

## *Superconductivity in aromatic hydrocarbons*

Yoshihiro Kubozono<sup>1,2,3</sup>, Hidenori Goto<sup>1</sup>, Taihei Jabuchi,<sup>1</sup> Takayoshi Yokoya<sup>1,2</sup>, Takashi Kambe<sup>4</sup>, Yusuke Sakai<sup>1</sup>, Masanari Izumi<sup>1</sup>, Lu Zheng<sup>1</sup>, Shino Hamao<sup>1</sup> Huyen L. T. Nguyen<sup>1</sup>, Masafumi Sakata,<sup>5</sup> Tomoko Kagayama<sup>5</sup> and Katsuya Shimizu<sup>5</sup>

- 1) Research Laboratory for Surface Science, Okayama University, Okayama 700-8530, Japan
- 2) Research Center of New Functional Materials for Energy Production, Storage and Transport, Okayama University, Okayama 700-8530, Japan
- 3) Japan Science and Technology Agency, ACT-C, Kawaguchi 332-0012, Japan
- 4) Department of Physics, Okayama University, Okayama 700-8530, Japan
- 5) Center of Science and Technology under Extreme Conditions, Osaka University, Osaka 560-8531, Japan.

Yoshihiro Kubozono: kubozono@cc.okayama-u.ac.jp

### **Abstract**

**‘Aromatic hydrocarbon’ implies an organic molecule that satisfies the  $(4n+2)$   $\pi$ -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  $Rb_x$ picene and  $Ca_x$ picene. A most serious problem is that the shielding fraction is  $\leq 15\%$  for  $K_x$ picene and  $Rb_x$ picene, and it is often  $\sim 1\%$  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.

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

## 1. 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 ( $K_x\text{picene}$ ) 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  $\beta'$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub> at 8.2 GPa [5]). However, the  $T_c$  of 18 K is lower than the highest  $T_c$ 's in metal-doped C<sub>60</sub>'s ( $T_c = 33$  K for RbCs<sub>2</sub>C<sub>60</sub> at ambient pressure (0 GPa) [6] and  $T_c = 38$  K for Cs<sub>3</sub>C<sub>60</sub>

at 0.7 GPa [7]), but higher than the highest  $T_c$ 's in metal-doped graphites (11.5 K for  $\text{CaC}_6$  at 0 GPa [8] and 15.1 K for  $\text{CaC}_6$  at 7.5 GPa [9]). Thus, the high  $T_c$  found in  $\text{K}_x\text{picene}$  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  $\text{K}_x\text{picene}$  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  $\text{K}_x\text{picene}$  was 15% at 4 K, while it was 1.2% for the 18 K phase of  $\text{K}_x\text{picene}$  [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  $\text{K}_x\text{picene}$  and other metal-doped picenes that exhibit a high shielding fraction. As reported in Ref. 4, we discovered a superconducting phase of  $\text{Rb}_x\text{picene}$ , in addition to  $\text{K}_x\text{picene}$ .  $\text{Rb}_x\text{picene}$  exhibited a  $T_c$  as high as 7 K and a shielding fraction of 10% at 4 K [4]. The first study on  $\text{Rb}_x\text{picene}$  showed the presence of only a single superconducting phase at 6.9 K. Very recently, we discovered an 11 K phase ( $T_c^{\text{onset}} = 11.5$  K,  $T_c = 11$  K) in  $\text{Rb}_x\text{picene}$ . 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  $\text{Rb}_x\text{picene}$  possesses two distinct superconducting phases, as does  $\text{K}_x\text{picene}$ . The  $T_c$ 's and shielding fractions of the superconducting aromatic hydrocarbons are listed in Table 1.

The nominal  $x$  values of  $\text{K}_x\text{picene}$  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  $\text{Rb}_x\text{picene}$  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 superconducting phase. The most powerful method to determine the exact  $x$  value may be Raman scattering. A pronounced peak is observed at  $1378\text{ cm}^{-1}$  in the Raman spectrum of pure solid picene, which can be assigned to superposition of the  $\nu_{20}$  and  $\nu_{21}$   $A_1$  vibration modes

of the picene molecule [10]. The subscripts of  $\nu_{20}$  and  $\nu_{21}$  refer to the 20th and 21st  $A_1$  vibration modes from the lowest vibration. Kato, Kambe and Kubozono reported that these vibration modes provided strong electron-phonon coupling [11]. When electrons are donated to picene molecules from alkali-metal atoms, the peak clearly shifts to a lower frequency. We measured the Raman scattering of picene,  $K_1$ picene,  $K_2$ picene,  $K_3$ picene,  $K_4$ picene and  $K_5$ picene solids, and the frequencies of the peak basically took three discrete values, 1378, 1344 and 1313  $\text{cm}^{-1}$ , which were consistent with those predicted theoretically for picene,  $\text{picene}^{2-}$  and  $\text{picene}^{3-}$  [10]. This implies that only the  $K_2$ picene and  $K_3$ picene solids can be prepared when doping picene solids with K atoms at nominal  $x$  values of 1 - 5. The same behavior was observed in  $\text{Rb}_x$ picene [10]. The observed frequencies were 1378, 1345 and 1313  $\text{cm}^{-1}$ , which could be assigned to picene,  $\text{picene}^{2-}$  and  $\text{picene}^{3-}$ , implying the presence of  $\text{Rb}_2$ picene and  $\text{Rb}_3$ picene. Systematic  $M / H - T$  plots were prepared for the  $K_x$ picene and  $\text{Rb}_x$ picene samples, and the correlation between the magnetic behavior and Raman scattering was fully investigated [10], revealing that **only samples containing** only  $K_3$ picene and  $\text{Rb}_3$ picene showed superconducting behavior. **In other words, the superconductivity may be associated with  $A_3$ picene phase (A: alkali metal atoms) or the phase relating to  $A_3$ picene.** Recent reports discuss the exact number of metal atoms required for superconductivity in other aromatic superconductors [12,13].

The crystal structures of superconducting  $K_x$ picene solids are a most important research subject. However, conclusive structures have never been found because of the low superconducting shielding fraction of the samples prepared. The crystal structures of 7 and 18 K phases in  $K_x$ picene were experimentally suggested by our group [3,9]. The X-ray diffraction (XRD) patterns showed that the pure picene solids had a monoclinic lattice (space group:  $P2_1$ ) (see Fig. 1(b)). The lattice constants,  $a$ ,  $b$ ,  $c$  and  $\beta$  are 8.472(2), 6.170(2), 13.538(7) Å and 90.81(4)°, respectively [4,13], which are consistent with those determined for pure picene single crystals [14]. In the crystals, the herringbone stacking-layer ( $ab$ -layer) laminates in the direction of the  $c$ -axis. For the  $K_x$ picene with the 7 K  $T_c$ , whose nominal  $x$  value was 2.9, lattice constant  $a$  expanded to 8.707(7) Å, while  $b$  and  $c$  shrank to 5.912(4) and 12.97(1) Å, respectively; the space group of  $P2_1$  still remained in  $K_x$ picene. The lattice constants of pure picene and  $K_x$ picene are listed in Table 2. The

lattice constants obtained for  $K_x$ picene suggest that K atoms are intercalated into the  $ab$ -plane so as to expand only lattice constant  $a$ . Theoretical calculation suggests that this is energetically the most stable structure [15].

On the other hand, we were able to selectively synthesize the 18 K phase in  $K_x$ picene with a liquid solvent technique using  $CH_3NH_2$  [10], and measured its XRD patterns. The experimental details are reported in Ref. 10. Raman scattering of the  $K_x$ picene (nominal  $x = 3.1$ ) after the complete removal of  $CH_3NH_2$  showed a red-shift of  $67\text{ cm}^{-1}$  (from the  $1378\text{ cm}^{-1}$  in pure picene) in the peak ascribable to the superposition of the  $\nu_{20}$  and  $\nu_{21}$   $A_1$  vibration modes, *i.e.* the  $K_3$ picene phase. The samples showed superconductivity with  $T_c = 18\text{ K}$ . A  $(CH_3NH_2)K_x$ picene sample (nominal  $x = 3.0$ ) can be prepared simply by not heating the material to 443 K to completely remove  $CH_3NH_2$  [10], and it shows no superconductivity. The XRD patterns of both samples were analyzed with the space group of  $P2_1$ . As seen in Table 2, the lattice constants  $a$  and  $c$  of the  $(CH_3NH_2)K_x$ picene sample are larger than those in pure picene, while the  $b$  remained almost constant. The  $c$  axis expanded markedly from  $13.538(7)$  to  $14.476(4)\text{ \AA}$ , suggesting that the  $CH_3NH_2$  molecules may be intercalated into the space between the herringbone layers ( $ab$ -layers). The lattice constants  $a$  and  $c$  in the  $K_x$ picene sample showing  $T_c = 18\text{ K}$  that was prepared using liquid  $CH_3NH_2$  were still larger than those of pure picene, but the  $c$  was smaller than that of  $(CH_3NH_2)K_x$ picene. For this  $K_x$ picene solid (nominal  $x = 3.1$ ) exhibiting a  $T_c$  of 18 K, we concluded that the K atoms might be intercalated into both the  $ab$ -plane and the space between  $ab$ -layers. The theoretical calculation suggested the presence of a metastable structure in  $K_3$ picene [16]. The structure is denoted as  $K_2K_1$ picene in Refs. 15 and 16, meaning that two K atoms are inserted into the  $ab$ -layer while one K atom is intercalated into the space between  $ab$ -layers, implying different placement of K atoms than in 7 K  $K_x$ picene. If this is the case, the  $T_c$  in  $K_3$ picene is closely related to the crystal structure, *i.e.*, the crystal structure is a key for determining  $T_c$ . However, at the present stage, although certain crystal structures are suggested for the samples, it remains uncertain whether the suggested structures are associated with the actual superconducting phases, as the sample's shielding fractions are too low.

The strength of electron-phonon coupling in K<sub>3</sub>picene was calculated considering intramolecular vibrations of picene<sup>3-</sup> [11], and the density of states on the Fermi level ( $D(\epsilon_F)$ 's) was evaluated by comparing the electron-phonon coupling and the experimental  $T_c$ 's of K<sub>3</sub>picene with McMillan's formula. The  $D(\epsilon_F)$ 's were 1.99 and 2.44 eV<sup>-1</sup> molecule<sup>-1</sup> spin<sup>-1</sup>, respectively, for 7 and 18 K phases; where the Coulomb pseudopotential describing electron-electron repulsion,  $\mu^*$ , was fixed at 0.1 [11]. In other words, if this superconductivity is explainable within the framework of the BCS theorem, the  $T_c$ 's observed can be reproduced with the above  $D(\epsilon_F)$  values. The experimental  $D(\epsilon_F)$  was evaluated to be 1.2 states eV<sup>-1</sup> molecule<sup>-1</sup> spin<sup>-1</sup> from the ESR spectrum for the 18 K phase of K<sub>3</sub>picene, which is on the same order as the theoretical value (2.44 eV<sup>-1</sup> molecule<sup>-1</sup> spin<sup>-1</sup>), while the  $D(\epsilon_F)$  of the 7 K phase could not be evaluated because of the low ESR signal. That is, a larger  $D(\epsilon_F)$  provides a higher  $T_c$ . Thus the approximate estimates of  $D(\epsilon_F)$  may roughly reproduce the  $T_c$ , although not completely. Casula *et al.* pointed out that the superconductivity could not be explained by considering only the intramolecular phonons, but that intermolecular phonons also play important roles in the emergence of superconductivity [17]. It was suggested that the intermolecular phonons' contribution accounts for ~50% of all the electron-phonon coupling that produces superconductivity. These theoretical calculations were based on the assumption that the superconductivity of K<sub>3</sub>picene substantially follows a BCS-type phonon-mediated mechanism [11,17].

Here, we should consider the interesting variation of  $T_c$  with pressure. The  $T_c$  of the 7 K phase decreased straightforwardly with increasing pressure ( $p$ ), so that  $dT_c / dp = -0.3$  K GPa<sup>-1</sup> [10]. This can reasonably be interpreted within the framework of the BCS theorem based on the band broadening caused by applied pressure, *i.e.*, the decrease in  $D(\epsilon_F)$ . But surprisingly, the  $T_c$  of the 18 K phase increased linearly with increasing pressure [10]. The  $T_c$  reached 30 K at around 1 GPa. The  $dT_c / dp$  was 12.5 K GPa<sup>-1</sup>, and much larger than in the CaC<sub>6</sub> superconductors that exhibit positive pressure-dependence, typically  $dT_c / dp = 0.5$  K GPa<sup>-1</sup> [9]. In the case of solid CaC<sub>6</sub>, the positive pressure dependence of  $T_c$  was explained within the framework of the BCS theorem by the softening of Ca-Ca phonon modes. However, the positive pressure dependence of  $T_c$  in

the 18 K phase of  $K_x$ picene cannot be simply explained within the BCS model. Aoki and Kariyado pointed out that the topology of the Fermi surface in the  $K_3$ picene and  $K_2K_1$ picene structures described above changes drastically under high pressure [18]. Such a change is called a ‘Lifshitz transition’. They suggested that the drastic change in the Fermi surface might explain the behavior in ways that go beyond simple band broadening.

The magnetic behavior of the 7 and 18 K phases of  $K_x$ picene, and the 7 and 11 K phases of  $Rb_x$ picene were fully investigated to determine their lower and upper critical fields ( $H_{c1}$  and  $H_{c2}$ ) and other important parameters related to superconductivity such as London’s penetration depth ( $\lambda_L$ ) and the Ginzburg-Landau coherence length ( $\xi_{GL}$ ). The  $M$  vs.  $H$  curve of  $Rb_{3.8}$ picene ( $T_c$  of 11 K) measured at 4.5 K provided an  $H_{c1}$  of 80 Oe (see Fig. 2(b)). This diamond curve shows clear superconductivity. The  $H_{c2}$  was evaluated as 2000 Oe at 4.5 K. The  $\lambda_L$  and  $\xi_{GL}$  were evaluated to be 170 and 41 nm, respectively, with the general equations relating  $H_{c1}$  and  $H_{c2}$  to  $\lambda_L$  and  $\xi_{GL}$  [19]. Table 3 lists the  $H_{c1}$ ,  $H_{c2}$ ,  $\lambda_L$  and  $\xi_{GL}$  for all metal-doped picene superconductors. Furthermore, it was pointed out that the  $\lambda_L$  that was found was larger than the crystalline size ( $L$ ) of the superconductor samples (see table 3), which was evaluated with the Debye-Scherrer equation. The fact that  $\lambda_L > L$  means that  $H$  must penetrate significantly to the superconducting phase and this penetration reduces the shielding fraction. The electrical resistivity ( $\rho$ ) of superconducting  $K_x$ picene solids was measured in four-terminal measurement mode, and the  $\rho$  of the pellet sample of  $K_{3.5}$ picene showed zero-resistivity below 8 K, clearly implying superconductivity [20]. The  $T_c$  determined from the crossing point of the two lines that map the variation of  $\rho$  above and below the  $T_c$  was 10.9 K (Fig. 2(a) in Ref. 20). The reproducibility of zero-resistivity was confirmed for the pellet sample of  $K_{3.1}$ picene, which showed a  $T_c$  of 6.7 K, and zero-resistivity was observed below 5 K [20]. This confirmation of zero-resistivity guarantees that  $K_x$ picene provides superconductivity. The Raman scattering of the samples showed that they contained the  $K_3$ picene phase.

For further confirming the superconducting transition in  $K_x$ picene from  $R - T$  plot, we measured the temperature dependence of  $R$  using the pressurized sample of  $K_x$ picene (nominal  $x = 3.0$ ); the sample showed the  $T_c$  of 6.5 K and the shielding fraction of 0.5%



at 2.5 K (Fig. 3(a)), *i.e.*, the 7 K phase of  $K_3$ picene. In this experiment, the temperature dependence of  $R$  was measured at 4.1 GPa. The superconducting transition ( $T_c^{\text{mid}} = 5.6$  K) was confirmed from the  $R - T$  plot (Figs. 3(b) and (c)) measured using the  $K_x$ picene sample with such a small shielding fraction; the experimental condition such as the current flow at low-temperature was carefully checked in this experiment.

Here we have to discuss why the drop of resistance or zero resistance was observed in the sample with such a low-shielding fraction. One possibility is that the  $R - T$  measurement was performed using pelletized sample or pressurized sample. In the pelletized sample or pressurized sample, the connection between superconducting parts must be improved so that the superconducting current flows. Furthermore, tunnel current caused by Josephson effect may flow across the insulating part which may lead to the observation of zero resistance or drop of resistance. Thus, the superconductivity of  $K_x$ picene was also evidenced from the resistance measurement using pelletized or pressurized sample. In addition, the  $T_c^{\text{mid}}$  shown in Fig. 3(c) follows the pressure dependence of  $T_c$  in the 7 K phase of  $K_x$ picene, which was measured previously [10].

The Photoemission spectroscopy (PES) reported by Okazaki *et al.* showed metallic behavior in thin films of K-doped picene [21,22], *i.e.*, the PES peak was observed at the Fermi energy with K-doping of picene thin films and the peak disappeared with excess K-doping. However, the PES reported by other groups showed no metallic behavior [23-25]. Okazaki *et al.* suggested that the observation of metallic behavior originated in the different crystal structures of picene thin-films, which change depending on the substrates used.

We also intercalated the alkali-earth metal atoms Ca and Ba into solid picene. With Ca atoms intercalated, a superconducting transition was confirmed at a nominal 1.5 parts Ca, *i.e.*,  $Ca_{1.5}$ picene [13], which indicated a three-electron donation to picene molecules in the superconducting sample, based on the oxidation state of +2 in Ca. The  $T_c$  was 7 K and the shielding fraction was 1.25% at 2 K. In the case of Ba, we observed a superconducting transition with  $T_c = 6$  K, but the shielding fraction was quite small (1% at 2.0 K). Thus, although the alkali-earth metal-doped picene showed superconductivity,

the shielding fraction was too small for us to determine the structure and physical properties.

We also tried K-doping picene using the liquid  $\text{NH}_3$  technique, analogous to the successful synthesis of  $\text{K}_x\text{picene}$  using  $\text{CH}_3\text{NH}_2$  [10]. The  $\text{Li}_x\text{picene}$  prepared using liquid  $\text{NH}_3$  showed superconductivity, with a  $T_c$  of 11 K. Thus,  $\text{NH}_3$  was also found to be useful in the synthesis of  $\text{K}_x\text{picene}$  solids. Recently, we observed superconductivity with a  $T_c$  as high as 14 K in  $\text{K}_x\text{picene}$  (nominal  $x = 3.0$ ), and a shielding fraction of 3.9% at 2 K (see Fig. 4(a)). This phase's  $T_c$  is different from the 7 and 18 K phases of  $\text{K}_x\text{picene}$ , and probably represents a new superconducting phase. Its structure and physical properties have not yet been determined, and the study of its characteristics is now in progress. Pressing the sample up to 0.2 GPa led to a higher shielding fraction than the above value (Fig. 4(b)), *i.e.*, a shielding fraction of 16% at 5 K was realized after pressing the sample, suggesting an increase in the size of superconducting grains due to a stronger connection. Furthermore, we speculated the stabilization of superconducting phase under pressure through the suppression of competitive electronic phase for superconductivity such as magnetic order which has often been observed in the  $\text{K}_x\text{picene}$  sample. Anyway, the pressing the sample improves the superconductivity.

We carefully checked the presence of elements (impurities) other than K and C elements in the  $\text{K}_x\text{picene}$  sample using energy dispersive X-ray (EDX) spectroscopy. As seen from Fig. 4(c), only peaks due to C and K were observed together with the small peaks due to O owing to oxidation of sample, Si owing to the glass (when cutting sample tube, Si was introduced to the sample), and Cu originating from Cu tape used for holding the sample. Notably, H cannot be detected by EDX. Thus, the EDX spectrum substantially suggests no elements other than K and C in  $\text{K}_x\text{picene}$ .

## **2. Metal-doping of solid hydrocarbons other than picene, and their superconductivity**

The first successful production of superconductivity by metal-doping of aromatic

hydrocarbons other than picene was achieved in phenanthrene, which has a W-shaped structure consisting of three fused benzene rings [12]. This work was done by Chen's group at the Chinese University of Science and Technology. The  $K_x$ phenanthrene sample (nominal  $x = 3$ ) provided a  $T_c$  of 4.95 K with a shielding fraction of 5.3%, while  $Rb_x$ phenanthrene (nominal  $x = 3$ ) showed a  $T_c$  of 4.75 K with a shielding fraction of 6.7%. Pressing the  $K_3$ phenanthrene sample increased the shielding fraction to 15.5%. Similar behavior was observed in superconducting  $K_x$ picene samples [4]. The Raman peak observed at  $1441\text{cm}^{-1}$  for pure phenanthrene downshifted to 1424 and  $1419\text{cm}^{-1}$ , respectively, for  $K_3$ phenanthrene and  $Rb_3$ phenanthrene, suggesting three-electron donation to the phenanthrene molecule, an electron transfer equal to that in superconducting metal-doped solid picene. Subsequently,  $Sr_{1.5}$ phenanthrene and  $Ba_{1.5}$ phenanthrene showed superconductivity, with  $T_c = 5.6$  and 5.4 K, respectively [26]. The shielding fraction of  $Ba_{1.5}$ phenanthrene was reported to be 65.4%. However, it was found that the samples of  $Ba_{1.5}$ phenanthrene contained La atoms, and two papers on specific heats were retracted. It should be noted that La metal shows superconductivity with  $T_c = 6$  K (face centered cubic (fcc)) and  $T_c = 5$  K (double hexagonal close packing (dhcp)) and also positive pressure-dependence of  $T_c$  ( $dT_c / dp = 1.2\text{ K GPa}^{-1}$  for fcc and  $1.1\text{ K GPa}^{-1}$  for dhcp) [27]. At the present stage, we cannot judge whether the superconductivity of the  $Ba_{1.5}$ phenanthrene sample exhibiting the high shielding fraction (~65%) originated from  $Ba_{1.5}$ phenanthrene. Further study of  $Ba_{1.5}$ phenanthrene may be required. We observed clear superconductivity in the  $Sr_{1.5}$ phenanthrene sample provided by the above group, which showed  $T_c = 5.3$  K and a shielding fraction of 4% at 2 K (Fig. 5(a)). X-ray photoelectron spectroscopy (XPS) of the  $Sr_{1.5}$ phenanthrene sample showed only C and Sr peaks (Fig. 5(b)), indicating that the superconductivity of the  $Sr_{1.5}$ phenanthrene sample can be assigned to Sr-doped phenanthrene. **In other words, no elements other than Sr and C were included in the sample.** The pressure dependence of  $T_c$  in  $K_3$ phenanthrene showed a positive-pressure effect, with the  $T_c$  increasing linearly with increasing pressure [12]. The  $1/T_c(0\text{ GPa}) \times dT_c / dp$  of  $K_3$ phenanthrene was  $0.26\text{ GPa}^{-1}$  which means  $dT_c / dp \sim 1.2\text{ K GPa}^{-1}$ . Our group also observed superconductivity in  $K_x$ phenanthrene with  $T_c = 4.5$  K and a shielding fraction of 1%.

Superconductivity was confirmed in K-doped dibenzopentacene ( $K_{3.45}$ DBP, DBP: dibenzopentacene) by Xue *et al.*, which showed a  $T_c$  as high as 33 K [28]. Multiple superconducting phases were observed in  $K_x$ DBP;  $T_c = 7.4$  K for  $K_3$ DBP and  $T_c = 28.2$  K for  $K_{3.17}$ DBP. Thus, the different  $x$ 's of  $K_x$ DBP provide different  $T_c$ 's. At present, the  $T_c$  of  $K_{3.45}$ DBP is the highest reported for metal-doped aromatic hydrocarbons. The shielding fraction of  $K_{3.45}$ DBP was 3.2% at 25 K, still fairly low. Our group also observed the superconducting transitions at  $T_c = 30$  and 7 K in  $K_x$ DBP, with a shielding fraction below 1%.

We prepared K-doped [6]phenacene using the liquid  $NH_3$  technique, and superconductivity was observed with  $T_c = 7$  K and a shielding fraction of 1%. Since the shielding fraction was so low, we could not characterize the structure and physical properties. Nevertheless, this is significant because it showed that a superconducting phase can be produced using phenacenes other than phenanthrene and picene. Subsequently,  $K_x$ [7]phenacene was prepared, which showed superconductivity with a  $T_c$  as high as 11 K. This sample was prepared using the normal annealing method. The shielding fraction was 0.1% at 2 K. Thus, we have prepared new superconductors with various phenacene molecules. We also observed superconductivity in metal-doped coronene [13] and corannulene, but the shielding fraction was still 1%. Such a low shielding fraction suggests the possibility of surface superconductivity, with only the surfaces of crystal grains doped with metal atoms. Furthermore, the degradation of molecules by the reaction of metal atoms with the hydrocarbons is also suggested. The samples exhibiting low shielding fractions should be more precisely characterized to clarify the origin of their superconductivity. The trial is now in progress independently by some groups.

Finally, we plotted the  $T_c$ 's of the hydrocarbon superconductors (both aromatic and non-aromatic) as a function of the number of benzene rings. As seen from Fig. 5(c), for superconductors with a higher shielding fraction, the  $T_c$  increases with an increasing number of benzene rings. In contrast, when the  $T_c$ 's of metal-doped hydrocarbons with low shielding fractions ( $\sim 1\%$ ) are plotted, the  $T_c$  does not increase straightforwardly. Metal-doped picene and dibenzopentacene possess multiple superconducting phases, so

various  $T_c$ 's are observed [4,28], but the  $T_c$ 's of metal-doped phenanthrenes range from 4.5 to 6.0 K [12,26]. The correlation between  $T_c$  and the number of benzene rings is confined to the maximum  $T_c$ 's in each sample that has a high shielding fraction. To firmly establish the correlation, we have to produce more hydrocarbon superconductors with high shielding fractions.

### 3. What was clarified for aromatic hydrocarbon superconductors?

This article has shown the problems to be solved concerning aromatic hydrocarbons. In the ~5 years since the discovery of superconductivity in metal-doped picene, many theoretical studies have appeared on aromatic hydrocarbon superconductors, but just a few papers on the preparation of aromatic hydrocarbon superconductors. The reason is probably the difficulty of preparing such superconductors. We fully reviewed superconductivity in carbon based superconductors, including aromatic hydrocarbons, in 2011 [13], and recently a review on aromatic hydrocarbon superconductors was published by Artioli and Malavasi [29]. In that review, Artioli and Malavasi pointed out that 'in order to make the hydrocarbon superconductors a solid future prospect much effort – starting from the experimental side – is still required'.

At the present stage, some groups have succeeded in preparing aromatic hydrocarbon superconductors with a shielding fraction of more than 10%. Very recently, Artioli *et al.* at University of Pavia (Italy) and University of Oslo (Norway) discovered the superconductivity in Sm doped [n]phenacenes (n = 3, 4 and 5); [n]phenacenes (n = 3, 4 and 5) refer to phenanthrene, chrysene and picene [30]. The  $T_c$ 's of Sm doped phenanthrene, chrysene and picene were 4.4, 5.4 and 4 K, respectively. Thus, new types of superconducting aromatic materials steadily increase. This allows us to conclude that superconducting materials can be prepared by metal intercalation into solid aromatic hydrocarbons, or if strictly saying, by reaction of metal with solid aromatic hydrocarbons. This is clearly established. However, the study of the structure and composition of these superconducting materials remains incomplete, as suggested in the above review article. Currently, the superconducting shielding fraction of 0.1 – 1.0% can be observed at the probability of 10% out of the  $K_x$ picene and  $Rb_x$ picene samples prepared, while remaining

90% samples mainly exhibited the Curie-type behavior, suggestive of localized magnetic state. The samples with more than 10% shielding fraction are sometimes found, but the clear protocol to synthesize the high-quality superconductor sample has not yet been established. Recently, some other groups, new to this field, have succeeded in preparing superconducting metal-doped picene solids, and some of their papers will be published soon. This may be the trigger for a more extensive pursuit of the origin of aromatic superconductivity.

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Table 1.  $T_c$ 's and shielding fractions (SF's) of metal-doped aromatic hydrocarbons. The  $T_c$  determination method is described in each reference. The  $T_c$ 's of the 14 K phase of  $K_x$ picene and 11 K phase of  $Rb_x$ picene were determined based on the crossing point of two lines (see Figs. 4(a) and 2(a)). The temperatures for SF evaluation are described in text or references. Nominal x values are described in text or references.

	$T_c$ (K)	SF (%)
$K_x$ phenanthrene <sup>a)</sup>	4.95	5.3
$Rb_x$ phenanthrene <sup>a)</sup>	4.75	6.7
$K_x$ picene (7 K phase) <sup>b)</sup>	6.9	15
$K_x$ picene (14 K phase)	14	3.9
		16 (after pressing)
$K_x$ picene (18 K phase) <sup>b)</sup>	18	1.2
$Rb_x$ picene (7 K phase) <sup>b)</sup>	6.9	10
$Rb_x$ picene (11 K phase)	11	14
$K_x$ dibenzopentacene <sup>c)</sup>	7.4	3.6
	28.2	5.5
	33	3.2

a) Taken from Ref. 12.

b) Taken from Ref. 4.

c) Taken from Ref. 28.

Table 2. Lattice constants of metal-doped aromatic hydrocarbons. Nominal x values are described in text or references.

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)	$V(\text{Å}^3)$
phenanthrene <sup>a)</sup>	8.453	6.175	9.477	98.28	490
K <sub>3</sub> phenanthrene <sup>a)</sup>	8.430	6.134	9.417	98.18	482
Rb <sub>3</sub> phenanthrene <sup>a)</sup>	8.450	6.139	9.442	97.99	485
picene <sup>b)</sup>	8.472(2)	6.170(2)	13.538(7)	90.81(4)	708
K <sub>x</sub> picene (7 K phase) <sup>b)</sup>	8.707(7)	5.912(4)	12.97(1)	92.77(5)	667
(CH <sub>3</sub> NH <sub>2</sub> ) <sub>z</sub> K <sub>x</sub> picene <sup>c)</sup>	8.927(5)	6.151(1)	14.476(4)	94.16(3)	793
K <sub>x</sub> picene (18 K phase) <sup>c)</sup>	8.571(5)	6.270(2)	14.001(3)	91.68(3)	752

a) Taken from Ref. 12.

b) Taken from Ref. 4.

c) Taken from Ref. 10.



Table 3. Parameters characterizing superconductivity in metal-doped aromatic hydrocarbons.

	$H_{c1}$ (Oe)	$H_{c2}$ (Oe)	$\lambda_L$ (nm)	$\xi_{GL}$ (nm)	$L$ (nm)
$K_x$ picene (7 K phase) <sup>a)</sup>	300	>10000	95	<18	14
$K_x$ picene (18 K phase) <sup>a)</sup>	400	>10000	77	<18	14
$Rb_x$ picene (7 K phase) <sup>a)</sup>	150	800	130	57	29
$Rb_x$ picene (11 K phase)	80	2000	170	41	66
$K_x$ dibenzopentacene <sup>b)</sup>	200	-	-	-	-

a) Taken from Ref. 4.

b) Taken from Ref. 28.

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## Figure captions

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  $Rb_x$ picene (nominal  $x = 3.8$ ).

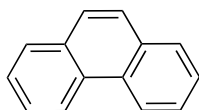
Fig. 3. (a)  $M / H$  vs.  $T$  plots (0 GPa) in ZFC and FC modes and (b)  $R$  vs.  $T$  plot (4.1 GPa) of 7 K phase of  $K_x$ picene (nominal  $x = 3.0$ ). (c) Expanded  $R$  vs.  $T$  plot of (b).

Fig. 4. (a)  $M / H$  vs.  $T$  plots (0 GPa) in ZFC and FC modes and (b)  $M / H$  vs.  $T$  plots in ZFC and FC modes measured at 0.2 GPa for  $K_x$ picene ( $x = 3.0$ ). (c) EDX spectrum for  $K_x$ picene ( $x = 3.0$ ).

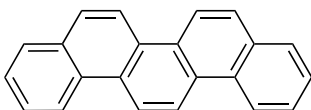
Fig. 5. (a)  $M / H$  vs.  $T$  plots (0 GPa) in ZFC and FC modes and (b) XPS spectrum for  $Sr_x$ phenanthrene (nominal  $x = 1.5$ ). (c) Plots of  $T_c$  against number of benzene rings in hydrocarbon superconductors. In (c), the dots (blue and red) refer to the high- $T_c$  and low- $T_c$  phase of picene, coronene and dibenzopentacene which have multiple superconducting phases. The blue dot of phenanthrene corresponds to the superconducting phase. The dots (green) refer to the superconducting phases of [6]phenacene and [7]phenacene.

Figure 1

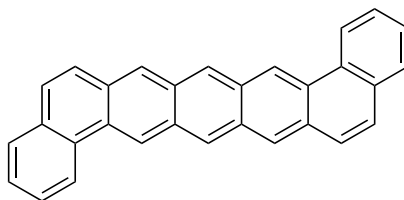
(a)



phenanthrene



picene



dibenzopentacene

(b)

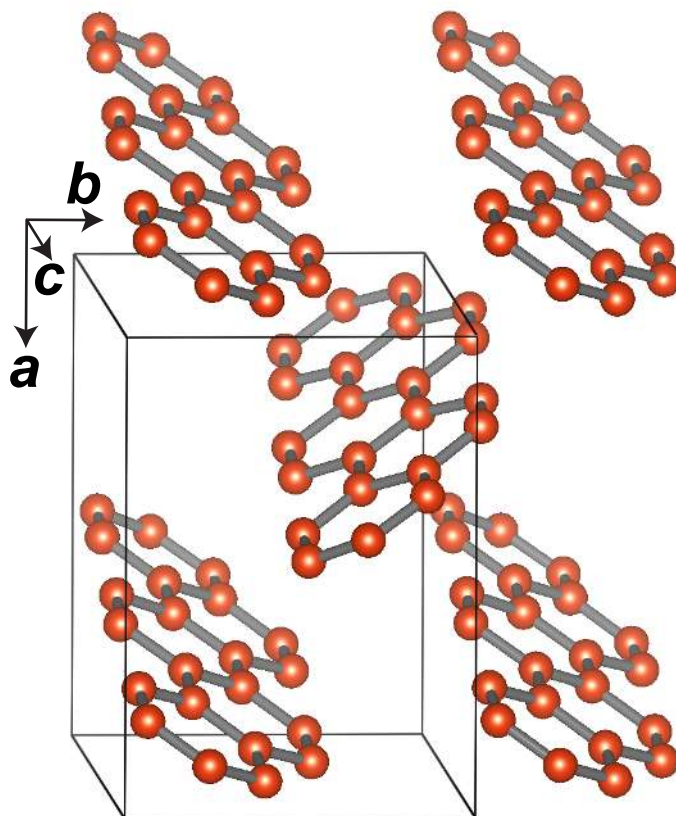


Figure 2

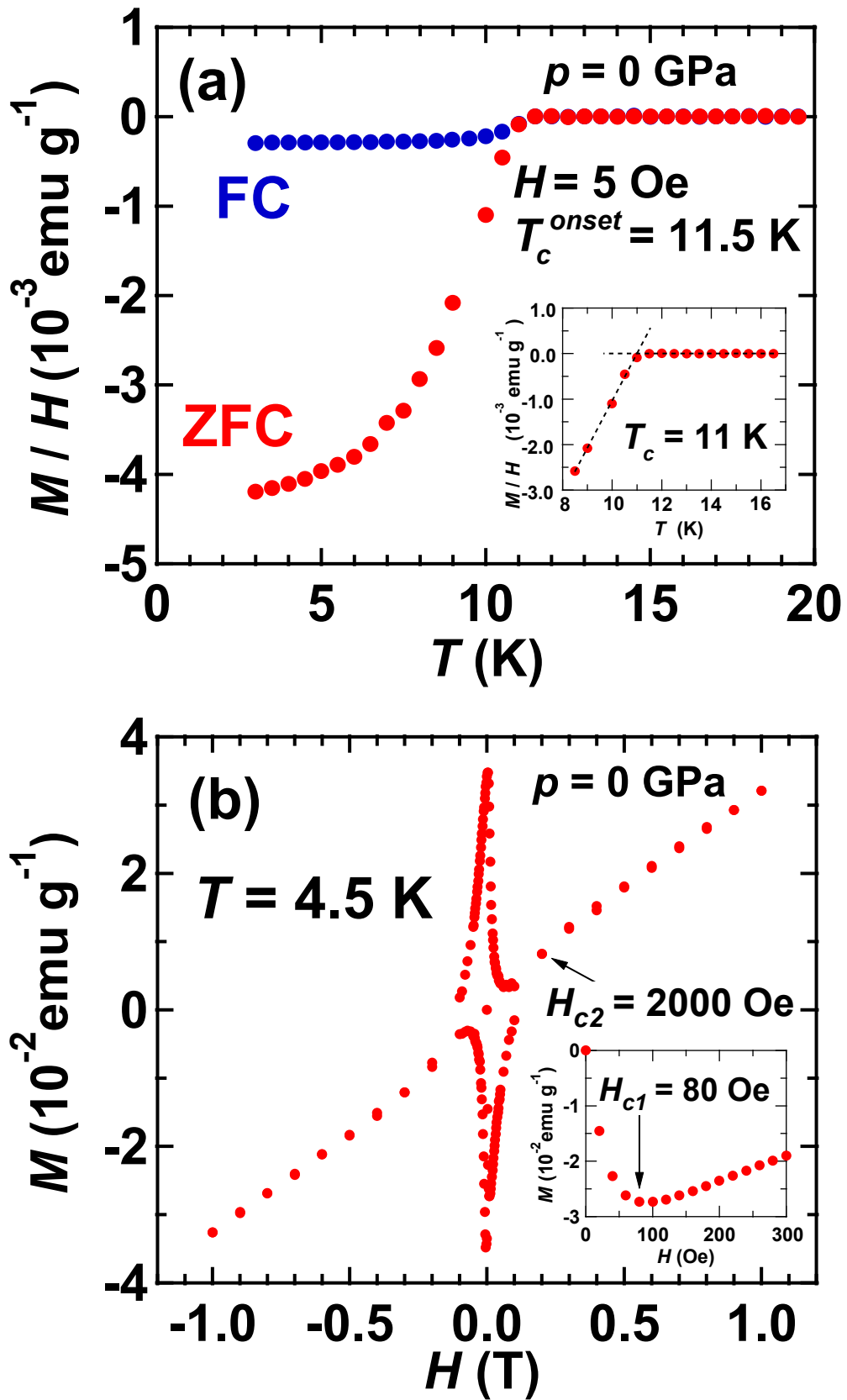


Figure 3

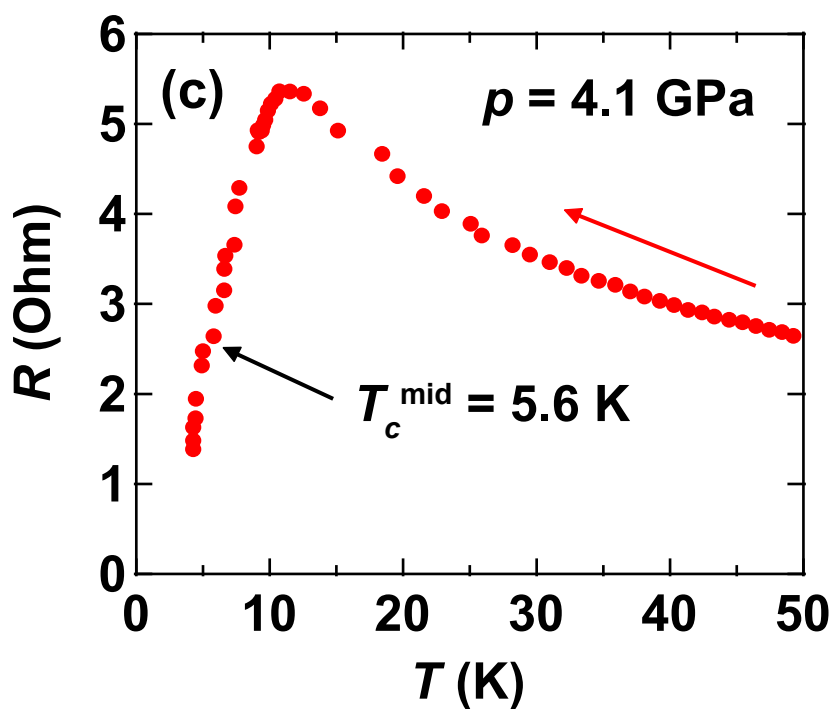
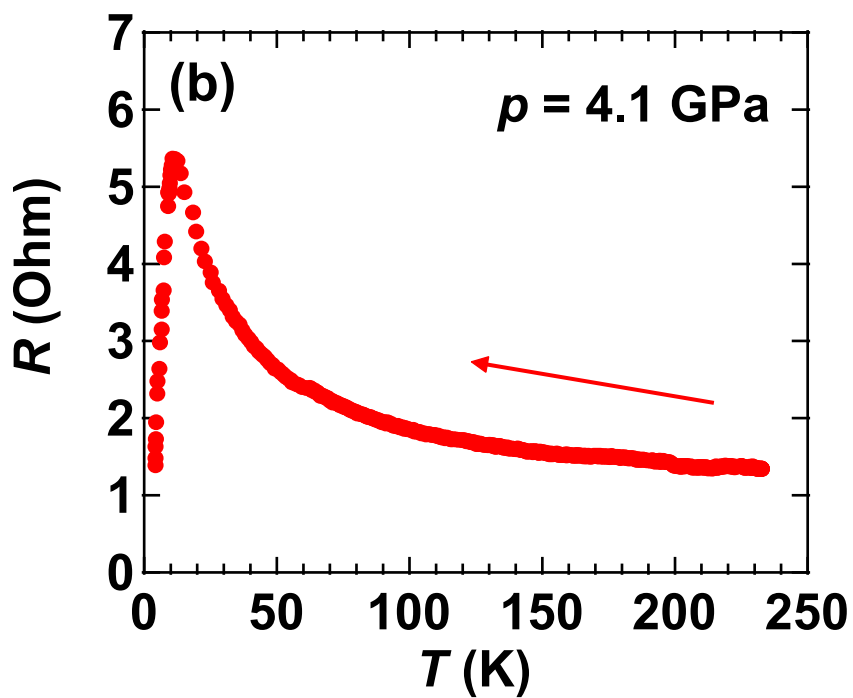
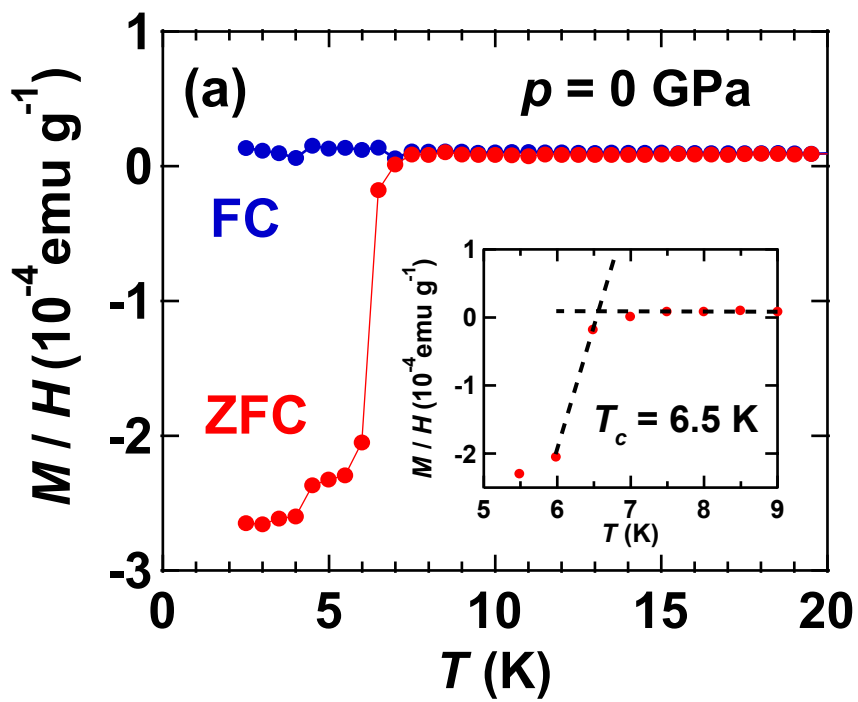


Figure 4

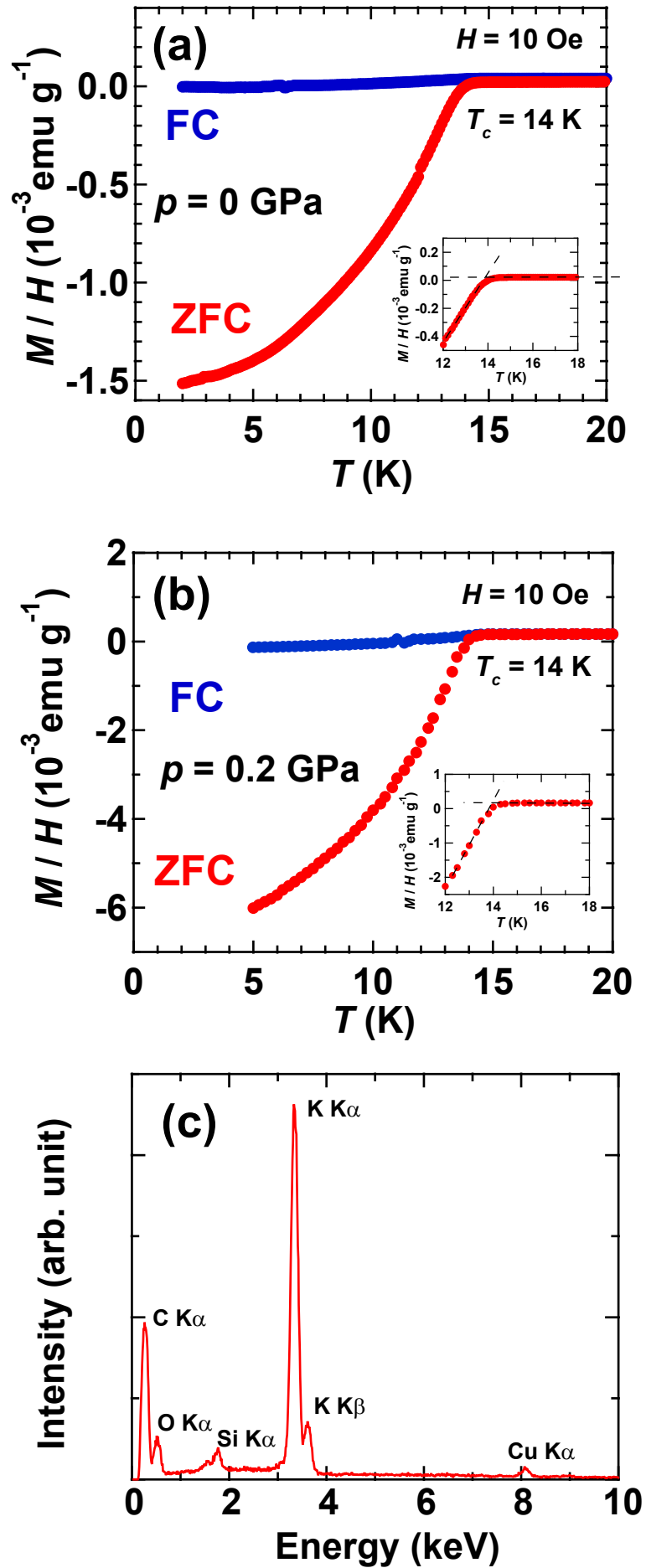




Figure 5

