Superconductivity in Sm-doped 1,3,5-triphenylenbenzene

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We report the discovery of superconductivity at about 4.3 K in the samarium doped 1,3,5-triphenylenbenzene. By using a solid state reaction method, the samarium doped 1,3,5-triphenylenbenzene samples are successfully synthesized. These samples are characterized by magnetization, X-ray diffraction (XRD), scanning electron microscope(SEM) and energy dispersive spectroscopy (EDS) measurements. The X-ray diffractions reveal that the sample crystallizes in a space group of P2_1/m. The magnetization measurements reveal a superconducting transition at about 4.3 K. However, the superconducting shielding fraction is only about 1%, which is similar to the previous reports of the superconductivity in other aromatic hydrocarbons. Magnetization hysteresis loops (MHLs) of the sample show that it is a typical type-II superconductor.

I. INTRODUCTION

Organic superconductors are widely concerned because it was predicted that the superconducting transition temperature may reach a high value. Actually later investigations reveal that the superconductivity of organic superconductors may not be driven by exchanging phonons, but rather by some exotic reasons. The first observation of superconductivity in organic materials can be traced back to 1980s, when Bechgaard et al. found superconductivity in 1,3,5-triphenylenbenzene samples with a transition temperature of 9.9 K under a pressure of 12 kbar in (TMTSF)_2PF_6. Here TMTSF represents tetramethyltetraselenafulvalene (C_10H_12Se_14) and is an electron donor molecule. Since then, researchers have found a series of superconductors of this type by replacing PF_6 with AsF_6, SbF_6, ClO_4, and so on. They are collectively referred to as the (TMTSF)_2X, where X represents the electron acceptor molecule, because they all have the same electron donor molecule TMTSF and the similar quasi-one-dimensional organic structures. Another major category of superconducting organic salts are (BEDT-TTF)_2X, where BEDT-TTF means bis(ethylenedithio)tetrathiafulvalene (C_10H_5S_8) and X can be I_3, Cu(SCN)_2, Cu[N(CN)_2]Br, Cu[N(CN)_2]Cl and so on. The highest superconducting transition temperature in potassium doped C_60 has been performed. There is a theoretical prediction that T_c of Cs_2RbC_60 can reach 33 K, and for Cs_3C_60 the T_c is 40 K at 15 kbar. There are many phonon modes for this kind of materials, thus the superconductivity may be attributed to the phonon based mechanism, however some other researchers have different opinions on the mechanism of superconductivity in these C_60 based superconductors. Further experimental evidence show that C_60 materials are strongly correlated electron systems with narrow energy band, thus superconductivity may originate from the electron correlation effect.

Recently, Aromatic hydrocarbons have attracted a lot attention because some of them can show superconductivity by doping alkali-metal or alkali-earth-metal. In 2010, researchers from Japan first synthesized K_3,3picene, which shows superconductivity with T_c of 7 K and 18 K. Subsequently the superconductivity with 5 K in potassium-doped phenantherene and superconductivity with 33 K in potassium-doped 1,2:8,9-dibenzopentacene were reported. Unfortunately, no repeating experiment about the superconductivity at 33 K has been performed. There is a theoretical prediction that T_c is directly proportional to the number of benzene rings in the constructing molecule. Not long ago, it was reported that there might be very high superconducting transition temperature in K_3p-terphenyl, whose T_c can be as high as 120 K. However, the diamagnetic volume at low temperature in K_3p-terphenyl is only about 0.04%, thus it is insufficient to conclude that diamagnetic behavior is derived from superconductivity. These experiments suggest that researchers can obtain superconductors with different T_c by adjusting the arrangement and number of benzene rings in molecular crystals. Clearly, the mystery of superconductivity mechanism in organic hydrocarbon has not been solved yet. The existence of positive pressure dependence of T_c and the local spin moments seem to suggest that these superconductors are unconventional ones. In this paper, we report the synthesis of a new aromatic superconductor by doping samarium, a magnetic rare-earth metal, into 1,3,5-triphenylenbenzene with molar ratio of 3 : 1. The
$T_c$ of Sm$_3$1,3,5-triphenylbenzene is about 4.3 K and the magnetic shielding fraction is only about 1%. This kind of small shielding fraction seems to be a common feature in aromatic hydrocarbons.$^{20}$

II. EXPERIMENT DETAILS

The samples are synthesized by means of solid state reaction. Samarium metal (>%99, GRINM) is ground into powder and mixed with 1,3,5-triphenylbenzene (>%99, Alfa Aesar) in a molar ratio 3:1. Then, the mixture is ground and pressed into pellets. All procedures are handled in a glove box filled with argon gas (O$_2$ and H$_2$O are less than 0.1ppm). The pellet is then put into an Al$_2$O$_3$ crucible and sealed in a quartz tube under a high vacuum. The quartz tube is put into furnace and heated up to 500 K in 600 minutes, and stayed at this temperature for 6 days. Finally we get samples with dark color. X-ray diffraction measurements are performed on the pristine material at room temperature with a Bruker D8 Advanced diffractometer with the CuK$_{α1}$ radiation. The XRD patterns are obtained in the 2θ range from 10$^\circ$ to 90$^\circ$ with a scanning rate of 0.2 sec/step. The morphology and surface compositions of Sm$_3$1,3,5-triphenylbenzene are investigated by scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) methods with the instrument of Phenom ProX (Phenom). An accelerating voltage of 15 kV is used for the EDS measurements. The magnetization measurements were carried out on a superconducting quantum interference devices with the vibrating sample option (SQUID-VSM, Quantum Design) with magnetic field ranging from 10 Oe to 1000 Oe.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of magnetic susceptibility $\chi$ for the bulk sample of Sm$_3$1,3,5-triphenylbenzene measured in zero-field-cooled (ZFC) and field-cooled (FC) modes under a magnetic field of 50 Oe. The $\chi$ versus $T$ in the inset shows a drastic decrease below 4.3 K which is determined as the superconducting transition temperature $T_c$. We can see that the transition is very sharp with width less than 1 K. The diamagnetic signal $\chi$ measured in the ZFC mode can be attributed to the magnetic shielding of the Meissner effect in the superconducting state. By subtracting ZFC data from FC data at 2.5 K, we can obtain $\Delta \chi$, which is about 2.5 × 10$^{-4}$ emu g$^{-1}$ Oe$^{-1}$. Assuming that the density of the sample is about 3.5 g/cm$^3$, according to formula $V_S = 4\pi \Delta \chi \rho$ (where $V_S$ means shielding fraction), we can get a magnetic shielding fraction of about 1%. It should be emphasized that, for all the PAH superconductors reported to date, the shielding fractions are all very small.$^{14,15}$ Although these shielding fractions can be increased by pressing the powder samples into tablets$^{14,15}$, it is still very small compared to other superconductors. It has been discussed that these small shielding fractions in powder samples may arise from the penetration depth of the magnetic field into the superconducting phase, because the sizes of these superconducting grains are smaller than the London penetration depth.$^{14}$ But this picture holds valid only when the sample is constructed by unconnected grains and superconducting phase is in the form of percolation. In general, the magnetic shielding volume in this type of superconductors is small, which needs further investigation to unravel the reason.

Figure 2 shows the temperature dependence of magnetic susceptibility $\chi$ measured in ZFC and FC modes under different magnetic fields.
measurements in ZFC and FC modes for the sample Sm$_3$1,3,5-triphenylbenzene. As we can see, the diamagnetic signals get smaller and smaller with increasing magnetic fields. However, even the magnetic field is increased up to 1000 Oe, we can still observe the drop of $\chi$ at 4 K. This result suggests that the $H_c$ of the sample may be large and far beyond 1000 Oe. It should be noted that even though the step-like transition still exists, above 200 Oe, the diamagnetic signal disappears, instead a paramagnetic background emerges. This may be understood in the way that the superconducting part inside the sample is very small, most areas of the sample are non-superconducting part which contributes a relatively large paramagnetic signal. Due to the paramagnetic background, the magnetic susceptibility of the non-superconducting part becomes more and more prominent when the magnetic field is getting higher and higher. Such clear paramagnetic background signals can be clearly seen in the following measurements of magnetization hysteresis loops (MHL). One can see from Figure 2 that, when the magnetic field is small, the signal shows some noise. This is due to the small superconducting signal of the sample compared with the resolution of the instrument.

Figure 3(a) shows the magnetization hysteresis loops (MHLs) of Sm$_3$1,3,5-triphenylbenzene with the range of magnetic field from -1000 Oe to 1000 Oe at different temperatures. The enlarged view of MHL at 4 K is showed in the inset of Figure 3(a). As we can see, the Meissner effect-like behaviors is still detectable, although a very strong paramagnetic background exists. From the Meissner effect-like behavior, we can roughly determine the $H_c$ of the sample at 4 K, which is about 40 Oe. This is smaller than the value of 175 Oe at 2 K in K$_3$phenanthrene with a $T_c$ of 5 K. Here $H_c$ means the threshold at which magnetic field starts to penetrate into the sample and is determined by the point of deviation from the linear line on the slope of the initial magnetization curve. The shielding behaviors of MHLs decay gradually with increasing temperature and disappear at 5 K. It should be emphasized that when the temperature is lower than 4 K, the hysteresis loop exhibit some jumps between 0 Oe and 1000 Oe. This phenomenon appears in repeated measurements, which we think may be induced by the flux jump effect. Figure 3(b) shows the subtracted magnetization hysteresis loops ($\Delta$MHLs) of Sm$_3$1,3,5-triphenylbenzene with MHL at 5 K as background, i.e., $\Delta M = M(H, T) - M(H, 5K)$. And the Meissner effect-like behaviors become more visible after subtracting the background.

Figure 4(a) shows the x-ray diffraction (XRD) patterns of the samarium doped 1,3,5-triphenylbenzene with molar ratio 3:1. Figure 4(b) shows the XRD pattern of the raw material of 1,3,5-triphenylbenzene, which crystallizes in a space group of $Pnma$. The lattice parameters determined here are $a = 7.47\text{Å}$, $b = 19.66\text{Å}$, $c = 11.19\text{Å}$, being consistent with the results reported before. Comparing the XRD results in Figure 4(a) and (b), it is ob-
FIG. 5. Scanning electron microscope image and element analysis of the Sm$_3$1,3,5-triphenylbenzene sample. The main panel shows the EDS spectrum from which Samarium, Carbon and Oxygen are visible. The inset shows the SEM image of one area of the sample. The rectangular frame with yellow color shows the area for the EDS measurement.

V. CONCLUSIONS

In conclusion, by using a solid state reaction method, we successfully synthesize the Sm$_3$1,3,5-triphenylbenzene samples. The magnetic susceptibility of the sample shows a diamagnetic transition at about 4.3 K. The diamagnetic transition is proved to be a superconducting transition by further measuring the temperature dependence of magnetization under different magnetic fields and MHLs. The MHLs and the ones with the background removed all indicate that the Sm$_3$1,3,5-triphenylbenzene is a type-II superconductor. Fitting to the index peaks of the XRD patterns of the sample Sm$_3$1,3,5-triphenylbenzene tells that the sample crystallize in a space group of $P2/m$. The SEM image shows that samarium uniformly distributes in the sample. Since the superconducting volume determined here is still quite small, we would not attribute the superconductivity to the determined structure, thus it is worthwhile to have further efforts to resolve the superconducting phase. However, we need to notify that, Sm doping is necessary for the emergence of superconductivity.

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