Enhanced superconductivity by rare-earth metal doping in phenanthrene

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Abstract
We successfully synthesized La- and Sm-doped phenanthrene powder samples and observed superconductivity in them at $T_c$ around 6 K. The $T_c$s are 6.1 K for La$_1$ phenanthrene and 6.0 K for Sm$_1$ phenanthrene, which are enhanced by about 1 and 0.5 K compared to those in A$_3$ phenanthrene (A = K and Rb) and in Ae$_{1.5}$ phenanthrene (Ae = Sr and Ba) superconductors, respectively. The superconductive shielding fractions for La$_1$ phenanthrene and Sm$_1$ phenanthrene are 46.1% and 49.8% at 2 K, respectively. The small effect of doping with the magnetic ion Sm$^{3+}$ on $T_c$ and the positive pressure dependence coefficient of $T_c$ strongly suggest unconventional superconductivity in the doped phenanthrene superconductors. The charge transfer to organic molecules from dopants of La and Sm induces a redshift of 7 cm$^{-1}$ per electron for the mode at 1441 cm$^{-1}$ in the Raman spectra, which is almost the same as those observed in A$_3$ phenanthrene (A = K and Rb) and Ae$_{1.5}$ phenanthrene (Ae = Sr and Ba) superconductors.

(Some figures may appear in colour only in the online journal)

The first observation of superconductivity in a carbon-based compound dates back to 1965, when superconductivity was observed in the first stage alkali-metal intercalated graphite CsK [1]. Up to now, superconductors based on carbon mainly consist of three types of materials: graphite intercalation compounds (GIC), doped fullerenes, and organic compounds. For all of these carbon-based superconductors, there are commonly 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 a $\pi$-orbital overlap between the adjacent molecules. At present, the highest-$T_c$ superconductor for these carbon-based materials is an alkali metal-doped fullerene, namely Cs$_3$C$_{60}$ under pressure ($\sim$12 kbar) with $T_c$ $\sim$ 38 K [2, 3]. Among the organic compounds, the previous record of $T_c$ was held by the tetraithiavalene derivative $\beta'-(BEDT-TTF)$_2$I$_2$ with $T_c = 14.2$ K under a high pressure of 8.2 GPa [4]. Very recently, this record of $T_c$ among superconducting organic materials was renewed by the potassium-doped picene (highest $T_c$ $\sim$ 18 K) [5] and subsequently the potassium-doped 1,2:8,9-dibenzopentacene ($T_c$ $\sim$ 33 K) [6], whose pristine organic molecules are composed of five and seven fused benzene rings, respectively. Alkali and alkali-earth metal-doped phenanthenes, whose pristine organic molecule phenanthrene consists of three fused benzene rings, are also found to be superconducting with $T_c$ $\sim$ 5 K [7, 8]. The discovery of superconductivity in these materials with fused benzene rings could open a novel broad class of hydrocarbon organic materials for superconductors, and suggests potential high-$T_c$ superconductivity in materials with long fused benzene rings. However, the mechanism for superconductivity in these organic hydrocarbons with long benzene rings remains unknown. There have been some hints of unconventional superconductivity in these materials, such as the positive pressure dependence of $T_c$ and the existence of local spin moments in the superconducting compounds [7, 8]. More detailed work should be conducted on this class of superconductors. The superconductivity in...
doped phenanthrene is a good candidate for investigating the physics in such organic superconductors, due to the relatively simple molecular structure of phenanthrene. In this work, we doped non-magnetic and magnetic rare-earth metal elements into phenanthrene to study the effect of magnetic ions on the superconductivity. Superconductivity in this class of organic hydrocarbons was realized by doping-induced charge (electron) transfer from the doped metal atoms to the molecules, which results in changes in the electronic structure and physical properties. Our previous works demonstrated that three electrons are required to transfer into one phenanthrene molecule to get superconductivity. In the present paper, we doped the rare-earth metals lanthanum and samarium, which are non-magnetic and magnetic respectively, into phenanthrene to realize superconductivity, with the nominal composition of La1 phenanthrene and Sm1 phenanthrene. Superconductivity was observed in these two compounds, with $T_c$ equal to 6.1 and 6.0 K for La1 phenanthrene and Sm1 phenanthrene, respectively. The superconductive shielding fraction is 46.1% in La1 phenanthrene and 49.8% in Sm1 phenanthrene at 2.5 K. Raman spectra show a redshift of $\sim$7 cm$^{-1}$ per electron due to charge transfer for both compounds, which is almost the same as those in $A_3$ phenanthrene ($A = K$ and Rb) and $Ae_{1.5}$ phenanthrene ($Ae = Ba$ and Sr) as well as that in $A_2C_{60}$ ($A = K$ and Rb). The pressure dependence of superconductivity in La1 phenanthrene shows a positive coefficient $d(T_c/T_c(0))/dP$ with the superconductive shielding fraction being almost unchanged.

Pristine phenanthrene (98%) was purified by a sublimation method [7]. Lanthanum (99.99%) and samarium (99.99%) were ground into a powder with a file and mixed carefully with the purified phenanthrene in molar ratio of 1:1. The synthesis of La1 phenanthrene and Sm1 phenanthrene is quite similar to the processes for Ba- and Sr-doped phenanthrene [8]. The mixture of rare-earth metal and phenanthrene was pressed into a pellet and sintered at 240°C in an evacuated quartz tube using the multiple-middle treatment process for a total of 8 days. Finally, products with a uniform dark black color were obtained. X-ray diffraction (XRD) and Raman measurements were carried out by sealing the samples in capillaries made of special glass (no. 10) and purchased from Hilgenberg GmbH. An XRD pattern was obtained in the 2-theta range from 5° to 65° with a scanning rate of 0.5° min$^{-1}$. Raman-scattering experiments were conducted by using the 780 nm laser line in a DXR Raman Microscope (Thermo Scientific). The scattering light was captured by using a single exposure of the CCD with a spectral resolution of 1 cm$^{-1}$. Low-temperature Raman spectra were obtained on a Raman Microscope (Horiba JY T64000) equipped with Janis ST-500 microscopy cryostat.

Figure 1 shows the XRD patterns of pristine phenanthrene and the superconducting La- and Sm-doped phenanthrene. Pristine phenanthrene crystallizes in the space group $P2_1$ [7, 9]. The lattice parameters for pristine phenanthrene are $a = 8.453(1)$ Å, $b = 6.175(2)$ Å, $c = 9.477(2)$ Å and $\beta = 98.28(3)^\circ$ [7, 9]. All the reflections in the XRD patterns of the rare-earth metal-doped phenanthrenes shown in figure 1 can be well indexed with the space group of $P2_1$ as for pristine phenanthrene, just the same as previously reported alkali and alkali-earth metal-doped phenanthrene. No impurity phase was found in the XRD patterns. From the XRD patterns shown in figure 1, lattice parameters are obtained as $a = 8.481(2)$ Å, $b = 6.187(2)$ Å, $c = 9.512(1)$ Å, $\beta = 97.95(4)^\circ$ for La1 phenanthrene and $a = 8.475(3)$ Å, $b = 6.180(2)$ Å, $c = 9.505(2)$ Å, $\beta = 98.10(3)^\circ$ for Sm1 phenanthrene. The lattice parameters are changed slightly relative to pristine phenanthrene. The unit cell volume expands from 489.5 Å$^3$ for pristine phenanthrene to 494.3 Å$^3$ for La1 phenanthrene and to 492.9 Å$^3$ for Sm1 phenanthrene. The expansion of the unit cell is similar to the previous alkali-earth metal-doped case. The smaller unit cell of Sm1 phenanthrene relative to La1 phenanthrene is consistent with the ion radius of Sm$^{3+}$ being smaller than that of La$^{3+}$.

Superconductivity of the La1 phenanthrene and Sm1 phenanthrene powder samples was characterized by magnetic susceptibility measurements at low magnetic field in zero-field-cooling (ZFC) and field-cooling (FC) processes. Figure 2(a) displays the temperature dependence of magnetic susceptibility $\chi(T)$ measured in the ZFC and FC processes under a magnetic field of 10 Oe for the powder samples of La1 phenanthrene and Sm1 phenanthrene. $\chi(T)$ exhibits a well-defined peak at $T_c$ and significant decreases in ZFC and FC measurements for both La1 phenanthrene and Sm1 phenanthrene at temperatures of 6.1 K and 6.0 K, respectively. The temperature at which magnetic susceptibility begins to drop is defined as the superconducting transition temperature ($T_c$). The diamagnetic signals from ZFC and FC measurements can be assigned to reflect the superconductive shielding volume fraction and Meissner volume fraction. As shown in figure 2(a), the shielding volume fraction and the Meissner volume fraction are 46.1% and 6.3% for La1 phenanthrene and 49.8% and 6.5% for Sm1 phenanthrene, respectively. The shielding fraction is much larger than that of alkali metal-doped
Figure 2. Temperature dependence of the magnetic susceptibility ($\chi$) for La$_1$ phenanthrene and Sm$_1$ phenanthrene. (a) $\chi$ plotted against $T$ for La$_1$ phenanthrene and Sm$_1$ phenanthrene in the zero-field-cooling (ZFC) and field-cooling (FC) measurements under a magnetic field of 10 Oe. (b) Magnetic susceptibility as a function of temperature for La$_1$ phenanthrene in the ZFC measurements under different magnetic fields. $H$ versus $T_c$ is plotted in the inset of (b).

The temperature dependence of the magnetic susceptibility measured at 5 T for La$_1$ phenanthrene and Sm$_1$ phenanthrene powder samples is displayed in figure 4. Curie–Weiss-like behavior is observed at high temperature for both samples, indicating the existence of local spin moments. By fitting the experimental data below 85 K (and above 15 K for Sm$_1$ phenanthrene) by using the Curie–Weiss formula $\chi = \chi_0 + C/(T + \theta)$, where $\chi_0$ is constant, $C$ is the Curie constant and $\theta$ is the paramagnetic Curie temperature, the effective magnetic moments are estimated to be 0.34 $\mu_B$ and 0.46 $\mu_B$ per chemical formula for La$_1$ phenanthrene and Sm$_1$ phenanthrene, respectively. This is very large in comparison to the 0.06 $\mu_B$ in pristine phenanthrene [7].
suggesting that there is quite large amount of local magnetic moment in these doped phenanthrene samples. Since La$^{3+}$ is non-magnetic, the induced local magnetic moments should arise from the charged phenanthrene molecules. In other words, some of the electrons which are transferred from La atoms to phenanthrene molecules give rise to local spin moments. The larger magnetic moments in Sm$_1$ phenanthrene could be due to the existence of the magnetic ions Sm$^{3+}$. It is well known that in conventional s-wave superconductors, local magnetic moments break up the spin singlet Cooper pairs and hence strongly suppress superconductivity (an effect known as pair-breaking). While in these rare-earth metal-doped phenanthrene samples, although the effective magnetic moments are larger than those obtained in superconducting K$_3$ phenanthrene (0.22 $\mu_B$ per chemical formula) and Rb$_3$ phenanthrene (0.21 $\mu_B$ per chemical formula) [7], superconductivity ($T_c$) is enhanced instead of being suppressed. This is a strong indication of the unconventional nature of superconductivity in the doped phenanthrene. Moreover, for Sm$_1$ phenanthrene there is an antiferromagnetic transition happening at $T_N \sim 15$ K, which is ascribed to the antiferromagnetic ordering of Sm$^{3+}$ ions. This $T_N$ is close to that in the elemental Sm (14.8 K) [10].

However, no reflection for elemental Sm can be recognized in the XRD pattern shown in figure 1. Actually, $T_N$ for Sm$^{3+}$ ions can vary from several kelvin to more than 20 K, and strongly depends on the particular compound [11–13]. While it was reported that no magnetic order is formed for Sm$^{3+}$ ions in Sm$_{12.75}$C$_{60}$ [14]. One can find that the existence of the magnetic Sm$^{3+}$ ions with antiferromagnetic order has negligible suppression effect on the superconductivity. All these results strongly suggest the unconventional nature of the superconductivity in the system.

As is well known, the effect of charge transfer into fused hydrocarbon rings can be studied by Raman spectroscopy. Figure 5(a) shows the Raman spectra at room temperature for pristine phenanthrene, La$_1$ phenanthrene and Sm$_1$ phenanthrene. As reported previously [7, 8], seven major peaks can be observed in pristine phenanthrene: 1524, 1441, 1350, 1037, 830, 411 and 250 cm$^{-1}$. All of these major peaks of the Raman spectrum can be classified to the A$_1$ mode, and are the vibrational assignments of C–C stretching (1350 and 1037 cm$^{-1}$), C–C rocking (1524 and 1441 cm$^{-1}$), ring bending (830, 411 and 250 cm$^{-1}$) [15–17]. A clear downshift can be observed for the peaks in the Raman spectra of La$_1$ phenanthrene and Sm$_1$ phenanthrene, relative to those of pristine phenanthrene. Such a phonon-mode softening effect is attributed to the charge transfer from La and Sm dopant atoms into phenanthrene molecules, which has been widely observed in doped fullerenes [18] as well as in doped phenanthrene as reported previously by us [7, 8]. In doped fullerences, a downshift of 6 cm$^{-1}$ per electron was observed due to the charge transfer [18]. In alkali or alkali-earth metal-doped phenanthrene, a downshift of $\sim 7$ cm$^{-1}$ per electron was observed due to the charge transfer [7, 8]. For the present two rare-earth metal-doped phenanthrene superconductors, this A$_1$ mode of 1441 cm$^{-1}$ in pristine phenanthrene moves to 1420 cm$^{-1}$ in La$_1$ phenanthrene and 1419 cm$^{-1}$ in Sm$_1$ phenanthrene. Consequently, the electron transfer from rare-earth metal atoms to the phenanthrene molecules induces redshifts of 21 and 22 cm$^{-1}$ in the Raman spectra for La$_1$ phenanthrene and Sm$_1$ phenanthrene, respectively, suggesting a redshift of about 7 cm$^{-1}$ per electron in both samples, well consistent with those observed in alkali or alkali-earth metal-doped phenanthrene samples.
metal-doped phenanthrene [7, 8]. Temperature dependent measurements of Raman scattering were also performed for La$_1$phenanthrene at temperatures ranging from 300 to 4.5 K. The selected Raman spectra are displayed in figure 5(b). Normally, phonon anharmonicity gives rise to the following temperature dependence of the linewidth (full width of half-maximum) $\Gamma$ and mode frequency $\omega$ [19]:

$$\Gamma(T) = \omega_0 \left(1 + \frac{2}{e^{2h\omega_0/k_B T} - 1}\right)$$

(1)

$$\omega(T) = \omega_0 + C \left(1 + \frac{2}{e^{2h\omega_0/k_B T} - 1}\right)$$

(2)

where $h\omega_0$ is the phonon frequency, $k_B$ is the Boltzmann constant, and $C$ is a constant. In figure 5(b), no shift more than 0.5 cm$^{-1}$ can be observed for both linewidth and mode frequency with the variation of the temperature from 300 to 4.5 K, indicating an unusual phonon decay with decreasing temperature. The nearly temperature independent $\Gamma(T)$ suggests $\omega_0 << \gamma$, so that lattice anharmonicity is no longer a dominant mechanism of the phonon decay in the present studied La$_1$phenanthrene. The mechanism for this unusual process of phonon decay is not yet understood. The interactions of phonons with other excitations (for instance, electrons in conducting materials) might affect the phonon lifetime and contribute to the phonon linewidth $\Gamma(T)$ because additional channels for phonon decay could be opened by them. More measurements with higher resolution must be done to explain the temperature-independent linewidth and mode frequency. It should also be pointed out that, as seen from figure 5(b), the Raman spectrum exhibits no obvious change as temperature cools down across $T_c$. However, all of these mode frequencies are much larger than $2\Delta_0 = 3.53k_BT_c$ and so most of these modes are not expected to be sensitive to the superconducting transition.

In summary, we have successfully fabricated the new superconductors La$_1$phenanthrene and Sm$_1$phenanthrene, which show $T_c = 6.1$ and 6.0 K, respectively. The positive pressure effect on $T_c$ was observed in La$_1$phenanthrene. Enhanced superconductivity was observed despite the increase in the effective magnetic moments compared to previously reported K$_1$phenanthrene and Rb$_1$phenanthrene. In particular, the antiferromagnetic order from the magnetic ion Sm$^{3+}$ has a negligible effect on $T_c$ in Sm$_1$phenanthrene. These results strongly suggest unconventional superconductivity in the doped phenanthrene-type superconductors.

Acknowledgments

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References

[1] Hannay N B, Geballe T H, Matthias B T, Andres K, Schmidt P and MacNair D 1965 Phys. Rev. Lett. 14 225
[2] Palstra T T M, Zhou O, Iwasa Y, Sulewski P E, Fleming R M and Zegarski B R 1995 Solid State Commun. 93 327
[3] Takabayashi Y et al 2009 Science 323 1585
[4] Taniguchi H, Miyashita M, Uchiyama K, Satoh K, Môri N, Okamoto H, Miyagawa K, Kanoda K, Hedo M and Uwatoko Y 2003 J. Phys. Soc. Japan 72 468
[5] Mitsuhashi R et al 2010 Nature 464 76–9
[6] Xue M Q, Cao T B, Wang D M, Wu Y, Yang H X, Dong X L, He J B, Li F W and Chen G F 2012 Sci. Rep. 2 389
[7] Wang X F, Liu R H, Gui Z, Xie Y L, Yan Y J, Ying J J, Luo X G and Chen X H 2011 Nature Commun. 2 507
[8] Wang X F, Yan Y J, Gui Z, Liu R H, Ying J J, Luo X G and Chen X H 2011 Phys. Rev. B 84 214523
[9] Trotter J 1963 Acta Crystallogr. 16 605–8
[10] Huray P, Nave S and Haire R 1983 J. Less-Common Met. 93 293
[11] Nandi S et al 2011 Phys. Rev. B 84 054419
[12] Prassides K, Lappas A, Buchgeister M and Verge P 1995 Europhys. Lett. 29 641
[13] Felner I, Mayer I, Grill A and Schieber M 1972 Solid State Commun. 11 1231
[14] Margadonna S, Iwasa Y, Takenobu T and Prassides K 2004 Struct. Bonding 109 127
[15] Bree A, Solven F G and Vilkos V V B 1972 J. Mol. Spectrosc. 44 298
[16] Godec J and Colombo L 1976 J. Chem. Phys. 65 4693
[17] Bandyopadhyay I and Manogaran S 2000 J. Mol. Struct. (Theochem) 496 107
[18] Dresselhaus M S, Dresselhaus G and Eklund P C (ed) Science of Fullerenes and Carbon Nanotubes (San Diego, CA: Academic) chapter 11 and references therein
[19] Maradudin A A, Flinn P A and Coldwell-Horsfall R A 1961 Ann. Phys. 15 337
Maradudin A A, Flinn P A and Coldwell-Horsfall R A 1961 Ann. Phys. 15 360
Balkanski M, Wallis R F and Haro E 1983 Phys. Rev. B 28 1928