

Novel Orientational Ordering and Reentrant Metallicity in K_xC_{60} Monolayers for $3 \leq x \leq 5$

Yayu Wang, R. Yamachika, A. Wachowiak, M. Grobis, K. H. Khoo, D.-H. Lee, Steven G. Louie, and M. F. Crommie
*Department of Physics, University of California at Berkeley, and Materials Sciences Division, Lawrence Berkeley Laboratory,
 Berkeley, California 94720-7300, USA*

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STM studies on K_xC_{60} monolayers reveal new behavior over a wide range of the phase diagram. As x increases from 3 to 5 K_xC_{60} monolayers undergo metal-insulator-metal reentrant phase transitions and exhibit a variety of novel orientational orderings, including a complex 7-molecule, pinwheel-like structure. The proposed driving mechanism for the orientational ordering is the lowering of electron kinetic energy by maximizing the overlap of neighboring molecular orbitals. In insulating (metallic) K_xC_{60} this gives rise to orbital versions of the superexchange (double-exchange) interaction.

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Orientational ordering is a classic example of spontaneous symmetry breaking. The highly symmetric icosahedral structure of a C_{60} ball makes the fullerenes ideal systems for studying novel orientational phases [1]. Orientational order also plays a key role in shaping the rich electronic phase diagram of the fullerenes that involves superconducting, metallic, insulating, and magnetic phases [2]. Many basic properties of these phases, such as superconductivity and metal-insulator transition, are controversial due to the difficulty of disentangling the interactions between orientational order and other degrees of freedom, such as intramolecular vibration and intermolecular hopping [3].

Monolayers (MLs) of K-doped C_{60} provide an excellent two-dimensional laboratory for exploring fullerene physics [4–11]. The effect of molecular orientation on electronic structure was seen in recent angle-resolved photoemission spectroscopy measurements that reveal significant differences between metallic K_3C_{60} MLs on Ag(111) and Ag(001) [12]. Long-range orientational ordering in an insulating phase was also observed in K_4C_{60} MLs on Au(111) by scanning tunneling microscopy (STM) [13]. K_4C_{60} MLs were shown to be insulating due to a molecular Jahn-Teller (JT) distortion that is accompanied by crosslike orientational ordering. The local properties of higher-doped K_xC_{60} MLs with $x > 4$, however, have not been explored, and the effects of adding electronic charge to the JT-insulating cross phase are unknown.

In this Letter, we report STM studies of the orientational order and electronic structure of K_xC_{60} MLs over a wide range of K contents in the higher-doped regime. We find that $K_{4+\delta}C_{60}$ MLs with $0.1 < \delta < 0.5$ exhibit C_{60} molecules that retain the JT-insulating state but display a new complex, 7-sublattice pinwheel-like orientational ordering. At $x = 5$ the system reenters a metallic phase that exhibits a novel orientational structure strongly related to the $x = 3$ metallic phase. In the JT-insulating K_xC_{60} MLs a novel superexchange-like mechanism is proposed to be a crucial driving force for the cross and pinwheel phases. In the metallic phases the dominant mechanism for orientational

ordering is the maximization of the overlap of occupied electron wave functions, analogous to the double-exchange interaction.

Our experiments were conducted using a homebuilt cryogenic STM. C_{60} molecules were deposited onto a clean Au(111) surface from a Knudsen cell evaporator. K atoms were dosed onto the C_{60} ML from a K getter. Both K and C_{60} evaporators were calibrated by directly counting the number of atoms or molecules in STM images. K_xC_{60} ML was annealed at 200 °C for 20 min before being cooled to 7 K for STM experiments. After STM measurements at one doping, higher dopings were obtained by adding more K atoms onto the existing ML followed by reannealing. For highly doped MLs with $x > 4.5$, lower annealing temperatures of ~ 140 °C were used to avoid K loss. This method enabled us to fabricate K_xC_{60} MLs with accurate average K contents between $0 \leq x \leq 5$.

Figure 1(a) shows a typical STM image of the new “pinwheel” phase that occurs in $K_{4+\delta}C_{60}$ ($0.1 < \delta < 0.5$) MLs. K deposition in the regime $4 < x < 5$ induces a rearrangement of the C_{60} molecules that destroys the long-range cross phase previously observed in stoichiometric K_4C_{60} [Fig. 1(a) inset], leading to a novel pinwheel-like local structural unit (highlighted in blue). dI/dV spectroscopy of the pinwheel molecules [Fig. 1(b)] reveals an electronic structure very similar to that of the insulating K_4C_{60} cross phase. This suggests that the pinwheel molecules in $K_{4+\delta}C_{60}$ still retain the energetically favorable C_{60}^{4-} JT-insulating charge state seen in the stoichiometric K_4C_{60} cross phase [13]. Thus the difference between the cross and pinwheel phases lies purely in the C_{60} lattice structure and intermolecular orientational order.

As shown in Fig. 2(b), each pinwheel consists of six “wheel” C_{60} molecules arranged hexagonally around a central “pin” molecule (each wheel molecule is rotated by $\sim 60^\circ$ relative to its neighbor). The seven molecules sit on a close-packed triangular lattice, which is a denser packing (by $\sim 5\%$) than the more open cross phase. Figure 2(a) shows an ordered domain of the 7-sublattice pinwheels forming a $\sqrt{7} \times \sqrt{7}R40.9^\circ$ hexagonal super-

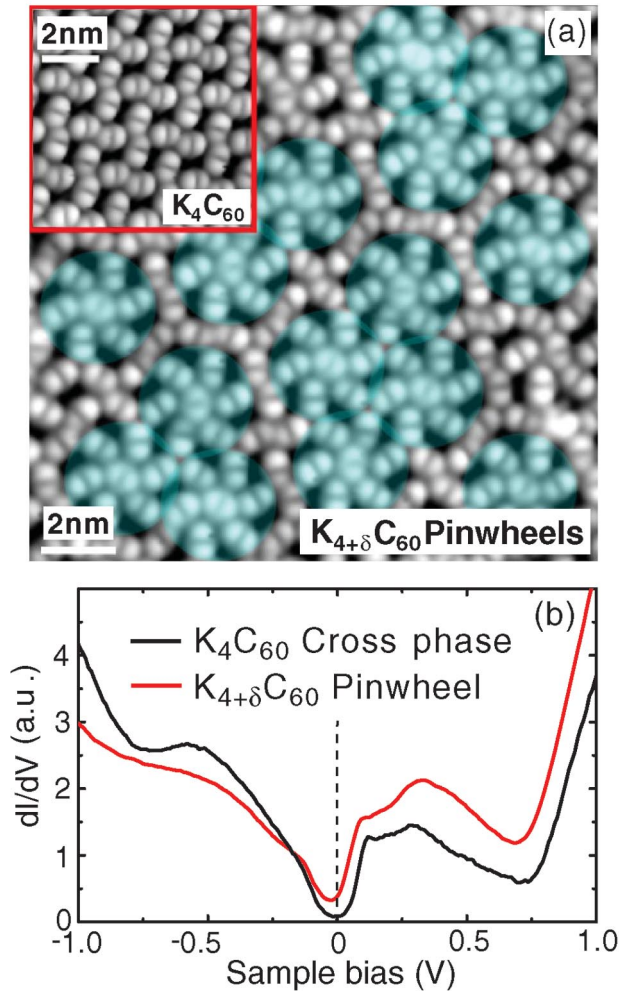


FIG. 1 (color). (a) STM topograph ($V = -0.2$ V, $I = 5$ pA) of a $K_{4+\delta}C_{60}$ ML ($\delta \sim 0.5$) displaying new 7-sublattice pinwheel structures (highlighted in blue). Inset: Topograph of the stoichiometric K_4C_{60} ML shows the cross phase. (b) dI/dV spectroscopy for a single pinwheel molecule (red curve) is similar to spectroscopy measured for molecules in the K_4C_{60} cross phase (black curve).

structure. This suggests that the pinwheels are the structural unit of a new phase rather than merely defects. Both the number and size of the domains grow continuously as the average K content increases from $x \sim 4.1$ to 4.5. This is accompanied by the growth of small C_{60} -free voids containing only K atoms on Au(111).

The orientation of the center pin molecule reveals another novel aspect of the pinwheel structure. Because of the threefold rotational symmetry of the underlying triangular lattice, the pin molecules are free to choose among three degenerate orientations. Experimentally the three possible orientations are randomly realized among the pin molecules, as shown in Fig. 2(a). This type of partial disorder is a hallmark of geometric frustration for orientational ordering on a triangular lattice.

When the K content is increased further to $x \sim 5$, a new stoichiometric, metallic phase emerges, as shown by the

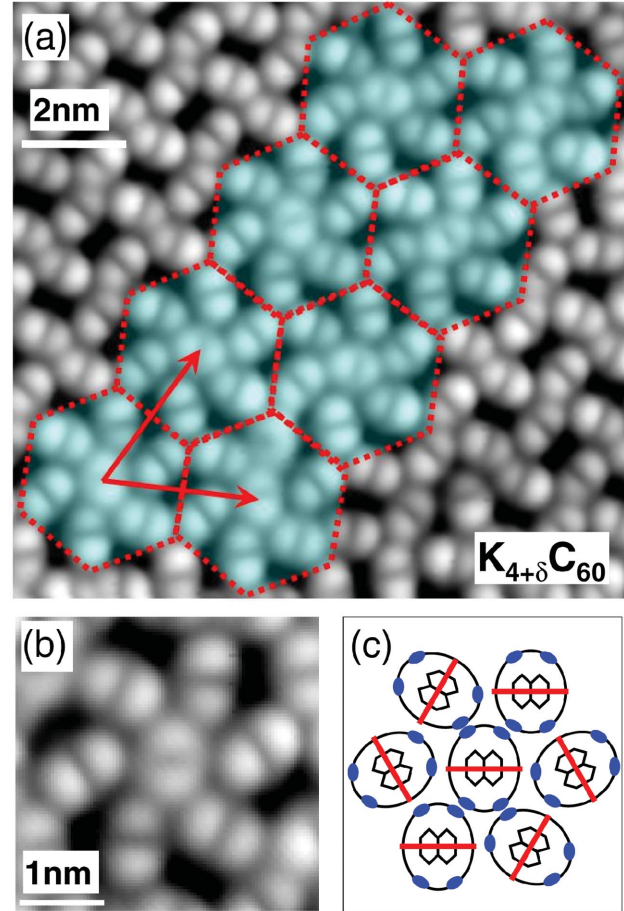


FIG. 2 (color). (a) STM image ($V = -0.2$ V, $I = 5$ pA) of a domain of pinwheels where the 7-sublattice pinwheels form a close-packed $\sqrt{7} \times \sqrt{7}$ superstructure. (b) A close-up image and (c) a schematic structure of a single 7-sublattice pinwheel. The observed line node in STM topography is represented here by a red line.

ordered domain of bright molecules in Fig. 3(a). dI/dV spectra [Fig. 3(b)] reveals that the JT-insulating gap disappears and a finite density of states exists at E_F , indicating a metallic ground state. This indicates that C_{60} molecules in this new phase are in a C_{60}^{5-} charge state where the fifth electron occupies an upper JT split band, as illustrated in Fig. 3(b) inset. The K_5C_{60} molecules form a triangular lattice with a prominent 2×2 superstructure composed of bright “tri-star” features. Each tri-star and its nearest neighbors form a “flowerlike” structural unit, where the tri-star (flower center) exhibits a hexagon facing up and the surrounding molecules (flower petal) exhibit a 6-6 bond facing up [Fig. 3(c)] [14].

The orientational ordering of K_5C_{60} closely resembles that found in the metallic K_3C_{60} ML [Fig. 3(a) inset] in which C_{60} molecules form a $\sqrt{3} \times \sqrt{3}$ superstructure of bright molecules [13]. Figures 3(c) and 3(d) present schematic models of the orientational structure of K_5C_{60} and K_3C_{60} . In both phases the C_{60} molecules form a triangular lattice with all neighboring C_{60} molecules (except the

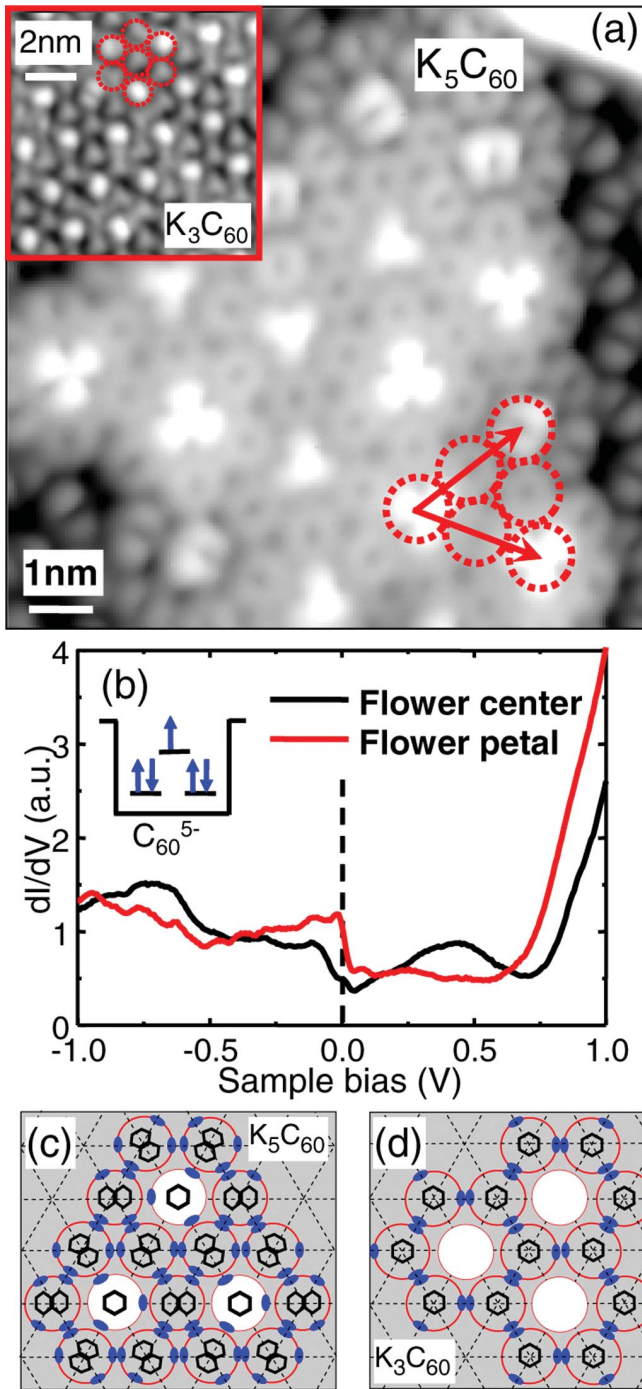


FIG. 3 (color). (a) STM topograph ($V = -0.2$ V, $I = 5$ pA) of K_5C_{60} flower phase exhibiting 2×2 reconstruction. Inset: Topograph of the K_3C_{60} ML. (b) dI/dV spectra of molecules in K_5C_{60} flower phase show finite density of state at E_F . Inset: Schematic K_5C_{60} electronic structure. (c),(d) Model structures for the K_5C_{60} and K_3C_{60} phases. Blue dots represent pentagons on the C_{60} equatorial plane.

central “bright” ones) contacting each other through their equatorial pentagons.

What drives these orientational orderings? The cross and pinwheel patterns are reminiscent of orderings arising from

electrostatic quadrupole interactions [15], which was proposed for other systems [16–18]. It is unlikely, however, that electrostatic quadrupole interactions drive the cross and pinwheel phases seen here because (1) the strength of the quadrupole interaction is too weak (estimated to be only ~ 1 meV between nearest C_{60} neighbors), and (2) our extensive computer simulations cannot reproduce the experimentally observed structures using only a quadrupole-based model [15].

We propose that the main mechanism for all K_xC_{60} orientational phases is the minimization of electron kinetic energy by maximizing the overlap of relevant molecular orbitals. For the JT-insulating cross and pinwheel phases ($4 \leq x < 5$) this leads to a novel superexchange-like mechanism, in which virtual hopping of an electron from the HOMO of one C_{60}^{4-} to the LUMO of its nearest

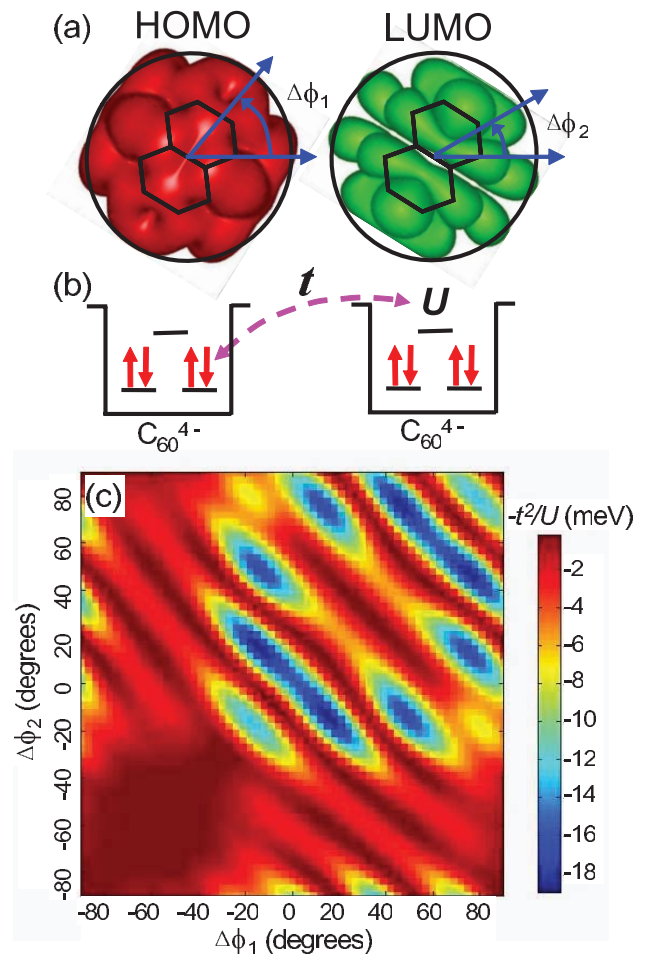


FIG. 4 (color). (a) Local electronic density of states for the HOMO and LUMO of a JT-distorted C_{60}^{4-} molecule calculated by tight binding. (b) Schematic diagram of the proposed superexchange mechanism between two neighboring C_{60}^{4-} molecules. (c) The orientational dependence of $-t^2/U$ obtained from tight-binding calculations for adjacent molecules. The angle (0,0) corresponds to the experimentally observed cross phase.

neighbor [Fig. 4(b)] gains an energy proportional to t^2/U , where t is the hopping amplitude and U is the HOMO-LUMO gap [19]. Here t depends on the overlap between the HOMO and LUMO of adjacent molecules, and thus depends on their relative orientations.

For the stoichiometric K_4C_{60} insulator, this superexchange favors the cross phase. Upon additional K deposition to $K_{4+\delta}C_{60}$ the new pinwheel ordering preserves the local K_4C_{60} stoichiometry and benefits energetically from the JT distortion and superexchange between C_{60}^{4-} molecules by increasing the C_{60} packing density over that of the more open K_4C_{60} cross phase. This occurs via the segregation of added K atoms into the previously mentioned C_{60} -free voids. Adding K atoms to the K_4C_{60} ML thus has essentially the same effect as applying an external pressure, a common driver for structural phase transitions.

This interpretation is supported by tight-binding calculations that we have performed to estimate the strength of intermolecular superexchange and its dependence on molecular orientations. For each carbon atom of the JT-distorted C_{60}^{4-} structure [13], one π orbital was kept and only nearest neighbor hopping was allowed. The hopping integral was assumed to be $-2.3 \times (0.145 \text{ nm}/d)^2 \text{ eV}$, where d is the distance between neighboring carbon atoms [20,21]. Under this approximation the HOMO and LUMO wave functions [Fig. 4(a)] are given by linear combinations of π orbitals located at different carbon atoms: $|\psi_{\text{HOMO}}\rangle = \sum_{i=1}^{60} a_i |\phi_i\rangle$, $|\psi_{\text{LUMO}}\rangle = \sum_{j=1}^{60} b_j |\phi_j\rangle$.

The strength of superexchange is estimated by calculating the HOMO-LUMO hopping integral for neighboring molecules as a function of their relative orientation using $t_{\text{HL}} = \langle \psi_{\text{HOMO}} | K | \psi_{\text{LUMO}} \rangle = \langle \sum_{i=1}^{60} a_i \phi_i | K | \sum_{j=1}^{60} b_j \phi_j \rangle = \sum_{i,j=1}^{60} a_i^* b_j t_{ij}$, where $t_{ij} = \langle \phi_i | K | \phi_j \rangle$. Following Ref. [21] we take $t_{ij} = V_0(r_{ij}/d_0) \exp[-(r_{ij} - d_0)/\lambda] \theta(d_c - r_{ij})$, where $\theta(x)$ is the step function, $r_{ij} = |\vec{r}_i - \vec{r}_j|$, $\lambda = 0.45 \text{ \AA}$, $d_0 = 1.54 \text{ \AA}$, $V_0 = 6.2 \text{ eV}$, and $d_c = 6.5 \text{ \AA}$ [21]. We computed the energy $-t^2/U$ between two adjacent molecules in the unit cell of the $x = 4$ cross structure. We summed the contributions from the two HOMO wave functions and used $U = 200 \text{ meV}$ (the experimental HOMO-LUMO gap). Both molecules were rotated in a plane and $-t^2/U$ values for different orientations were plotted in Fig. 4(c). Here $\Delta\phi_1$ and $\Delta\phi_2$ are the angles of the two molecules relative to the observed cross-phase orientation, whose angle is defined as (0,0). We find (0,0) to be in the trough of a local minimum in $-t^2/U$, with a value of -15 meV . This represents a significant energy gain for the cross-phase structure, and is much larger than the estimated quadrupole interaction. We take this level of agreement as an encouraging sign for our superexchange proposal.

In the metallic K_3C_{60} and K_5C_{60} phases the superexchange mechanism is not applicable. The likely mecha-

nism for orientational ordering here is enhancement of first-order electron hopping via maximization of the overlap of occupied electron wave functions, analogous to the double-exchange interaction. Density-functional theory calculations suggest that in the metallic phases the occupied state density peaks near the C_{60} pentagons [14,19]; hence, it is energetically favorable to have close intermolecular contact between pentagons to maximize electron hopping. As shown in Figs. 3(c) and 3(d), the orientational structures of both metallic phases indeed satisfy this requirement.

In conclusion, we find that K_xC_{60} MLs undergo a reentrant metal-insulator-metal transition as x is varied from 3 to 5. Each electronic phase has a novel orientational ordering associated with it. This includes a highly complex, 7-sublattice pinwheel orientational structure in the insulating $K_{4+\delta}C_{60}$ phase. The proposed superexchange and double-exchange mechanisms highlight the close interplay between orientational order and electronic structure in the fullerides.

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