Superconductivity in alkali-earth metals doped phenanthrene

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We discover superconductivity in alkali-earth metals doped phenanthrene. The superconducting critical temperatures \( T_c \) are 5.6 K and 5.4 K for Sr\(_{1.5}\)phenanthrene and Ba\(_{1.5}\)phenanthrene, respectively. The shielding fraction of Ba\(_{1.5}\)phenanthrene exceeds 65%. The Raman spectra show 8 cm\(^{-1}\)/electron and 7 cm\(^{-1}\)/electron downshifts for the mode at 1441 cm\(^{-1}\) due to the charge transfer to organic molecules from the dopants of Ba and Sr. Similar behavior has been observed in A\(_3\)phenanthrene and A\(_3\)C\(_{60}\)(A = K and Rb). The positive pressure effect in Sr\(_{1.5}\)phenanthrene and Ba\(_{1.5}\)phenanthrene together with the lower \( T_c \) with larger lattice indicates unconventional superconductivity in this organic system.

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Superconductors, materials that conduct electricity without resistance and completely eject the magnetic field lines, are mostly inorganic materials. Organic superconductors are very intriguing in condensed matter physics community due to low dimensionality, strong electron-electron and electron-phonon interactions and the proximity of antiferromagnetism, insulator states and superconductivity. Basically, there are mainly two types of organic superconductors: i) the quasi-one-dimensional Bechgaard and Fabre salts- (TMTSF)\(_2\)X (TMTSF = tetramethyltetraselena fulvalene) and (TMTTF)\(_2\)X (TMTTF = tetramethyltetrafulvalene, X = monovalent anions); ii) quasi-two-dimensional salts derived from the donor molecule (BEDT-TTF)\(_2\)X (BEDT-TTF = [bis(ethylenedithio)tetrafulvalene]). The recent discovery of superconductivity in doped organic crystals containing an extended phenanthrene-like structural motif, which is designated as \([n]\)phenacens\((n = 3\) and \(5\)), has provided new empirical substance to the occurrence of superconductivity in organic, \(\pi\)-molecular materials. Organic materials are generally considered as electrical insulators. Both phenanthrene \((n = 3)\) and picene \((n = 5)\) are semiconductors with band gaps of 3.16 eV\(^{10}\) and 3.3 eV\(^{2}\), respectively. Superconductivity is introduced by doping alkali-metals into the interstitial sites of the pristine compounds. The charge (electron) transfer from alkali-metal atoms to the molecules results in changes of the electronic structure and the physical properties to realize superconductivity.

All the reported organic superconductors, including the doped phenanthrene type, contain five-member rings or six member rings with conjugated \(\pi\)-orbital interactions among these rings. The \(\pi\)-electron can delocalize throughout the crystal, giving rise to metallic conductivity due to \(\pi\)-orbital overlap between adjacent molecules. The molecule and crystal structure of organic materials are completely different from the inorganic system, which makes the understanding of superconductivity in organic system quite difficult and complicated. The superconductivity in doped phenanthrene-type materials offers an excellent candidate for studying physics in organic, \(\pi\)-molecular superconductors. However, the superconducting fraction was reported to be rather small in both phenanthrene and picene system. The maximum shielding fractions in the powder samples of K-doped picene and phenanthrene are 1.2\(^{2}\) and 5.3\(^{2}\), respectively. This makes it difficult to investigate intrinsic superconducting properties in phenanthrene-type systems. Obtaining high-quality samples and pursuing new superconductors in this hydrocarbon superconducting family are the central issues for investigating intrinsic physical properties and understanding the superconducting mechanism in organic, \(\pi\)-molecular superconductors. Here we report the discovery of superconductivity in strontium and barium doped phenanthrene, and the superconducting transition temperature is \( T_c \) of 5.6 K and 5.4 K for Sr\(_{1.5}\)phenanthrene and Ba\(_{1.5}\)phenanthrene, respectively. The shielding fraction is up to 65.4% in Ba\(_{1.5}\)phenanthrene at 2 K. Raman spectra show 8 cm\(^{-1}\)/electron and 7 cm\(^{-1}\)/electron downshifts due to the charge transfer, which are similar to those of A\(_3\)phenanthrene and A\(_3\)C\(_{60}\)(A = K and Rb). The pressure dependence of superconductivity shows a positive coefficient \(d(T_C/T_C(0))/dP\) and an enhancement of the shielding fraction.

Barium (99%), Strontium (99%), phenanthrene (98%) were purchased from Alfa Aesar. The phenanthrene was purified by sublimation method. Barium and strontium were ground into powder with file. The purified phenanthrene and Ba/Sr powder were mixed with chemical stoichiometry ratio. The mixture was ground carefully and then pressed into pellets. The samples were sealed in quartz tube under vacuum less than \(5 \times 10^{-4}\) Pa. The sample was heated at 230°C for 8 days with intermediate grinding and pelleting for three times. Finally, the products with uniform dark black color were obtained. The X-ray diffraction and Raman measurement were carried...
out by sealing the samples in capillaries made of special glass No. 10 and purchased from Hilgenberg GmbH.

Figure 1 shows the X-ray diffraction (XRD) patterns of the pure, and Ba- and Sr-doped phenanthrene, respectively. Fig.1(a) shows the XRD pattern of pure phenanthrene. There are three fused benzene rings in the molecule of phenanthrene, as shown in the inset of Fig.1(a). The phenanthrene crystallizes in the space group of $P_{2_1}$. The lattice parameters for pristine phenanthrene are $a = 8.453 \text{Å}$, $b = 6.175 \text{Å}$, $c = 9.477 \text{Å}$ and $\beta = 98.28^\circ$, being consistent with the results reported before. Fig.1(b) shows the XRD patterns of Sr- and Ba-doped phenanthrene, respectively. All the peaks can be well indexed with the $P_{2_1}$ space group. No impurity phase was found in the XRD pattern. Lattice parameters are $a = 8.471 \text{Å}$, $b = 6.181 \text{Å}$, $c = 9.491 \text{Å}$, $\beta = 97.55^\circ$ for Sr$_1$phenanthrene; $a = 8.479 \text{Å}$, $b = 6.177 \text{Å}$, $c = 9.502 \text{Å}$, $\beta = 97.49^\circ$ for Ba$_1$phenanthrene. It indicates that the superconducting phase discussed below is responsible for the superconductivity. The lattice parameters show slightly changes compared to pristine phenanthrene. The unit cell volume increases slightly from 489.5 Å$^3$ for phenanthrene to 492.6 Å$^3$ for Sr$_1$phenanthrene and 493.4 Å$^3$ for Ba$_1$phenanthrene, which is consistent with doped TMTSF case. With monovalent anions injection, the unit cell volume of (TMTSF)$_2$PF$_6$ expands to 345.5 Å$^3$ per TMTSF molecule from 316 Å$^3$ per TMTSF in the pristine compound. While in K$_x$picene, the unit cell volume shows significantly shrinkage due to potassium doping. Generally, there are two effects of foreign atom/ionic intercalation on unit cell volume. Firstly, the lattice will expand because of the volume of foreign atom. Secondly, the attracting force becomes electrostatic attraction from Van der Waals force, which will reduce the unit cell volume. The change of lattice parameter induced by intercalation of Sr and Ba indicates former fac-

FIG. 1: X-Ray diffraction patterns for phenanthrene, Sr$_1$phenanthrene and Ba$_1$phenanthrene. (a): X-ray diffraction pattern for pristine phenanthrene, the molecule and crystal structure are shown in the inset. (b): X-ray diffraction patterns for Sr- and Ba-doped phenanthrene.

FIG. 2: Temperature dependence of magnetic susceptibility ($\chi$) for Sr$_1$phenanthrene and Ba$_1$phenanthrene. (a): $\chi$ versus $T$ plots for Sr$_1$phenanthrene and Ba$_1$phenanthrene in the zero-field-cooling (ZFC) and field-cooling (FC) measurements under the magnetic field of 10 Oe. The inset shows M-H curve of Ba$_1$phenanthrene at 2 K. (b): $\chi$ versus $T$ curve for Ba$_1$phenanthrene in the ZFC measurements under different magnetic fields. The $H$ versus $T_C$ plot is shown in the inset.
corresponding to the sharp drop is defined as the superconducting transition temperature ($T_c$). The superconducting transition temperatures are higher than the $T_c$ of 4.95 K and 4.75 K for K$_3$phenanthrene and Rb$_3$phenanthrene, respectively. The intercalation of larger atom results in a lower $T_c$, which is consistent with the alkali-metal doped phenanthrene. The evolution of $T_C$ with the radii of intercalating atoms for doped phenanthrene is quite different from the doped C$_{60}$, whose superconducting transition temperatures increase monotonically as the unit cell size increases$^{16}$. It cannot be understood in BCS theory because the density of states (DOS) increases with lattice expansion, and increase of DOS should lead to enhancement of $T_C$ based on BCS theory. However, $T_C$ of Sr$_{1.5}$phenanthrene is little higher than that of Ba$_{1.5}$phenanthrene with larger unit cell volume. In this sense, Sr$_{1.5}$phenanthrene and Ba$_{1.5}$phenanthrene superconductors should be unconventional. Diamagnetic signals from zero-field-cooling and field-cooling measurements can be assigned to shielding and Meissner effects. As shown in Fig.2(a), the shielding fraction and the Meissner fraction are 65.4% and 3.4% for the powder sample of Ba$_{1.5}$phenanthrene, 39.5% and 9.5% for the sample of Sr$_{1.5}$phenanthrene, respectively. The shielding fraction is much larger than that of alkali-metal doped picene and phenanthrene. The superconducting transition width is $\sim$ 0.8 K, which is comparable with K$_3$phenanthrene and Rb$_3$phenanthrene. The $M$ versus $H$ plot is shown as the inset of Fig.2(a). The lower critical field $H_{C1}$ of Ba$_{1.5}$phenanthrene is 720 Oe at 2 K, which is larger than the value of 380 Oe at 5 K in K$_3$picene with $T_C$ of 18 K and 175 Oe at 2 K in K$_3$phenanthrene with $T_C$ of 5 K.

Figure 2(b) shows $\chi$ versus $T$ plots for Ba$_{1.5}$phenanthrene superconductor under different magnetic fields. The diamagnetic signal is gradually suppressed and the superconducting transition become significantly broad with the application of magnetic fields. One can clearly observe a superconducting transition at 3.5 K with the magnetic field up to 2000
When the field is higher than 5000 Oe, it is difficult to observe the superconducting transition from magnetization curve. The magnetic field H versus $T_C$ plot is shown in the inset of Fig.2(b). It is difficult to precisely determine the upper critical field $H_{c2}$ from $H-T_C$ curve, but it is obvious that it exceeds 2000 Oe.

Figure 3(a) and 3(b) show the temperature dependence of $\chi$ for Sr$_{1.5}$phenanthrene and Ba$_{1.5}$phenanthrene in ZFC measurements under different pressures, respectively. The most remarkable result is that $T_C$ for both of Sr$_{1.5}$phenanthrene and Ba$_{1.5}$phenanthrene increases with increasing applied pressure. The shielding fraction also becomes larger. It indicates that the superconductivity is enhanced with the pressure. As shown in Fig.3(c), $d(T_C(P)/T_C(0))/dP$ are $\sim 0.21$ GPa$^{-1}$ and 0.23 GPa$^{-1}$ for Sr$_{1.5}$phenanthrene and Ba$_{1.5}$phenanthrene, respectively. The positive pressure effect is similar to that of Kphenanthrene. According to BCS theory, the decrease of $T_C$ is expected with application of pressure because the density of states $N(E_F)$ at the Fermi level decreases. The unusual positive pressure effect indicates unconventional superconductivity in Sr$_{1.5}$phenanthrene and Ba$_{1.5}$phenanthrene superconductors.

Figure 4 shows the Raman scattering for pristine phenanthrene, Sr$_{1.5}$phenanthrene and Ba$_{1.5}$phenanthrene. There are seven major peaks in pristine phenanthrene: 1524, 1441, 1350, 1037, 830, 411 and 250 cm$^{-1}$. The major peaks of the Raman spectrum belong to A$_1$ mode due to the C-C stretching vibration. The phonon modes in Sr$_{1.5}$phenanthrene and Ba$_{1.5}$phenanthrene show redshift relative to the pristine phenanthrene. Such phonon-mode softening effect arises from the charge transfer into phenanthrene molecule from dopants of Ba and Sr. The main mode shifts from 1441 cm$^{-1}$ in pristine phenanthrene to 1416 cm$^{-1}$ in Sr$_{1.5}$phenanthrene and 1419 cm$^{-1}$ in Ba$_{1.5}$phenanthrene. There are 25 and 22 cm$^{-1}$ downshifts for Sr$_{1.5}$phenanthrene and Ba$_{1.5}$phenanthrene, respectively. It indicates 8 cm$^{-1}$/electron downshift for Sr$_{1.5}$phenanthrene and 7 cm$^{-1}$/electron downshift for Ba$_{1.5}$phenanthrene due to the charge transfer. This is consistent with that of Kphenanthrene(6 cm$^{-1}$/electron) and Rb$_3$phenanthrene(7 cm$^{-1}$/electron).

Such similar behavior has been observed in A$_3$C$_{60}$ (A=K, Rb, Cs), in which 6 cm$^{-1}$/electron redshift at 1460 cm$^{-1}$ occurs. The Raman shift induced by charge transfer is nearly the same, and independent of dopants, being similar to that of alkali-metal doped C$_{60}$.

In summary, we discover the superconductivity in Sr- and Ba-doped phenanthrene-type system. Sr$_{1.5}$phenanthrene and Ba$_{1.5}$phenanthrene show superconductivity at 5.6 K and 5.4 K, respectively. The positive pressure effect in Sr$_{1.5}$phenanthrene and Ba$_{1.5}$phenanthrene and lower $T_c$ with larger lattice indicate unconventional superconductivity in this organic system. The superconductivity can be realized by doping alkali-earth metals to provide charge and transfer it to organic molecules.

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