several days at $\sim$ 320 K, so the metastable orthopolymer is obtained even with quite slow cooling.

We found a *third* KC_{60} structure by quenching a capillary sample from 573 K into ice water and then immediately cooling further. A 298 K x-ray profile obtained less than 20 min after the quench showed nothing new; phase separation was largely suppressed, and we observed mainly the rocksalt structure with $\mathbf{a}$= 13.98 Å. Maintained at 298 K, the rocksalt gradually transformed to the orthopolymer rather than to the *equilibrium* two-phase mixture with $x\sim$ 0 and 3; the transformation rocksalt $\rightleftharpoons$ orthopolymer involves motions $<$1 Å (Ref. 9) while the macroscopic K diffusion required for phase separation is evidently too slow at 298 K. *On the other hand*, when the quenched sample was immediately loaded into a closed-cycle cryostat and cooled to 19 K, a *new* structure appeared, shown by (+) in Fig. 1. This showed no observable change after 5 days at 120 K. Initial indexing based on the stronger peaks yielded a fundamental body-centered orthorhombic cell at 19 K with $\mathbf{a}$ = 9.609(3) Å, $\mathbf{b}$ = 9.784(3) Å, and $\mathbf{c}$ = 14.156(3) Å, which resembles that of the orthopolymer except that the $\mathbf{a}$ parameter is relatively less shortened (albeit still considerably shorter than in other known intercalation compounds of C_{60}). However, careful inspection reveals several low-angle weak peaks (denoted by asterisks in the inset to Fig. 1), which can only be accounted for by an enlarged cell, doubled along the $\mathbf{a}$ and $\mathbf{c}$ axes, as shown in Fig. 2. The strongest supercell reflection, indexed as (1/2 0 1/2) in the fundamental cell, occurs at a d-spacing of 15.9 Å; thus the true parameters are $\mathbf{a}$ = 19.218(5) Å, $\mathbf{b}$ = 9.784(3) Å, and $\mathbf{c}$ = 28.312(5) Å, roughly $\sqrt{2}\mathbf{a}_0$, $\mathbf{a}_0/\sqrt{2}$, $2\mathbf{a}_0$. The observed peaks satisfy the reflection condition $h+l=$ even, consistent with space group $Bmmm$.

It is easy to establish by structure factor calculations that no C_{60} orientational state can possibly account for such strong superlattice intensities. It is therefore necessary to consider substantial shifts of either the K ions or the C_{60}'s from their ideal positions in the fundamental cell. Models based on K shifts gave very unsatisfactory results, but reasonable agreement was obtained with shifts of adjacent C_{60}'s toward each other along $\mathbf{a}$ so as to form dimer pairs, accompanied by a small rotation about $\mathbf{b}$ to optimize the molecular packing, as illustrated in Fig. 2(b). The formation of such pairs accounts for both the doubling of $\mathbf{a}$ and its contraction ($\mathbf{a}/2$ = 9.61 Å) relative to the rocksalt cell ($\mathbf{a}_0/\sqrt{2}$ = 9.89 Å), while the doubling of $\mathbf{c}$ and the body-centered cell are natural consequences of the optimized packing arrangement shown in Fig. 2(b). However, the combination of dimer formation and rotation results in the loss of two of the $Bmmm$ mirror planes; the reduced symmetry is monoclinic, space group $C2/m$ with $\mathbf{a}_{\text{mono}}$ = 17.109 Å, $\mathbf{b}_{\text{mono}}$ = 9.784 Å, $\mathbf{c}_{\text{mono}}$ = 19.218 Å, β_{mono}= 124.17° [Fig. 2(b)], with K ions and C_{60} molecules at the positions listed in Table I. If the structure is assumed to be completely dimerized, the observed superlattice intensities and the displacements listed in Table I are consistent with a center-to-center separation of 9.34 Å for the dimer pairs,[12] and a rotation angle of $\sim$1°, giving distances of 9.85–9.88 Å for adjacent molecules except for neighbors along $\mathbf{b}$ which are slightly closer at 9.78 Å. The average distances between K(1) and K(2) to the C_{60}

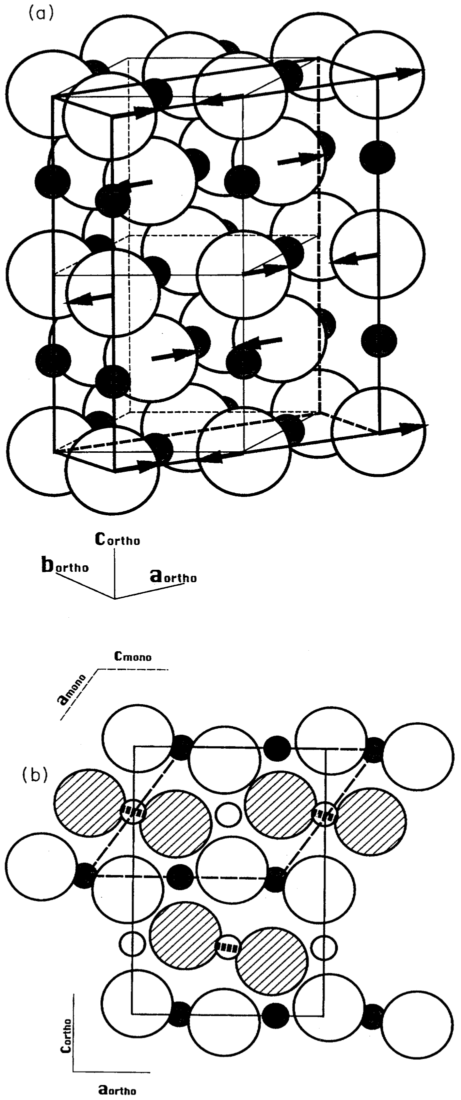

FIG. 2. (a) Three-dimensional perspective illustrating the orthorhombic supercell (heavy outline). The light lines represent two stacked rocksalt cells. Arrows pointing between neighboring C_{60}'s indicate the shifts observed in the formation of dimer pairs. (b) Projection of the KC_{60} structure at 19 K perpendicular to the $\mathbf{b}_{ortho}$ axis, showing the formation of dimer pairs (connected with heavy lines) along the $\mathbf{a}_{ortho}$ axis and rotation about the $\mathbf{b}_{ortho}$ axis. The enlarged orthorhombic unit cell is shown by solid lines, and for clarity, all shifts and rotations have been amplified. The *C*2/*m* monoclinic cell is shown by heavy broken lines. *Large* empty and shaded circles indicate C_{60} at $y=0$ and 1/2, *small* light and dark shaded circles indicate K at $y=0$ and 1/2, respectively.

spheres are 3.34 and 3.41 Å, slightly less than in the rocksalt phase (3.43 Å).

In view of the low symmetry and large unit cell, an unconstrained Rietveld refinement based on the present data was not feasible. We used instead the LeBail technique for pattern decomposition[13] (which does not require a structural model) to extract the unit cell and peak shape parameters. This process was complicated by the presence of some untransformed rocksalt phase (not readily apparent from Fig. 1). The results are summarized in Table II, and provide strong evidence for a small monoclinic distortion, with $\mathbf{a}_{mono}=17.092(1)$ Å, $\mathbf{b}_{mono}=9.771(1)$ Å, $\mathbf{c}_{mono}=19.209(2)$ Å, $\beta_{mono}=124.06(1)°$. Simulated patterns based on this structure with small admixtures of fcc KC_{60} and K_3C_{60} account very well for the main features of the observed pattern, including the superlattice peaks, in the low-angle region where the scattering function for C_{60} is insensitive to the molecular orientations.

TABLE I. C_{60} and K coordinates in the low-temperature dimer phase of KC_{60}, space group *C*2/*m*, $\mathbf{a}_{mono}$ = 17.109 Å, $\mathbf{b}_{mono}$ = 9.784 Å, $\mathbf{c}_{mono}$ = 19.218 Å, $\beta_{mono}=124.17°$. The displacements of the C_{60} molecules are estimated from the intensities of the weak superlattice peaks with the C_{60} molecular scattering factor approximated by a spherical Bessel function $\sin(QR)/QR$ with $R=3.55$ Å.

	Site	Position
C_{60}	4(*i*)	0.006, 0, 0.246
K(1)	2(*b*)	0, 1/2, 0
K(2)	2(*d*)	0, 1/2, 1/2

X-ray scans of selected regions between 19–300 K showed no detectable change up to ~270 K, above which point the superlattice peaks disappeared abruptly [Fig. 3(a)]. This may be compared to the 257 K orientational ordering transition in C_{60}, and we suggest that the transformation *metastable* rocksalt → *metastable* dimer is driven by orientational ordering of the C_{60} molecules, the slight increase in temperature being due to the weak effect of octahedral K on the orientational potential.[14] On further heating to 300 K, drastic changes in the x-ray pattern were observed [Fig. 3(b)], corresponding to the disappearance of the dimer structure and the reappearance of the rocksalt phase together with another phase, tentatively identified as orthopolymer. Cooling again to 260 K showed some irreversible changes in the pattern, with a diminished amount of dimer. This result indicates that the polymer may be formed more readily when the dimer is heated above the ordering transition. We also found that the dimer axis $\mathbf{c}_{mono}$ has essentially zero thermal expansion, a feature shared by the orthopolymer.[9]

Differences in cell volumes are informative. $\Delta V/V$ from quenched rocksalt to orthopolymer (298 K) is ~5.2%, but only ~1.8% from rocksalt to the new dimer structure. The latter is only slightly greater than the 0.9% contraction which accompanies the orientational ordering of C_{60}.[15] The trends

TABLE II. Results of pattern decomposition by the LeBail technique for the 19 K x-ray profile of Fig. 1 ($R_p=2.54\%$, $R_{wp}=3.35\%$, $\chi^2=1.44$).

Phases	Molar Frac.	Lattice parameters
dimer-KC_{60}	90%	$\mathbf{a}=17.092(1)$, $\mathbf{b}=9.771(1)$, $\mathbf{c}=19.209(2)$, $\beta=124.06(1)°$
fcc-KC_{60}	6%	$\mathbf{a}=13.910(5)$
fcc-K_3C_{60}	4%	$\mathbf{a}=14.169(4)$

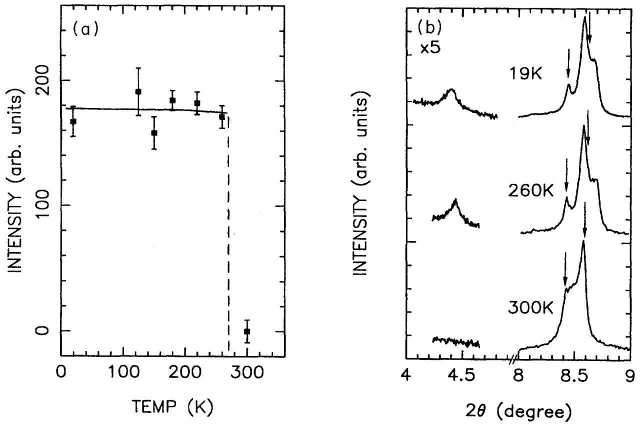

FIG. 3. (a) Variation of (101) superlattice peak integrated intensity upon heating. (b) X-ray data in the regions of the orthorhombic supercell (101) and (012)/(202) peaks at 19, 260, and 300 K, respectively. The (111) reflections from the minority fcc KC_{60} and K_3C_{60} phases are shown by arrows.

in cell volumes suggest that near 300 K the orthopolymer is more stable than the dimer structure, which in turn is more stable than the quenched rocksalt, consistent with the present measurements.[16]

The existence of metastable monoclinic dimer and orthopolymer structures indicates the tendency of C_{60} molecules to coalesce. Calculations show an energy gain of at least 0.2 eV through dimerization.[17] Dimer formation may be driven by orientational ordering, which in turn hinders polymerization.[10,18] The fact that we observed formations of polymer and dimer at such moderate temperatures ($\leq$298 K) suggests the dimerization is not thermally induced, but rather that Coulomb attraction and empty tetrahedral sites which bring adjacent C_{60}'s close together[4] play key roles in the formation of the polymer and dimer phases. Nothing is known about the electronic structure of the dimer phase; the lattice doubling relative to the metallic orthopolymer suggests insulating behavior due to a Peierls transition. There remain many questions to be answered about the dimer structure—distortion from icosahedral symmetry due to intermolecular bond formation,[9] molecular orientations, possible residual disorder, and the nature of the 270 K transition.

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