Superconductivity in an organometallic compound

This work reports superconductivity with $T_c$ of 3.6 K in a potassium-doped organometallic compound – tri-o-tolylbismuthine – grown by a two-step method, i.e. ultrasound treatment and low temperature annealing. Using magnetic-susceptibility and electrical-resistivity measurements, the superconductivity in synthesized samples is supported by both the Meissner effect and the zero-resistivity state. The superconducting phase and its composition are determined by the combined studies of X-ray diffraction and theoretical calculations as well as Raman spectroscopy. The present work enriches the physical properties of organometallic compounds in superconductivity.

As featured in:

Organometallic compounds constitute a very large group of substances that contain at least one metal-to-carbon bond in which the carbon is part of an organic group. They have played a major role in the development of the science of chemistry. These compounds are used to a large extent as catalysts (substances that increase the rate of reactions without themselves being consumed) and as intermediates in the laboratory and in industry. Recently, novel quantum phenomena such as topological insulators and superconductors were also suggested in these materials. However, there has been no report on the experimental exploration of the topological state. Evidence for superconductivity from the zero-resistivity state in any organometallic compound has not been achieved yet, though much effort has been made. Here we report the experimental realization of superconductivity with a critical temperature of 3.6 K in a potassium-doped organometallic compound, i.e. tri-o-tolylbismuthine, with evidence of both the Meissner effect and the zero-resistivity state through dc and ac magnetic susceptibility measurements. The obtained superconducting parameters classify this compound as a type-II superconductor. The benzene ring is identified to be the essential superconducting unit in such a phenyl organometallic compound. The superconducting phase and its composition are determined by combined studies of X-ray diffraction and theoretical calculations as well as Raman spectroscopy measurements. These findings enrich the applications of organometallic compounds in superconductivity and add a new electron-acceptor family of organic superconductors. This work also points to a large pool for finding superconductors from organometallic compounds.

1 Introduction

Organometallic compounds, first discovered by Zeise of Denmark in 1827, have been an active frontier in organic, inorganic, coordination and biological chemistry. These compounds usually contain at least one chemical bond connecting a carbon (C) atom of an organic molecule and a metal element (M). Their extensive prospects have been found in applications as catalysts (most famously, Ziegler–Natta catalysts), organic synthesis reagents (commonly, Grignard reagents), anticancer drugs (e.g. metalloene dihalides), and other special reagents (such as antiseptics, sterilizers, and insecticides). However, the applications of their physical properties have not been widely addressed as expected. Recently, these compounds were suggested theoretically as candidates for topological insulators due to their lattice symmetry and strong spin–orbit coupling. In general, many topological insulators can become superconductors by chemical doping or the application of external pressure. It is interesting to examine whether such organometallic compounds could eventually exhibit superconducting properties through some external modifications.

As a typical organometallic compound, tri-o-tolylbismuthine (o-TTB) with the structure of three methyls connected to triphenylbismuth (TPB) in the ortho-position of the C–Bi bond is one example of inexpensive and nontoxic organobismuth reagents. These reagents are widely used in chemical synthesis such as in the preparation of transition metal complexes or as catalysts for polymerization reactions in medicinal chemistry. Very recently, the Meissner effect was reported in potassium (K)-doped TPB, although the evidence for superconductivity from electrical transport measurements is still absent. Meanwhile, tri-p-tolylbismuthine (p-TTB), a methyl derivative of TPB, was found to possess superconductivity at 3.6 and/or 5.3 K after K doping. Here, we choose an o-TTB molecule to examine possible superconductivity by doping an alkali metal. Differing from TPB, one surrounding hydrogen in each phenyl is replaced by methylphenyl in o-TTB.
Although both compounds still share similar physicochemical properties, adding CH₃ in o-TTB affects the molecular geometry due to the different steric hindrance. This in turn induces additional C–H intermolecular interactions. Previous studies have shown that the Bi–Bi distance increases from 5.11 to 5.71 Å from TPB to o-TTB. This may facilitate metal-doping in o-TTB molecules from a spatial arrangement perspective. On the other hand, the addition of methyl generally reduces the symmetry because of the introduction of the lattice distortion. As a result, the symmetry space group changes from C2/c for monoclinic TPB to P1 for triclinic o-TTB. This degradation in structural symmetry as well as intercalation of metal atoms can lead to an increase of the carrier concentration, which helps to enhance the electrical conductivity. Therefore, o-TTB is expected to exhibit better electrical transport properties by simple addition of functional groups.

2 Experimental and computational methods

2.1 Experimental details

Synthesis of potassium-doped o-TTB is the same method as that of intercalated triphenylbismuth, completed by a two-step synthesis method, i.e. ultrasound treatment and low temperature annealing. Alkali-metal potassium (99% purity, Sinopharm Chemical Reagent) was cut into patches and mixed with o-TTB (> 98% purity, Tokyo Chemical Industry). The original stoichiometric ratio (K:o-TTB) is x : 1 (x = 3 and 2). The mixture was sealed in quartz tube with a high vacuum (10⁻⁴ Pa). Then novel ultrasonic processing at 90 °C for 10 h has the advantage of sufficient mixing. The low temperature annealing can avoid KH to yield quality doped crystals. To measure the physical properties of the doped samples, the obtained material was placed into different airtight containers to prevent the dissociation of the sample. A nonmagnetic capsule, diamond anvil cell (DAC), capillary and mylar film were used for sample protection to take magnetization, resistivity, Raman scattering and X-ray diffraction measurements, respectively. The magnetization measurements were completed using a Magnetic Properties Measurement System (Quantum Design MPMS3). The resistivity was measured using a Physical Properties Measurement System (Quantum Design PPMS) with the help of the standard four-probe method. The X-ray diffraction patterns for pure and doped o-TTB were collected using an X-ray diffraction spectrometer using Cu Kα radiation (Bruker D8). The Raman spectra were collected on an in-house system with a spectrometer (Princeton Instruments) at a wavelength of 660 nm and a power less than 1 mW to avoid any damage of the samples.

2.2 Computational details

Our theoretical calculations were performed by using the plane-wave pseudopotential method as implemented in the Vienna ab initio simulation package (VASP) program. The generalized gradient approximation with the Perdew–Burke–Ernzerhof formula for the exchange-correlation potential and the projector-augmented wave method for the ionic potential were used to model the electron–electron and electron-ion interactions. Plane wave basis sets with an energy cutoff of 450 eV and a 3 × 3 × 3 Monkhorst–Pack k-point mesh were adopted for geometry optimization. A finer 5 × 5 × 5 k-point sampling scheme was used for calculating the density of states. The convergence criteria for the energy and max force are set to 10⁻⁴ eV and 0.015 eV Å⁻¹, respectively.

3 Results and discussion

The Meissner effect and zero-resistance are two essential characters for superconductivity. The Meissner effect in K-doped o-TTB with the original stoichiometric ratio of 3 (labeled by A) is confirmed by both dc and ac magnetic susceptibility measurements. Fig. 1(a) shows the temperature dependence of the dc magnetic susceptibility (χₜ) with zero-field cooling (ZFC) and field cooling (FC) runs at a magnetic field of 10 Oe. One can see a sudden drop in χₜ around 3.6 K in both the ZFC and FC runs. The sudden drop of χₜ originating from the well-defined Meissner effect, indicates the occurrence of superconductivity in the studied organometallic compound. $T_c$ is defined as the temperature where a sharp drop takes place. The shielding fraction extracted from $\chi_{dc}$ at a temperature of 1.8 K is about 17%. This is around five times higher than the reported one (3.74%) in K-doped TPB. This significant improvement could benefit from the contributions of the functional group –CH₃. Fig. 1(c) shows the magnetic hysteresis [M–H] loop with scanning the magnetic field up to 2 kOe in the temperature range of 2–3 K. The clear diamond-like hysteresis loop shrinks with increasing temperature. This behavior coincides with the feature of a typical type-II superconductor. $M$ decreases linearly with increasing $H$ in the initial stage until the applied field $H$ exceeds the lower critical field ($H_{c1}$). The temperature-dependent $H_{c1}$ is shown in Fig. 1(d). The inset of Fig. 1(d) shows the method for determining the value of $H_{c1}$ at 2 K, namely the field deviation from linear behavior. An $H_{c1}(0)$ value of 62 ± 2 Oe is thus obtained from the extrapolation to zero temperature based on the empirical law $H_{c1}(T)/H_{c1}(0) = 1 - (T/T_c)^2$. In Fig. 1(b), the diamagnetic signal in the Meissner state is gradually suppressed until being completely faded by the applied magnetic field up to 2 kOe. This is an intrinsic property of a type-II superconductor.

The Meissner effect was also observed below 3.6 K in one sample with a mole ratio of 2 : 1 (labeled as sample B, see Fig. S1 in the ESI†). The observation of superconducting transitions with a near-unanimous $T_c$ in the samples with different starting stoichiometric ratios indicates that the actual mole ratio of synthetical K-doped o-TTB is independent of the original stoichiometric value. The superconducting shielding fraction of sample B estimated from $\chi_{dc}$ at 1.8 K is 8.9%, almost half of sample A.

The ac magnetic susceptibility $\chi_{ac}$ measurements provide further evidence for the occurrence of the Meissner effect, as shown in Fig. 1(e). As a common technology for the identification of the existence of superconductivity, the real component $\chi'_{ac}$ of the ac susceptibility reveals the magnetic shielding, and the imaginary part $\chi''_{ac}$ is a measure of the magnetic irreversibility. Both components of $\chi_{ac}$ exhibit exquisite
changes at around 3.6 K. This temperature is exactly the same as that detected from the temperature dependence of $\chi_{ac}$. Due to the absence of magnetic flux in the normal state, the values of both parts are close to zero. Below $T_c$, the diamagnetic signal in $\chi_{ac}$ drops fast with lowering the temperature due to the exclusion of magnetic flux. In the imaginary part, the flux penetrating the sample falls behind the applied flux to form a positive peak signal. Such a peak signal in $\chi_{ac}'$ implies a tendency to form zero-resistivity in the superconducting state at a qualitative level.

Now we check the existence of the zero-resistivity in K-doped $o$-TTB. Fig. 2(a) displays the resistivity measurements on this compound at ambient pressure. It can be seen that the change of the resistivity with temperature is not regular. There seemingly exists a hump at around 120 K. Above that, the resistivity shows a non-metallic feature. It changes to metallic-like behavior at low temperatures. This phenomenon is probably due to the weak linkage inside the sample or the poor contact between the sample and electrode. However, as the temperature is decreased, the resistivity suddenly shows a sharp drop and then reaches zero at a certain temperature. This observation serves as solid evidence for supporting the existence of superconductivity in this organometallic compound. The onset temperature, below which a sudden drop of the resistivity is observed, is just the critical temperature for this new superconductor. Its value is exactly the same as that detected from the magnetic susceptibility measurements (Fig. 1). The inset of Fig. 2(a) shows the enlarged view of the low temperature resistivity. Zero-resistivity behavior with $T_c \sim 3.6$ K can be clearly observed. Therefore, K-doped $o$-TTB is identified as a new organic superconductor from both the Meissner effect and zero-resistivity state. In comparison with TPB,$^{12}$ adding the $-\text{CH}_3$ group in $o$-TTB does not make much difference for $T_c$ rather than bringing about the increase of the superconducting shield fraction. This indicates that the phenyl is the essential unit for holding superconductivity in phenyl organometallic compounds. The enhancement of the superconducting shield fraction is a key factor for the realization of the zero-resistivity state in K-doped $o$-TTB. Therefore, introducing the functional groups offers a simple but effective means to improve the superconducting properties in organometallic compounds.

The superconducting parameters can be obtained from the field dependences of both the magnetic susceptibility and resistivity. Fig. 2(b) shows the temperature dependence of the resistivity at a pressure of 5 kbar and at various magnetic fields up to 1.3 Tesla. The suppression of superconductivity can be found by the application of magnetic fields. The temperature-dependent resistivity curve systematically shifts toward lower temperatures with increasing magnetic fields. Meanwhile, the temperature span of the superconducting transition broadens significantly as the magnetic field is increased. Superconductivity is completely destroyed at a magnetic field of 1.3 Tesla in the studied temperature range. The temperature-dependent resistivity curves at various magnetic fields allow the determination of an
important superconducting parameter – the upper critical field \( (H_{c2}) \). \( H_{c2} \) is defined by using the onset \( T_c \) criterion, which is determined by the first dropped point deviating from the linear resistivity curve. The inset of Fig. 2(b) summarizes the temperature dependence of \( H_{c2} \). Based on the Werthamer–Helfand–Hohenberg equation,\(^{20} \)

\[
H_{c2}(0) = 0.693\left((dT_c/dH)\right)_{T_c} T_c,
\]

one can obtain the value of \( H_{c2}(0) \) for the compound at pressure of 5 kbar. The calculated \( H_{c2}(0) \) is about 1.78 ± 0.10 Tesla at 0 K. The colorful area is extrapolated by using the formula \( H_{c2}(T) = H_{c2}(0)\left(1 - \left(T/T_c\right)^2\right)^{1/2} \)

\[
[1 + \left(T/T_c\right)^2].
\]

Since the \( T_c \) values at ambient pressure and at a pressure of 5 kbar are almost the same, we can assume the same \( H_{c2}(0) \) value for the ambient condition. By using the equations for the critical fields,\(^{21} \)

\[
H_{c2}(0) = \Phi_0/2\pi \xi_0^2 \quad \text{and} \quad H_{c1}(0) = (\Phi_0/4\pi \xi_0^2) \ln(\lambda_1/\xi_0),
\]

with \( \Phi_0 \) being the flux quantum, we obtained a zero-temperature superconducting coherence length \( \xi_0 \) of 136 ± 3 Å and a London penetration depth \( \lambda_1 \) of 2840 ± 4 Å. The Ginzburg–Landau parameter \( \kappa = 20.9 \pm 0.4 \) is thus obtained based on the expression \( \kappa = \lambda_1/\xi_0 \), supporting the feature of a type-II superconductor.\(^{21} \)

The obtained superconducting parameters in K-doped \( \sigma \)-TTB are reasonably comparable to those for low-dimensional organic salts\(^{23} \) and metal-doped fullerides.\(^{23} \)

One may wonder what the superconducting phase of K-doped \( \sigma \)-TTB could be. The crystal structures of pristine and K-doped \( \sigma \)-TTB are shown in Fig. 3. The powder X-ray diffraction (XRD) patterns of pure \( \sigma \)-TTB (Fig. 3(a)) can be indexed well as a triclinic class with the space group \( P1(1) \). There are eight molecules of \( \text{C}_2\text{H}_2\text{Bi} \) in a unit cell with lattice parameters \( a = 38.3100 \, \text{Å}, b = 5.2520 \, \text{Å}, \) and \( c = 20.2200 \, \text{Å} \) together with angles \( \alpha = 90.00^\circ, \beta = 121.00^\circ, \) and \( \gamma = 90.00^\circ, \) as shown in Fig. 3(c). The crystal structure of this organometallic compound changes dramatically after doping with the alkali metal (Fig. 3(b)), implying the formation of a distinct structure after adding potassium. The crystal structure of K-doped \( \sigma \)-TTB is obtained on the basis of K-doped TPB.\(^{12} \) Both compounds show very similar XRD patterns (Fig. 3(b)). While replacing TPB with \( \sigma \)-TTB in the unit cell of K-doped TPB, we performed the full relaxation of atomic positions for mole ratios of 4 : 1 and 3 : 1. The optimized results showed that the XRD pattern of 3 : 1 fairly matches with the measurements. For such a structure, three molecules of \( \text{C}_2\text{H}_2\text{Bi} \) and nine K atoms distribute in a nearly cubic unit cell with dimensions \( a = 9.5450 \, \text{Å}, b = 9.5810 \, \text{Å}, \) and \( c = 9.5530 \, \text{Å} \) together with angles \( \alpha = 89.62^\circ, \beta = 90.39^\circ, \) and \( \gamma = 89.85^\circ, \) as shown in Fig. 3(d). Here K atoms represented by blue balls are intercalated in the interstitial space of bismuth and the methylphenyl rings. In addition, a metal Bi trace is also observed in the XRD patterns of the doped sample (marked by the symbol *), indicating partial decomposition of \( \sigma \)-TTB into Bi atoms and methylbenzene (colorless liquid, removed). A similar situation has been discussed for K-doped TPB.\(^{12} \) Therefore, K\(_3\)\( \sigma \)-TTB is the most possible superconducting phase from the comparison of the experimental observation and theoretical calculations. The atomic positions of C and Bi in \( \sigma \)-TTB and those of C, H, Bi, and K in K\(_3\)\( \sigma \)-TTB are given in the ESL.\(^{1} \)

A comparison of potassium-doped \( \sigma \)-TTB, TPB,\(^{12} \) and \( p \)-TTB\(^{13} \) indicates that the three materials have a nearly cubic unit cell with close lattice constants. However, the steric hindrance of methyl groups reduces the interstitial space for accommodating potassium atoms in the unit cell, leading to a smaller mole ratio (3 : 1) for potassium-doped \( \sigma \)-TTB and \( p \)-TTB than the one (4 : 1) for potassium-doped TPB. In addition, different spatial distributions of methyl groups make potassium atoms occupy different positions in potassium-doped \( \sigma \)-TTB and \( p \)-TTB.

Raman spectroscopy measurements were performed to understand the formation of the superconducting phase. Fig. 4 shows Raman spectra of pristine and doped \( \sigma \)-TTB in the frequency range of 0–1800 cm\(^{-1} \). Pure \( \sigma \)-TTB (red curve) displays four regions of vibrational modes for the lattice and Bi-phenyl, C–C–C bending, C–H bending, and C–C stretching, from low to high frequencies.\(^{24} \) By intercalating K into \( \sigma \)-TTB, the lattice and C–C–C bending regions vanish abruptly. In addition, the other zones (C–H bending and C–C stretching) change dramatically. In the C–H bending region, three Raman peaks (637, 1010 and 1197 cm\(^{-1} \)) for \( \sigma \)-TTB exhibit distinct red shifts upon doping. This indicates a phonon-mode softening effect, arising from charge-transfer between the...
alkali metal and organobismuth molecule. This downshift effect has been generally observed in C-bearing superconductors such as alkali-metal doped hydrocarbons.\textsuperscript{25-27} This has been widely accepted as an approach to determine actual doping concentration in these superconductors. For K-doped o-TTB, there are 21–23 cm\textsuperscript{-1} redshifts in the frequencies for the mentioned three phonon modes. A downshift of 6 or 7 cm\textsuperscript{-1} in Raman spectra usually corresponds to transfer of one electron. The redshift in our K-doped o-TTB gives a number of transferred electrons of about 3. This is in good agreement with the result determined from the analysis of the XRD data (Fig. 3). On the other hand, the frequencies in the C–C stretching region increase with K doping. This behavior results from the phenyl polarization when a benzene ring is connected to the metal.\textsuperscript{28} Therefore, the complicated behavior of the Raman spectra of this superconductor is the product of competition between the charge-transfer effect and benzene polarization. We would like to point out there exists an important difference in the Raman spectra of potassium-doped o-TTB and p-TTB.\textsuperscript{13} While the highest C–C stretching mode at 1573 cm\textsuperscript{-1} in o-TTB shifts up by 7 cm\textsuperscript{-1}, the similar mode at 1581 cm\textsuperscript{-1} in p-TTB shifts down slightly. This difference can be understood by taking the effect of the methyl group into account. Owing to the similar electron-donating nature of the methyl group to Bi, its connection to the ortho or para position of the C–Bi bond will result in an increased or decreased polarization of the phenyl rings, which then causes different Raman shifts.
4 Conclusions

The discovery of superconductivity in K-doped o-TTB enriches the physical properties and adds to the potential technological applications of organometallic compounds as superconductors. The introduction of methyl in pristine organometallic molecules leads to a nearly five-fold increase of the superconducting shield fraction compared to K-doped TPB\textsuperscript{12} due to the possible delocalization effect and/or the increase of the carrier concentration. This offers an effective method to tune (super)conductivity by the simple addition of functional groups. Our findings add a new electron-acceptor family for organic superconductors distinguished from the M(dmit)\textsubscript{2} (M = Ni or Pd) system,\textsuperscript{25,26} polyaromatic hydrocarbons,\textsuperscript{25,26} and \(p\)-oilphenyls.\textsuperscript{30-36} This work also points to a new pool for producing superconductors from organometallic compounds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work at HPSTAR was supported by the National Key R&D Program of China (Grant No. 2018YFA0305900). The work at Hubei University was supported by the National Natural Science Foundation of China under Grants No. 11574076, 11674087, and 91221103.

Notes and references