

Spectroscopic evidence of low-energy gaps persisting up to 120 K in surface-doped *p*-terphenyl crystals

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Using high-resolution photoemission spectroscopy on *in situ* potassium surface-doped *para*-terphenyl crystals, we uncover a low-energy spectral gap of 12 meV. This spectral gap displays a strong temperature-dependent gap-filling behavior and persists up to 120 K, which is consistent with the onset temperature of a weak steplike diamagnetic transition found in this material. Among a few potential candidates for the origin of the observed gaps, we argue that electron pairing is a plausible origin—a possibility consistent with fluctuating Cooper pairs forming near 120 K.

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Multiple studies have reported a step-shape diamagnetic transition in potassium-doped *para*-terphenyl, which shows a high temperature onset of around 120 K [1,2]. The original study has pointed to the Meissner effect and high-temperature superconductivity [1]; however, the Meissner-like signals in these studies were extremely weak, with a volume fraction of about 0.04%. To date, zero resistivity has not been reported from this material, and the origin of this high-temperature magnetic transition remains unsettled. Aiming to spectroscopically explore the high-temperature transition, we present a photoemission study on pristine *p*-terphenyl single crystals with controlled *in situ* potassium metal (K) surface doping in ultrahigh vacuum.

Para-terphenyl is a simple organic molecule composed of three benzene rings arranged end-to-end, as illustrated in Fig. 1(a). These molecules can be packed together in single-crystalline form [Fig. 1(c)], in which case the molecules arrange themselves in a unidirectional stacking as shown in Fig. 1(b). The experiments that reported the weak step-shape diamagnetic transition above 120 K [1,2] were prepared from noncrystalline *p*-terphenyl powders annealed with potassium in an evacuated tube.

Our single-crystal samples of *p*-terphenyl were grown by the zone-refining method [3]. Their crystal structure was identified using x-ray diffraction [3]. Three crystals of similar size (around $0.2 \times 0.5 \times 0.5$ mm) were used. Figure 2(a) shows a schematic of the experiment. The crystals were initially annealed in ultrahigh vacuum at 100 °C, which due to the high vapor pressure of *p*-terphenyl will sublime off any dirty exterior layers. Submonolayer coverages of K were then consecutively dosed onto the clean surface at $T = 300$ K, with the surfaces monitored by x-ray core-level spectroscopy

(XPS) as well as by high-resolution photoemission of the near-Fermi-level features. Figure 2(b) shows spectra for a variety of consecutive doses. There are at least four peaks in the spectra at binding energies (energy below E_F) near 5, 7, 9, and 13.5 eV, respectively, corresponding to various peaks in the valence band/occupied molecular orbitals. For the pristine compound, there is vanishingly small spectral weight for the first 2 eV below the chemical potential, consistent with the optical gaps that are of order 3–4 eV [4]. With consecutive K surface dosings, a potassium 3*p* core level develops at the binding energy around 18 eV, indicating that potassium is incorporated onto/into the surface. Even in the presence of K dosing, the original valence peak features remain robust. This indicates that the potassium doping is perturbative in nature, only minimally modifying the large-scale electronic structure of *p*-terphenyl. On the other hand, the peak positions were monotonically shifted away from E_F , indicating a change in chemical potential and the spectral weight in the vicinity of the chemical potential grows [not visible in the wide scale scan of Fig. 2(b)]. This is consistent with the idea that potassium donates extra electrons to the lowest energy conduction bands.

To date, minimal angle-dependent changes have been observed, which is presumably due to two possibilities. (a) The very weak dispersion expected in organic crystals in which the constituent components are far separated with weak orbital overlap. A flat dispersion [5] combined with strong electronic correlations can cause a strong broadening effect and heavily smear out the momentum-dependent features. (b) Possible disorder of the underlying crystal lattice, or K overlayers which were not annealed after the K deposition can provide extra scattering of the electron, which would smear the momentum-dependent features. For this reason, the present spectra are not labeled by momentum-space positions and should be viewed as representing the average effect across the Brillouin zone.

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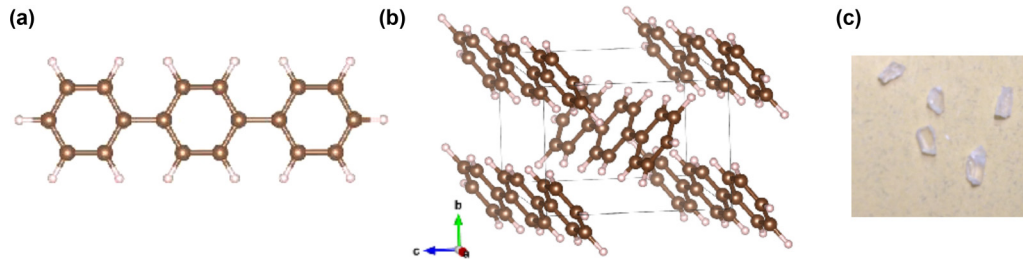


FIG. 1. *p*-terphenyl molecule and crystal: (a) *p*-terphenyl molecule, (b) *p*-terphenyl molecules arranged in a single crystal, and (c) pictures of our bulk crystals of *p*-terphenyl.

With sufficient K dosing, very weak metallic spectral weight appeared near the chemical potential and the material became much more conductive, as also evidenced by the lack of sample charging at low temperatures (see Fig. S1 in the Supplemental Material [6]). This result has similarities to some other doped aromatic organic compounds such as picene and coronene, in which minimal electronic weight was found at the Fermi level [26,27], and is different from doped C_{60} that does show strong spectral weight at E_F [28,29]. A more detailed discussion about the metallic but weak spectral weight at E_F is contained in the Supplemental Material [6].

Figure 3(a) shows the leading edge of the 10-K spectrum, which is pulled away from the chemical potential, as also evidenced by an overlay of this spectrum with that from a metallic gold film measured under identical conditions right after the measurement of the doped *p*-terphenyl. Figure 3(b) shows the very-low-energy regime for sample no. 3 as a function of temperature between 10 and 200 K (see Figs. S3 and S5 in the Supplemental Material [6] for some data on samples 1 and 2). An alternative view of the same spectra is presented in Fig. 3(c), which shows the data of Fig. 3(b) symmetrized about E_F , which has been developed as a powerful way to remove the effect of the Fermi function and better visualize the presence of any low-energy gaps [30].

Here we see that there is a strong suppression of low-energy spectral weight (a gap or pseudogap) that gradually disappears as the temperature is raised. Figure 4(a) shows the spectral weight lost at E_F (integrated over ± 3 meV) that is removed by the low-energy gap, normalized to a maximum effect of 1 at our lowest temperature. It is seen that the low-energy spectral weight is fully recovered at a temperature near 120 K, above which there are minimal changes. This temperature is within error the same as the observed onset of the diamagnetic transition in Refs. [1] and [2], suggesting that the gaps we observe are related to the weak diamagnetic transition.

A few candidate mechanisms for the temperature-dependent low-energy gap exist: (a) The formation of local Cooper pairs at $T = 120$ K, i.e., a gap or pseudogap due to superconductivity or fluctuating superconductivity. (b) The onset of charge density wave (CDW) or spin density wave (SDW) gaps. (c) A Coulomb gap or polaronic gap. Among these we argue that the electron pairing (a) is the most plausible origin because (b) no evidence for a CDW or SDW so far exists in these compounds, and (c) a Coulomb gap or polaronic gap would usually have a much “softer” or slowly varying character as a function of energy. Further, none of the others would be expected to have the temperature dependence shown in Fig. 4(a), while a pairing gap would, especially

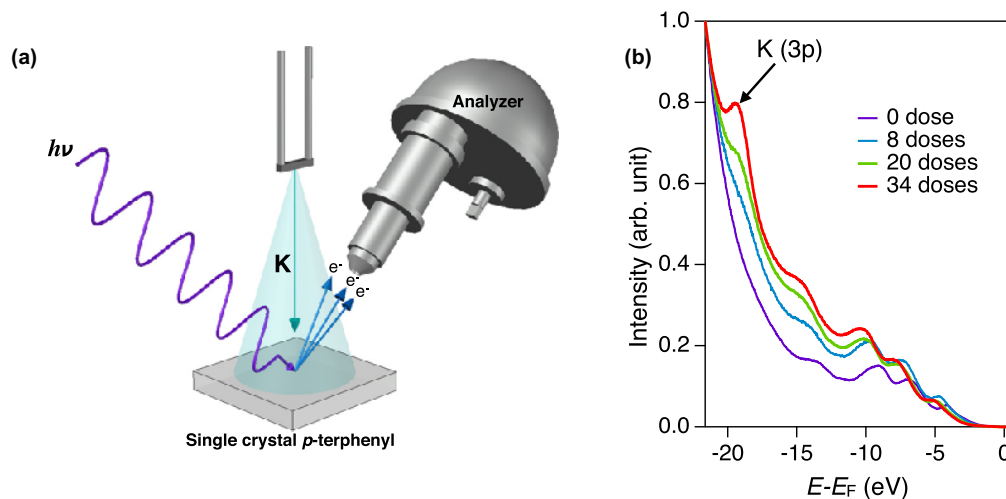


FIG. 2. Experimental setup and overview of photoemission intensity vs doping. (a) The experimental schematic. K was repeatedly dosed onto the surfaces of the crystals, with photoemission spectra taken at these different doses. (b) A wide overview of photoemission intensity vs doping level. The growing intensity of the humps and peak around 18 eV (K 3p) in the photoemission spectra indicate the increasing doping level that follows the number of doses. The shift of the four spectral peaks of the valence band around 5, 7, 9, and 13.5 eV shows the consistent change of chemical potential.

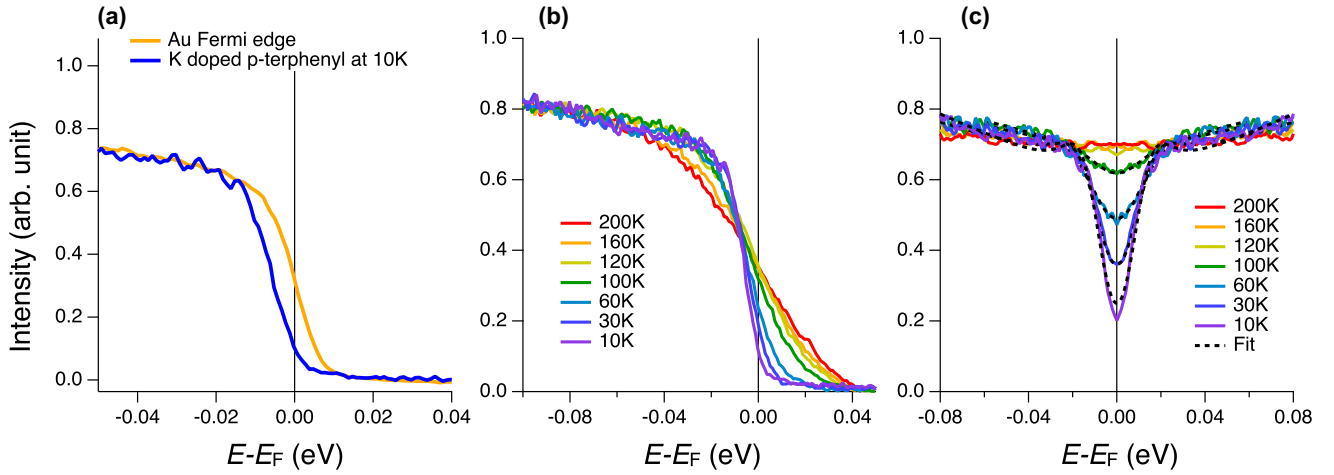


FIG. 3. Spectral gaps from sample no. 3. (a) Comparing sample spectrum to Fermi level reference. The spectrum of the sample shows a leading edge well pushed away from that of the Au reference spectrum. (b) Temperature dependence of the very-low-energy photoemission spectra. (c) The spectra of panel (b) symmetrized about E_F so as to remove the effect of the Fermi function. This data clearly shows the presence of a gap at low temperatures, with the gap “filling in” as the temperature is increased. The dashed lines are fits to the data using Eq. (1), which has two key parameters: a gap Δ and a scattering rate Γ .

considering the onset temperature of the diamagnetic transition. Such a temperature evolution of the lost spectral weight was shown as a signature behavior in the pairing gap of cuprate high- T_C superconductors (see Fig. 3 in Ref. [31]). After our original result was posted on the arXiv [32], a spectral gap on K-dosed *p*-terphenyl was observed with scanning tunneling microscopy (STM) by Ren *et al.* [33]. Although they studied monolayer thin films grown *in situ* instead of the single crystal we used in this study, the STM gap size is very similar to ours, and the gap is found to be particle-hole symmetric, a key signature of a pairing gap. And while STM gaps were insensitive to the application of magnetic fields up to 11 Tesla and so could be considered as in opposition to a pairing gap, it is noted that 11 Tesla is very small compared to the upper critical field of many superconductors, especially those with high pairing energy scales or transition

temperatures—for example, YBCO has upper critical fields up to 100 T, the alkali-metal-doped fulleride superconductor has upper critical fields up to 90 T, etc. [34,35]. Because of this mismatch in field scales compared to the large gap size that both angle-resolved photoelectron spectroscopy and STM observe, we feel that the field insensitivity of the STM studies leaves open the possibility that the observed gap is of pairing/preparing origin. Indeed, the STM work in Ref. [33] also considers the preparing gap as a plausible origin. Regardless of this, it is noted that the magnetic transition signal remains extremely weak and that no clear evidence for zero electrical resistance has yet been reported. The formation of electron pairs does not guarantee superconductivity, where long-range phase coherence between pairs is required. Possible reasons for this will be discussed near the end of the paper.

The gap data of Fig. 3(c) clearly shows the gap-filling behavior with temperature, similar to the cuprate high-temperature superconductors [36–38]. Such a “filling-in” behavior as well as weak or absent “coherence peaks” at the gap edge is most commonly and simply modeled with the Dynes model for the superconducting density of states $N_{SC}(E, T)$ [39]:

$$N_{SC}(E, T) = N_N(E) \text{Re} \left(\frac{E - i\Gamma(T)}{\sqrt{[E - i\Gamma(T)]^2 - \Delta(T)^2}} \right), \quad (1)$$

where $N_N(E)$ is the normal state density of states, and $\Gamma(T)$ represents a scattering rate effect that competes with the pairing gap $\Delta(T)$. The dotted lines in Fig. 3(c) show fits to the experimental data using this equation convolved with the measured experimental resolution function, and with $N_N(E) = a + bE$, i.e., a linearly varying density of states. The parameters extracted from these fits are shown in Fig. 4(b). The gap has a low-temperature magnitude of $\Delta(0) \sim 12$ meV and is roughly constant as the temperature is increased to 60 K or above. The fits also show that Γ , which fills in the gaps, starts small and rises rapidly with temperature, which is a well-known characteristic for cuprate high-temperature

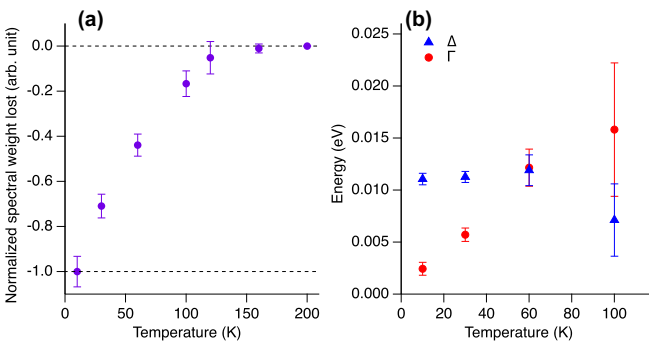


FIG. 4. Spectral weight lost, gap size, and scattering rate. (a) Integrated spectral weight lost ($E_F \pm 3$ meV) in the gap region vs temperature, normalized to the lowest temperature measurement. The error bars denote the standard deviations of the spectral weight lost extracted using different energy ranges for normalizing the spectra. (b) The gap Δ and scattering rate Γ as a function of temperature from the fits of Fig. 3 panel (c). The error bar denotes the 3σ return from the fitting.

superconductors (see Fig. S7 in Supplemental Material [6] and in Refs. [36–38]). With Δ considered as a pairing gap, our fits show that Γ becomes larger than Δ at approximately 60 K. Above this temperature the rate at which pairs are broken will be faster than the rate at which they are created, so we expect that the formation of long-range phase coherence above 60 K would be especially difficult. Our results above 60 K are therefore also strongly reminiscent of the pseudogap (preparing) state in the cuprates, which are widely (but not universally) discussed as a state with preformed Cooper pairs that have not yet condensed into the phase-coherent superconducting state [31,37,40].

The success of the simple Dynes model fitting, as well as the general resemblance of our observed phenomenology to the pairing/preparing gaps of cuprates, enhances the likelihood of electron pairing in this class of materials and indicates that the host of this effect should be the K-doped or K-intercalated *p*-terphenyl itself. In contrast to the original report [1,41] in which the end product is arguably a mixture of different components, in our experiment it is highly unlikely that chemical reactions substantially modified the material phase. Our results also suggest two main possibilities for the extremely weak Meissner-like signal and the absence of the zero-resistance state in measurements to date: (1) This is potentially due to a very weak overlap between various grains in the existing bulk doped (polycrystalline) compounds, which would have to be Josephson coupled to enable superconductivity, therefore leaving a weakened diamagnetic transition signal with all other potential superconducting properties weakened as well [42]. (2) Alternatively, the weak signals might be due to the intrinsically weak electronic overlap between individual terphenyl molecules, which could host local pairing similar to that in a Bose-Einstein condensation picture [43] but have a difficult time fully condensing into a coherent superconducting state with high phase rigidity. This is partly evidenced by the large pair-breaking Γ term shown in Fig. 4(b), by the weak diamagnetic signal, and by the lack of zero resistance so far observed (see a more detailed discussion in Supplemental Material [6]). Such a weak intermolecular overlap is expected in the herringbone stacking pattern of

molecules that pristine *para*-terphenyl crystals are known to crystallize in [Fig. 1(b)]. On the other hand, a planar stacking configuration should have much greater electronic overlap between molecules, so if they can be enticed into this configuration in a doped compound there should be a greatly enhanced possibility for the material to support phase coherence between molecules.

The mechanism of the possible pairing in these materials is also potentially quite different, not just because of the high temperature scales but also because of the unusual structure and chemistry of organic molecular solids. Little's original proposal suggested that a fully electronic (nonphononic) mechanism may be possible [44] and other proposals for organic superconductors including resonating valence bond (RVB) physics [45] as well as bipolaronic pairing mechanisms [46] have been discussed in the context of organic superconductivity. However, since the proposed bipolaron energy scale from Raman spectroscopy is of the order of 180 meV in these materials [1], it is not obvious whether we can connect bipolaron physics to the much lower energy scale gaps that are observed here. The present findings therefore potentially open new and exciting venues into the most fundamental aspects of superconductivity as well.

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