Evidence for phase formation in potassium intercalated 1,2;8,9-dibenzopentacene

Friedrich Roth,1 Andreas König,1 Benjamin Mahns,1 Bernd Büchner,1 and Martin Knupfer1

1IFW Dresden, P.O. Box 270116, D-01171 Dresden, Germany

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We have prepared potassium intercalated 1,2;8,9-dibenzopentacene films under vacuum conditions. The evolution of the electronic excitation spectra upon potassium addition as measured using electron energy-loss spectroscopy clearly indicate the formation of particular doped phases with compositions Kx-dibenzopentacene (x = 1, 2, 3). Moreover, the stability of these phases as a function of temperature has been explored. Finally, the electronic excitation spectra also give insight into the electronic ground state of the potassium doped 1,2;8,9-dibenzopentacene films.

I. INTRODUCTION

Molecular crystals—built from π conjugated molecules—are in the focus of research for a number of reasons. Within this class of materials, almost every ground state can be realized at will, spanning from insulators to semiconductors, metals, superconductors or magnets. Due to their relatively open crystal structure their electronic properties can be easily tuned by the addition of electron acceptors and donors. In some cases, this resulted in intriguing and unexpected physical properties. For instance, carbon based superconductors have a long history dating back to 1965, when superconductivity was found in alkali-metal doped graphite, with transition temperatures of \( T_c < 1 \) \( \text{K} \). Recently, the \( T_c \) was increased up to 11.5 K for calcium intercalated graphite.\(^2\)

However, more than 25 years later the discovery of a superconducting phase in the alkali metal doped fulleride\(^10\) represented a breakthrough in the field of superconductivity and attracted a lot of attention, also because of rather high transition temperatures up to 40 K.\(^6\) In this context, further interesting phenomena were observed in alkali metal doped molecular materials such as the observation of an insulator-metal-insulator transition in alkali doped phthalocyanine,\(^4\) a transition from a Luttinger to a Fermi liquid in potassium doped carbon nanotubes,\(^11\) or the formation of a Mott state in potassium intercalated pentacene.\(^11\)

In the case of organic superconductors, transition temperatures similar to those of the fullerides could not be observed in other molecular crystals until 2010, when superconductivity has been reported for another alkali metal doped molecular solid, K-picene, with a \( T_c \) up to 18 K.\(^12\) Furthermore, after this discovery superconductivity was also reported in other alkali metal intercalated polycyclic aromatic hydrocarbons, such as K-phenanthrene (\( T_c = 5 \text{K} \)), K-coronene (\( T_c = 15 \text{K} \)) and K-(1,2;8,9-dibenzopentacene) (\( T_c = 33 \text{K} \)).\(^13\) Especially in the latter case, the \( T_c \) is higher than in any other organic superconductor besides the alkali-metal doped fullerides. Now, a thorough investigation of the physical properties of 1,2;8,9-dibenzopentacene in the undoped as well as in the doped state is required in order to develop an understanding of the superconducting and normal state properties.

Apart from the introduction of charge carriers, the addition of potassium to dibenzopentacene can also lead to stable phases with particular stoichiometries. A very important prerequisite for detailed studies as well as the understanding of physical properties is the knowledge about such phases and their existence and stability regions. For instance, the physical properties and the conclusive analysis of experimental data of alkali metal fullerenes have been demonstrated to be strongly dependent on the existing phases and their characterization.\(^14\) We discuss the changes that are induced in the electronic excitation spectrum as a function of doping, and we provide clear evidence for the formation of three doped phases with K\(_1\)C\(_{30}\)H\(_{18}\), K\(_2\)C\(_{30}\)H\(_{18}\) and K\(_3\)C\(_{30}\)H\(_{18}\) composition. Moreover, temperature dependent investigations also allowed first insight into the stability regions of those phases, and the electronic excitation spectra suggest insulating as well as metallic ground states.

II. EXPERIMENTAL

1,2;8,9-dibenzopentacene (C\(_{30}\)H\(_{18}\)) is a molecule formed by seven benzene rings as depicted in Fig. 1. It looks like a pentacene molecule with one snapped off benzene ring on both ends. Up to now, no details of the crystal structure are published. Thin films of dibenzopentacene (BGB Analytik AG, 4461 Boeckten, Switzerland) were prepared by thermal evaporation under high vacuum conditions (base pressure lower than \( 10^{-8} \text{mbar} \)) onto single crystalline KBr substrates kept at room temperature with a deposition rate of 0.3 nm/min and an evaporation temperature of about 530 K. The film thickness was about 100 nm. These dibenzopentacene films were floated off in destilled water, mounted onto standard electron microscopy grids and transferred into the spectrometer. Prior to the EELS measurements the films were characterized \emph{in situ} using electron diffraction. The diffraction spectra show no sig-
significant pronounced texture which leads to the conclusion that our films are essentially polycrystalline.

All measurements were carried out using the 172 keV spectrometer described in detail elsewhere. We note that at this high primary beam energy only singlet excitations are possible. The energy and momentum resolution were chosen to be 85 meV and 0.03 Å⁻¹, respectively. We have measured the loss function Im[⁻¹/ε(q, ω)] for a momentum transfer q parallel to the film surface, which probes the electronic excitations of the films [ε(q, ω) is the dielectric function]. In addition, the C1s and K 2p core level excitations were measured with an energy resolution of about 200 meV and a momentum resolution of 0.03 Å. In order to obtain a direction independent core level excitation information, we have determined the core level data for three different momentum directions such that the sum of these spectra represent an averaged polycrystalline sample. The core excitation spectra have been corrected for a linear background, which has been determined by a linear fit of the data 10 eV below the excitation threshold. Since molecular crystals often are damaged by fast electrons, we repeatedly checked our samples for any sign of degradation. In particular, degradation was followed by watching an increasing amorphous-like background in the electron diffraction spectra and a broadening of the spectral features in the loss function. It turned out that under our measurement conditions the spectra remained unchanged for about 14 h at 20 K and 8 h at room temperature. Samples that showed any signature of degradation were not considered further but replaced by newly prepared thin films. The results from the different films have been shown to be reproducible.

Potassium was added in several steps by evaporation from a commercial SAES (SAES GETTERS S.p.A., Italy) getter source under ultra-high vacuum conditions (base pressure lower than 10⁻¹⁰ mbar). In each doping step, the sample was exposed to potassium for several minutes, the current through the SAES getter source was 6 A and the distance to the sample was about 30 mm. Further details of the doping procedure are discussed below.

![FIG. 1. Schematic representation of the molecular structure of 1,2;8,9-dibenzopentacene (C₃₀H₁₈).](image)

III. RESULTS AND DISCUSSION

The amount of potassium in our doped dibenzopentacene films was determined using core level excitation spectra. In Fig. 2, we show C1s and K 2p core level excitations of undoped and potassium doped dibenzopentacene. These data can be used to analyze the doping induced changes of the potassium doped films. Moreover, the C1s excitations represent transitions into empty C 2p-derived levels, and thus allow to probe the projected unoccupied electronic density of states of carbon-based material. All spectra were normalized at the step-like structure in the region between 291 eV and 293 eV, i.e. to the σ* derived intensity, which is proportional to the number of carbon atoms. For the undoped case (red line), we can clearly identify a sharp and strong feature in the range between 283 - 286 eV, which can be assigned to transitions into π* states representing the unoccupied electronic states. The step-like structure above 291 eV corresponds to the onset of transitions into σ*-derived unoccupied levels.

By doping the sample with potassium the spectrum is still dominated by a sharp excitation feature right after the excitation onset at 283 eV and, in addition, by K 2p core excitations, which can be observed at 297.2 eV and 299.8 eV, and which can be seen as a first evidence of the successful doping of the sample. Importantly, a reduction of the spectral weight of the first C1s excitation feature is observed in Fig. 2 upon doping, which can be seen as a further signal of successfully doping because it represents the filling of the conduction band.

The stoichiometry analysis can be substantiated by comparing the K 2p and C1s core excitation intensities in comparison to other doped molecular films with well known stoichiometry, such as K₆C₆₀. Details of this procedure can be found in previous publications. The results shown in the Fig. 2 indicate three different doping levels with KₓC₃₀H₁₈, K₂C₃₀H₁₈ and K₃C₃₀H₁₈ composition, which are discussed in more detail in the
Initial potassium addition to dibenzopentacene causes major changes in the electronic excitation spectrum as revealed in Fig. 3 (left panel), where we show a comparison of the spectra in an energy range of 0–10 eV measured using EELS for different doping steps. These data are taken with a small momentum transfer of 0.1 Å⁻¹, which represents the optical limit. During potassium addition, the dibenzopentacene films have been kept at room temperature.

For undoped dibenzopentacene (red open circles), we can clearly identify maxima at about 5 eV, 5.9 eV, 6.6 eV and 7.3 eV as well as a broad shoulder at about 3.75 eV, which are due to excitations between the occupied and unoccupied electronic levels. Zooming into the energy region around the excitation onset reveals an optical gap of 2 eV. This onset also represents a lower limit for the band gap (or transport energy gap) of solid dibenzopentacene. The excitation onset is followed by three rather weak electronic excitations at about 2.28 eV, 2.43 eV, and 2.62 eV. The main features of our spectrum are in good agreement with previous optical absorption measurements in solution. In general, the lowest electronic excitations in organic molecular solids usually are excitons, i.e. bound electron-hole pairs. We assume that this is also true for dibenzopentacene, a detailed analysis however of e.g. the exciton binding energy requires the knowledge of the so-called transport energy gap, which to our knowledge has not been determined yet.

Fig. 3 (left panel) reveals that upon initial doping, the spectral features become broader. The low energy structures representative of undoped dibenzopentacene decrease in intensity while three new peaks become visible at 1.76 eV, 2.93 eV and 3.7 eV. The latter steadily increase with doping until a particular doping level (labelled with 4 min K doped in Fig. 3) is reached. Most importantly, all spectra in the series as shown in Fig. 3 (left panel) can be simulated by a corresponding superposition of the spectra of undoped and 4 minutes doped dibenzopentacene. This is demonstrated in the inset in Fig. 3 where we show a comparison of the spectrum of a 2 min doped film and a superposition of the two spectra of undoped and 4 min doped dibenzopentacene weighted by 0.55 and 0.45, respectively. In addition, further potassium addition causes qualitative changes of the spectral shape, in particular the appearance of a new feature at 0.65 eV (see right panel of Fig. 3). Consequently, these two facts strongly indicate the formation of a potassium doped dibenzopentacene phase, and our core level measurements signal that we reached a doping level of x = 1. Interestingly, this K₁dibenzopentacene is stable up to 100 °C, i.e. heating up the sample to this temperature did not induce visible changes in the valence band as well as in the core level spectra. Going to 150 °C however resulted in a loss of potassium from the films as could be seen by a reduction of the excitation feature at 1.76 eV. In regard of the electronic ground state of the phase with K₁dibenzopentacene composition, the data in Fig. 3 indicate an energy gap of about 0.9 eV, i.e. this K₁-phase is insulating.

Starting from the above discussed phase (K₁dibenzopentacene) and adding further potassium while the films are kept at room temperature leads to a second doped phase, which is characterized by the additional peak in the electronic excitation spectrum at 0.65 eV, and which according to our core level analysis has a stoichiometry of K₂dibenzopentacene. Moreover, adding more potassium at this stage leads to the formation of a potassium overlayer on our films as signalled by the appearance of the charge carrier plasmon excitation of metallic potassium at 3.75 eV. This indicates that there is no further diffusion of potassium into a film with K₂dibenzopentacene composition at room temperature. Intriguingly, keeping the films at room temperature in our ultra high vacuum chamber results in a loss of potassium after several minutes as signalled by a loss the spectral weight around 0.65 eV, i.e. potassium diffuses out of the film. Cooling a K₂dibenzopentacene film down to 20 K, however, allows to keep the composition stable for at least 15 hours. Again spectra with intermediate composition can be well simulated by the superposition of the spectra of K₁dibenzopentacene + K₂dibenzopentacene.

To summarize at this point, we have prepared two potassium doped phases of dibenzopentacene, K₁dibenzopentacene and K₂dibenzopentacene, which can be achieved by potassium addition at room temperature under UHV conditions and which are well distinguished by corresponding features in the electronic excitation spectra. The temperature stability of these two phases is rather different since the former can be heated to about 100 °C without noticeable changes while the latter is only stable at very low temperatures (20 K).

However, the observation of superconductivity was reported for samples with even higher doping level, between x = 3 and 3.5. In order to realize such high doping levels, we had to change our doping procedure. In detail, we heated up the films during potassium addition (which lasted 15 minutes) to temperatures of 60 - 80 °C, and we annealed the films after each doping step at 80 °C for about 15 minutes. Finally, at least three doping and annealing cycles were necessary to identify clear changes in the electronic excitation spectra as revealed in Fig. 3 (right panel). The feature typical for K₂dibenzopentacene at 0.65 eV disappears and instead a shoulder centered at 0.85 eV shows up. Furthermore, there are slight changes in the double peak structure at 2.93 eV and 3.7 eV. Our measurements of the C 1s and K 2p core level excitations display a doping level of x ≈ 3 (cf. Fig. 2). The necessary annealing during and after potassium addition clearly signals, that potassium diffusion into the dibenzopentacene films requires much higher activation energy at higher doping levels. Interestingly, the observation of superconductivity in samples with about three potassium per dibenzopentacene molecule was made after long time annealing of the doped samples which also indicates hindered potassium diffusion at room temper-
Similar to what we have observed for the K$_1$-dibenzopentacene phase, our films with a K$_3$-dibenzopentacene composition also are stable at 100 °C for more than 15 hours. Further, higher temperatures (150 °C) again results in a loss of potassium from the films, and we observe spectral changes towards the spectral shape as observed for K$_1$-dibenzopentacene. Consequently, this infers a potassium binding energy that is rather similar for these two potassium doped dibenzopentacene phases.

Finally, the excitation spectra for the K$_2$- and the K$_3$-phase do not show clear evidence for an energy gap in contrast to what is observed for K$_1$-dibenzopentacene. Also measurements with higher momentum transfer do not show the opening of a band gap. This could be taken as evidence for a metallic ground state of these phases, in agreement with the observation of a superconducting phase at higher doping levels$^{10}$. However, the presence of the elastic line in our spectra does not allow the determination of the true ground state, metallic or insulating. In general, the doping induced excitation at about 1.76 eV could be interpreted as a transition from the now filled lowest unoccupied molecular orbital (LUMO) of dibenzopentacene to the LUMO+1 level. The lowest energy feature around 0.65 eV then could be interpreted as a charge carrier plasmon of the metallic phases. On the other hand, recent photoemission investigations of potassium doped picene and coronene, two other recently reported superconductors, were not able to identify any metallic doped phase, which might be related to the importance of electron-electron correlation effects$^{19}$. Given these facts, further work is required in order to unambiguously demonstrate well defined and well characterized metallic phases of doped hydrocarbon molecular solids.

IV. SUMMARY

To conclude, we have investigated potassium doping of thin films of dibenzopentacene using electron energy-loss spectroscopy. The doping induced changes in valence band as well as core level excitations, and the temperature dependence of the measured spectra clearly indicate the formation of phases with K$_1$-dibenzopentacene,
Our results thus provide insight into the phase behavior of K$_3$ dibenzopentacene, which we summarize in a provisional phase diagram as depicted in Fig. 4. This schematic diagram also includes a solid solution of potassium in the dibenzopentacene films denoted α, which would form first upon doping. We note that all our experiments have been carried out at a pressure of about 10$^{-10}$ mbar, and that the temperatures as given in Fig. 4 do not represent the atmospheric pressure behavior. Furthermore, film growth and doping by deposition from the vapor phase is characterized by the interplay between thermodynamics and kinetics, which can be nicely seen by the annealing steps that are necessary to achieve a doping level of K$_3$ dibenzopentacene. Finally, our data suggest that K$_3$ dibenzopentacene has an insulating ground state with an energy gap of about 0.9 eV, while K$_3$ dibenzopentacene and K$_3$ dibenzopenta- cene might well be metallic, because we do not find signatures of an energy gap in the electronic excitation spectra.

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