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Superconductivity in aromatic hydrocarbons

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ABSTRACT

'Aromatic hydrocarbon' implies an organic molecule that satisfies the $(4n + 2)$ π-electron rule and consists of benzene rings. Doping solid aromatic hydrocarbons with metals provides the superconductivity. The first discovery of such superconductivity was made for K-doped picene ($K_x$picene, five benzene rings). Its superconducting transition temperatures (T_c's) were 7 and 18 K. Recently, we found a new superconducting $K_x$picene phase with a T_c as high as 14 K, so we now know that $K_x$picene possesses multiple superconducting phases. Besides $K_x$picene, we discovered new superconductors such as Rb_xpicene and Ca_xpicene. A most serious problem is that the shielding fraction is ⩽15% for $K_x$picene and Rb_xpicene, and it is often ∼1% for other superconductors. Such low shielding fractions have made it difficult to determine the crystal structures of superconducting phases. Nevertheless, many research groups have expended a great deal of effort to make high quality hydrocarbon superconductors in the five years since the discovery of hydrocarbon superconductivity. At the present stage, superconductivity is observed in certain metal-doped aromatic hydrocarbons (picene, phenanthrene and dibenzopentacene), but the shielding fraction remains stubbornly low. The highest priority research area is to prepare aromatic superconductors with a high superconducting volume-fraction. Despite these difficulties, aromatic superconductivity is still a core research target and presents interesting and potentially breakthrough challenges, such as the positive pressure dependence of T_c that is clearly observed in some phases of aromatic hydrocarbon superconductors, suggesting behavior not explained by the standard BCS picture of superconductivity. In this article, we describe the present status of this research field, and discuss its future prospects.

Contents

1. General Introduction

'Aromatic hydrocarbon' generally implies a molecule that has $(4n + 2)$ π electrons and consists of benzene rings. The crystal and electronic structures of these molecules have been extensively

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studied by chemists. These molecules are semiconductors with characteristic band gaps, and have recently attracted significant attention from materials scientists and physicists because of their potential application in transistors and solar cells. Also, some hydrocarbons incorporating benzene rings have been investigated for their potential as new conductors. In 1937, London suggested the possibility of ‘supraconductivity’ in aromatic hydrocarbons. This is the first indication of the relationship of aromatic compound to superconductivity [1]. In the 1950s, Inokuchi and Akamatsu found high conductivity in complexes of perylene with halogens [2]. This pioneer work opened the way toward the realization of an organic conductor. In the 1970s, the main target for an organic conductor changed from aromatic hydrocarbons to charge-transfer complexes such as tetracyanoquinone because of their higher conductivity [3]. Therefore, as suggested above, the development of transistor and solar cell devices has recently focused on using various hydrocarbon molecules, including aromatic hydrocarbons. Thus, the most popular use of organic hydrocarbon molecules is in research on transistor and solar cell devices, and searches on ‘hydrocarbon/transistor’ find several hundred papers. This implies that hydrocarbons are now some of the most important materials in materials science. In 2010, we reported superconductivity in alkali-metal-doped picene [4], which is classed as an ‘aromatic superconductor’; the molecular structures of aromatic hydrocarbons are shown in Fig. 1 together with the lattice structure of picene. This article describes the research on aromatic superconductors reported in the 5 years since this discovery.

2. Superconductivity and features of metal-doped picene solids

When intercalating alkali-metal atoms (K and Rb) into solid picene, superconductivity was observed. The superconducting transition temperatures (T_c's) found for K-doped picene ($K_x$picene) were 7 and 18 K [4]. The 18 K T_c was a new record for organic superconductors, breaking the old record of 14.2 K (in β'-(BEDT-TTF)$_2$ICl$_2$ at 8.2 GPa [5]). However, the T_c of 18 K is lower than the highest T_c's in metal-doped C_{60}'s (T_c = 33 K for $RbCs_2C_{60}$ at ambient pressure (0 GPa) [6] and T_c = 38 K for Cs_3C_{60} at 0.7 GPa [7]), but higher than the highest T_c's in metal-doped graphites (11.5 K for CaC_6 at 0 GPa [8] and 15.1 K for CaC_6 at 7.5 GPa [9]). Thus, the high T_c found in $K_x$picene has attracted much attention because of the expectation of higher T_c's yet to come. Furthermore, superconductivity in metal-doped aromatic hydrocarbons might lead to a new research field in superconductors because of the diversity of hydrocarbons. Thus, finding superconductivity in $K_x$picene was quite significant for basic science, especially in solid state physics and materials science.

However, a most serious problem with metal-doped aromatic hydrocarbon superconductors is that their shielding fraction is still low. The shielding fraction for the 7 K phase of $K_x$picene was 15% at 4 K, while it was 1.2% for the 18 K phase of $K_x$picene [4]. The low shielding fraction made it impossible to identify the superconducting phases for determination of their crystal structure. During the five years since the discovery of superconductivity in 2010, our group has made an effort to synthesize $K_x$picene and other metal-doped picenes that exhibit a high shielding fraction. As reported in Ref. [4], we discovered a superconducting phase of Rb_xpicene, in addition to $K_x$picene. Rb_xpicene exhibited a T_c as high as 7 K and a shielding fraction of 10% at 4 K [4]. The first study on Rb_xpicene showed the presence of only a single superconducting phase at 6.9 K. Very recently, we discovered an 11 K phase (T_c^{onset} = 11.5 K, T_c = 11 K) in Rb_xpicene. The M/H *vs.* temperature (T) curves are shown in Fig. 2(a), in which M and H refer to the magnetization and applied magnetic field, respectively. The shielding fraction of the 11 K phase was 14% at 3 K. Thus, it was found that Rb_xpicene possesses two distinct superconducting phases, as does $K_x$picene. The T_c's and shielding fractions of the superconducting aromatic hydrocarbons are listed in Table 1.

The nominal x values of $K_x$picene showing T_c = 7 and 18 K were 3.3 [4], implying that doping of picene solids with similar amounts of K provides distinct superconducting phases. The nominal x values of Rb_xpicene exhibiting T_c = 6.9 and 11 K were 3.1 and 3.8, respectively. It is important to determine the exact x values in each

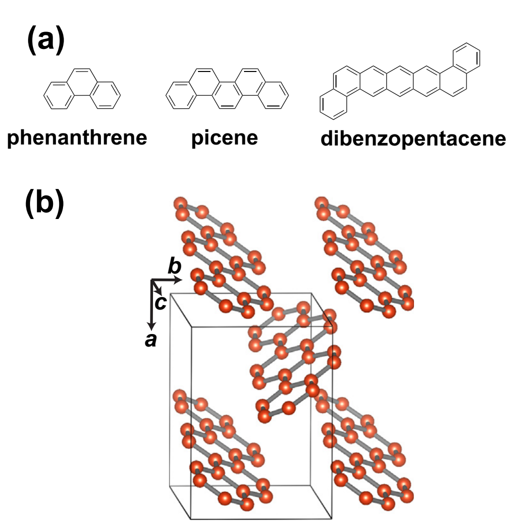

Fig. 1. (a) Molecular structures of some aromatic hydrocarbons and (b) lattice structure of picene.

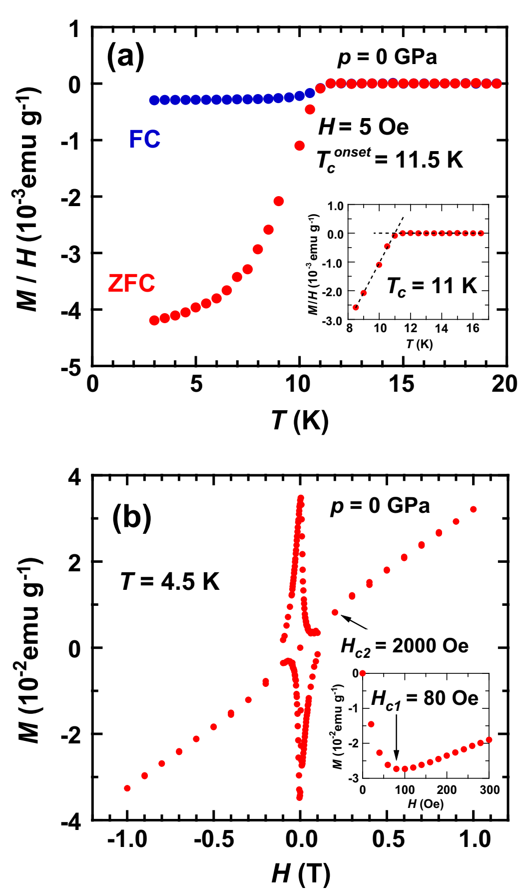

Fig. 2. (a) M/H *vs.* T plots (0 GPa) in ZFC and FC modes and (b) M *vs.* H plot (0 GPa) at 4.5 K for Rb_xpicene (nominal x = 3.8).