Revised manuscript

Fabrication of new superconducting materials, $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($0 < x < 1$)

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ABSTRACT

Metal intercalation to graphite produces various types of superconductors. The highest superconducting transition temperature T_c (onset temperature, T_c^{onset} , of 11.5 K) was found in Ca intercalated graphite, denoted CaC_6 . T_c^{onset} increased up to 15.1 K at 7.5 GPa, implying a positive pressure dependence. However, no new metal-intercalated graphite superconductors with T_c^{onset} higher than 11.5 K at ambient pressure have so far been reported. To search for new graphite superconductors, we successfully synthesized binary-element-intercalated graphite, $\text{Ca}_x\text{K}_{1-x}\text{C}_y$. Their structure resembles that of KC_8 . T_c increased continuously with increasing x . Furthermore, the pressure dependence of T_c in $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ was investigated over a wide pressure range from 0 to 43 GPa. T_c (= 9.6 K at 0 GPa) increased to 11.6 K at 3.3 GPa, and decreased to 2.0 K at 41 GPa. This behavior is similar to that of CaC_6 , albeit with a lower maximum T_c . X-ray diffraction patterns were measured under high pressures of 0 to 24 GPa, and suggest a structural transition at 15 GPa. Evidence is given for superconducting graphite involving binary metal intercalation.

1. Introduction

Superconductivity in Ca-intercalated graphite (CaC_6) has generated much interest for its superconducting transition temperature T_c , which is greater than in other metal-doped graphites. The onset superconducting transition temperature T_c^{onset} is 11.5 K for CaC_6 [1,2], compared to 136 mK for KC_8 and 25 mK for RbC_8 [3-5]. After the discovery of superconducting CaC_6 in 2005, new graphite superconductors YbC_6 ($T_c^{\text{onset}} = 6.5$ K [2]), SrC_6 ($T_c^{\text{onset}} = 1.65$ K [6]), and $\text{Li}_3\text{Ca}_2\text{C}_6$ ($T_c^{\text{onset}} = 11.15$ K [7]) were successfully synthesized and characterized. The superconductor BaC_6 ($T_c = 65$ mK) was also discovered very recently [8].

The pressure dependence of superconductivity in CaC_6 was investigated at pressures ranging from 0 to 16 GPa [9]. T_c^{onset} reached 15.1 K at 7.5 GPa and decreased rapidly above 8 GPa. Such a pressure dependence in T_c was also observed for other metal-doped graphite superconductors. The maximum T_c^{onset} values were 1.7 K (1.5 GPa [10]) and 7.1 K (1.8 GPa [11]) for KC_8 and YbC_6 , respectively. Thus, a positive pressure dependence is characteristic of graphite superconductors. In other words, metal-doped graphite is one of exotic superconductors. In the case of CaC_6 , the increase in T_c reportedly originates from the softening of in-plane Ca-Ca phonons [9,12] and the rapid decrease in T_c is attributed to the order-disorder transition relating to a large softening of lattice under pressure [13].

The $T_c^{\text{onset}} = 11.5$ K observed in CaC_6 remains the highest value reported to date. To beat this record, we tried to synthesize $\text{Ca}_x\text{K}_{1-x}\text{C}_y$, in which two metal elements are intercalated in the graphite. Here, we report on these new superconducting $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ compounds, synthesized by immersing highly oriented pyrolytic graphite (HOPG) in molten Li/K/Ca alloy. The superconducting $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ thus synthesized showed an increase in T_c from 0.136 to 11.2 K with increasing x , confirming the successful binary intercalation of Ca and K in the graphite. X-ray

diffraction (XRD) patterns of $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($x \neq 1$) suggest a KC_8 -type structure (face-centered orthorhombic, space group No. 70, $Fddd$ [14]). In the present study, we applied pressures ranging from 0 to 43 GPa to the $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$. The magnetic susceptibility (χ_g in $\text{cm}^3 \text{g}^{-1}$) of $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ at ambient pressure (0 GPa) showed clear superconducting behavior ($T_c = 9.6$ K, shielding fraction = 90% at 2.5 K). T_c increased to 11.6 K at 3.3 GPa as the pressure was increased, and subsequently decreased at still higher pressure. T_c was 4.0 K at 16 GPa and slowly decreased with pressure increasing to 43 GPa. The pressure dependence of the XRD pattern reflects a structural change, probably to hexagonal-diamond structure (non-graphite structure), above 15 GPa, consistent with the $T_c - p$ plot.

2. Experimental

The $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ samples were prepared using the liquid-alloy technique. Ca and K, mixed in appropriate molar ratios, were placed in an iron vessel with excess Li. The vessel was then heated to 300°C, at which temperature the Ca/K/Li alloy is already melted. The HOPG was then immersed in the melted Ca/K/Li alloy for one week. The entire preparation was done in an Ar-filled glove box (O_2 and H_2O concentrations were maintained below 0.1 ppm). The $\chi_g - T$ curves for the $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ samples were measured with a SQUID magnetometer (Quantum Design, MPMS2). XRD patterns at ambient pressure were measured at 295 K with an X-ray diffractometer (Rigaku, RINT-TTR III) equipped with a $\text{CuK}\alpha$ source ($\lambda = 1.5418 \text{ \AA}$).

The pressure dependence of the resistance (R) – temperature (T) relationship of $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ sample was measured in AC four-terminal-measurement mode. The sample was placed in a diamond anvil cell (DAC). A 60- μm -thick stainless-steel (SUS 310) gasket with a 200- μm -diameter hole was placed on the diamond with a 500 μm culet. The gasket was covered with

Al_2O_3 and a Kapton (polyimide) film was placed onto the $\text{Al}_2\text{O}_3/\text{SUS}$ gasket. The Cu electrodes were connected to the Kapton film. The $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ sample was placed onto the Cu electrodes, and the sample was pressed by another diamond. The pressure medium was not used in this experiment to avoid sample degradation. The pressure was determined by monitoring the fluorescence peak of a small piece of ruby placed inside the DAC. The resistance R was recorded using an AC resistance-bridge (Lakeshore, 370-type Resistance Bridge), limiting the applied current to less than 1 mA. The sample was cooled using liquid He, and the temperature was controlled with a temperature controller (Oxford, ITC503 Temperature Controller).

The XRD patterns under high pressure were measured at 295 K using synchrotron radiation ($\lambda = 0.4135 \text{ \AA}$) from the BL10XU beamline of the SPring-8, Japan; an incident beam is focused by a stacked compound X-ray refractive lens. A 40- μm -thick CuBe gasket with a 100- μm (or 200- μm) diameter hole was placed on the diamond with a 300- μm (or 600- μm) culet, and the sample was introduced into the hole. Finally the sample was pressed by another diamond. The sample set in the DAC without a pressure medium was used for the first XRD measurement, while lubricant oil (Idemitsu Co., Ltd., Daphne 7373) was loaded together with samples as a pressure medium in the second XRD measurement. The pressure was determined by monitoring the fluorescence peak of a piece of ruby set in the DAC. The X-ray diffraction signals were collected by imaging plate (IP) X-ray area detector system (Rigaku Co., R-Axis IV).

3. Results and discussion

3-1. Synthesis of binary-intercalated graphite ($\text{Ca}_x\text{K}_{1-x}\text{C}_y$).

Figure 1a shows the T dependence of the magnetic susceptibility χ_g , measured during zero-field cooling (ZFC) or field cooling (FC) in $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_y$ prepared by the melted-alloy method at ambient pressure (1 bar $\sim$ 0 GPa). The value of y in $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_y$ was determined experimentally, in section 3-2. The $\chi_g - T$ curves for $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_y$ show a clear drop at 10.5 K, which we assign to T_c^{onset} . T_c is defined from the intersection of the two lines representing the normal state and the state with decreasing χ_g , as shown in the inset of Figure 1a. T_c for $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_y$ was determined as 9.6 K. The shielding fraction of $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_y$ was determined as 90% at 2.5 K, suggesting bulk superconductivity. A T_c value of 9.6 K in $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_y$ is lower than 11.2 K, found in CaC_6 prepared in this study (result not shown); the T_c^{onset} for this CaC_6 sample was 11.5 K, consistent with previous reports [1,2]. The shielding fraction was 100% at 2.5 K.

All the $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ samples ($0 < x \leq 1.0$) provided the different superconducting transition temperatures (T_c^{onset} 's and T_c 's) and high shielding fractions ($\sim 100\%$), suggesting that the binary intercalation of Ca and K within graphite can produce bulk superconducting phases. Figure 1b plots T_c versus x for $\text{Ca}_x\text{K}_{1-x}\text{C}_y$. $T_c = 136$ mK [4] at $x = 0$, corresponding to KC_8 . This plot was made by averaging multiple $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ samples for each x ; the T_c of only one sample is plotted for $\text{Ca}_{0.7}\text{K}_{0.3}\text{C}_y$. The estimated standard deviation (error bar) about the mean T_c is shown on the graph. T_c varies continuously as a function of x in the range 136 mK and 11.2 K, which implies that the nominal x value is probably consistent with the actual stoichiometric value.

Fig. 1. (a) Magnetic susceptibility $\chi_g = M/H$ as a function of T for the zero-field-cooling (ZFC) and field-cooling (FC) modes of $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_y$. (b) T_c versus x for $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($0 \leq x \leq 1$). The dashed and dotted curves refer to the fitted ones for the experimental data found for $x = 0 - 1.0$. The $T_c - x$ behavior at $x = 0.7 - 1.0$ (dotted curve) is still unclear.

3-2. Structure of $\text{Ca}_x\text{K}_{1-x}\text{C}_y$.

XRD patterns for $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($0 < x < 1$) are shown in Figure 2a, together with simulated spectra for Li, LiC_6 , KC_8 , and CaC_6 . The KC_8 structure is denoted ‘ $\text{A}\alpha\text{A}\beta\text{A}\gamma\text{A}\delta$ ’ [14], where ‘A’ refers to the graphene sheet, and α , β , γ , and δ refer to the four sites occupied by the metal atoms (see Figure 2b). The crystal structure is an orthorhombic lattice with the space group $Fddd$ (No. 70). The lattice constants a , b , and c of KC_8 were 4.92, 8.52, and 21.40 Å, respectively [14]. On the other hand, the CaC_6 structure is denoted ‘ $\text{A}\alpha\text{A}\beta\text{A}\gamma$ ’, where the metal atoms occupy three different sites (Figure 2b). This crystal structure is rhombohedral with the space group $R\bar{3}m$ (No. 166) [1]. The lattice constants a and c of CaC_6 were 4.33 and 13.57 Å, respectively [1,15], and are shown in the hexagonal structure. As seen in Figure 2a, the XRD patterns for $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($0 < x < 1.0$) are similar to the simulation for KC_8 , implying that the materials have the structure of KC_8 . In other words, $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($0 \leq x < 1$) can be expressed as $\text{Ca}_x\text{K}_{1-x}\text{C}_8$. We henceforth use the

Fig. 2. (a) XRD patterns for the $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_y$ samples ($x = 0.2 - 0.6$), shown with simulated spectra for CaC_6 , KC_8 , LiC_6 and Li . (b) Schematic representation of the crystal structures of KC_8 and CaC_6 . (c) Graphene-sheet plane spacing d_{AA} versus x for the $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($0 \leq x \leq 1$) samples. The structure was determined as ' $\text{Ca}_x\text{K}_{1-x}\text{C}_8$ ' for $x \neq 1$.

chemical formula $\text{Ca}_x\text{K}_{1-x}\text{C}_8$ when referring to all the cases $0 \leq x < 1$. Furthermore, the XRD patterns for $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($x = 0.2, 0.33$ and 0.4) show no clear impurity peaks, implying the presence of only these $\text{Ca}_x\text{K}_{1-x}\text{C}_y$, whereas the XRD pattern of $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($x = 0.6$) shows some impurity peaks that can be assigned to the high-stage graphite intercalation compounds with the structures of KC_{24} and KC_{36} . These impurities are not superconducting.

Figure 2c shows the x dependence of the graphene-sheet plane spacing d_{AA} , for $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($0 \leq x \leq 1.0$). This spacing is almost x -independent for $\text{Ca}_x\text{K}_{1-x}\text{C}_8$ ($0 \leq x < 1.0$), whereas d_{AA} for CaC_6 (or $\text{Ca}_x\text{K}_{1-x}\text{C}_6$ ($x = 1.0$)) is much smaller. This reflects the smaller ionic radius of Ca and the

stronger interaction between the 4s orbital of Ca and the $2p_\pi$ orbital of C. The value of d_{AA} equals $c/4$ in the KC_8 structure, and $c/3$ in the CaC_6 structure. It is worth emphasizing that the KC_8 structure is maintained even when the molar ratio of Ca exceeds 0.5, e.g., $Ca_{0.6}K_{0.4}C_y$. The independence of d_{AA} on x ($x < 1$) suggests that the KC_8 lattice is governed by the K atoms. This hypothesis is reasonable because the ionic radius of K^+ , 1.38 Å (for a coordination number 6), is greater than that of Ca^{2+} , 1.00 Å (for a coordination number 6).

3.3. Pressure dependence of superconductivity in $Ca_{0.6}K_{0.4}C_8$.

The temperature dependence of R in $Ca_{0.6}K_{0.4}C_8$ was measured over a wide pressure range from 2.0 to 43 GPa. Some typical $R - T$ curves are shown in Figure 3a. R drops rapidly toward zero below 10.5 K at 2.0 GPa. Again, T_c was determined from the intersection of two regimes, as described in Figure 1a. R decreases slowly with decreasing temperature in the entire temperature range before reaching the superconducting transition in the $R - T$ curves under 2 – 20 GPa (see Figure 3b), implying simple metallic behavior. On the other hand, as seen from Figure 3b, R increases slowly with decreasing temperature below 100 K in the high-pressure range 31 – 43 GPa, *i.e.*, exhibiting insulating behavior in the low temperature range (see inset of Figure 3(b)). At 22 – 28 GPa the R increases slightly with decreasing temperature below 50 K, but it was recognized as still metallic in the entire temperature range (1.9 – 300 K) because of its small change below 50 K. These results imply a clear emergence of metal-insulator transition at low temperature above 30 GPa.

The $R - T$ curves at 4.5 GPa were measured in applied magnetic fields H ranging from 0 to 1.0 T (see Figure 3c), to confirm that the vanishing resistance indicates a superconducting transition.

Figure 3. Resistance R versus T for $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ at temperatures ranging from (a) 1.9 to 20 K and (b) 1.9 – 200 K, at different pressures. Inset of (b) shows the expanded $R - T$ plot at 31 GPa, and the MI means metal-insulator transition. Resistance values are normalized at (a) 20 K and (b) 200 K. (c) R versus T curves for $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ in different magnetic fields under a pressure of 4.5 GPa. Inset of (c) shows the $H - T$ phase diagram determined from (c). (d) T_c versus p for $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$.

H was applied perpendicular to the aa -plane of $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ (see Figure 3c). T_c decreases with increasing H and the resistance remains positive even at 0.10 T, which supports the occurrence of superconductivity in $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ under high pressure. This therefore makes the study of the pressure dependence of T_c , as determined from the $R - T$ curves, worthwhile and useful. The $H - T_c^{\text{onset}}$ plot was made from the T_c^{onset} 's at different H values (Figure 3c). Inset of Figure 3c shows the $H - T$ phase diagram for $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ at 4.5 GPa; the H on the plot (or fitted line) refers to upper critical field H_{c2} . The H_{c2} at 0 K, $H_{c2}(0)$, was evaluated to be 1.46 T which is smaller than Pauli limit.

A clear superconducting transition is observed below a pressure $p = 31$ GPa, and therefore superconductivity can be closely associated with metallic behavior, as seen from Figure 3b. The pressure dependence of T_c is shown in Figure 3d. It increases as the pressure increases to 3.3 GPa, where it reaches a maximum of 11.6 K, and then rapidly decreases up to 15 GPa, before settling around 3.6 K. There is a slow decrease thereafter. The value of T_c at 43 GPa was not confirmed down to 1.9 K. This behavior is qualitatively similar to that observed with CaC_6 ; however, the present T_c values are lower in the pressure range up to 12 GPa [9]. In the case of CaC_6 , the maximum T_c^{onset} was 15.1 K, and T_c was close to T_c^{onset} , as evidenced from the $R - T$ curves. The increase in T_c was explained by the softening (hardening) of Ca-Ca phonon (Ca-C phonon) [9,12], and the decrease in T_c was assigned to the order-disorder transition originating from random off-center displacement of Ca atoms in the plane which accompanies the lattice-softening [13]. This scenario should explain the dome-like $T_c - p$ behavior observed in $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ below 15 GPa. The T_c values for $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ exceed those of CaC_6 above 12 GPa [15]. Superconductivity in $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ was observed at temperatures down to 1.9 K, even for pressures above 20 GPa, whereas it was not observed in CaC_6 above 20 GPa.

More precisely, a high- T_c phase ($T_c = 5.0$ K at 26 GPa and $T_c = 12.5$ K at 35 GPa) other than the superconducting phase ascribable to $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ emerged above 24 GPa, but it was assigned to Li or CaLi_2 originating from the Li and Ca used in the sample preparation [16,17]. In Figure 3d, the T_c values due to Li or CaLi_2 are not plotted, but only the T_c values ascribable to the $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ sample under high pressure are plotted; the low T_c values ascribable to $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ could be clearly recorded because the high- T_c phase due to Li or CaLi_2 exhibits only a small drop (no zero-resistance) in $R - T$ plot. A low T_c was continuously observed in $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ up to 41 GPa, and disappeared completely at 43 GPa. When reducing the pressure from 43 GPa, T_c did

not follow the $T_c - p$ trajectory plotted in Figure 3d. In other words, the pressure dependence of T_c was irreversible, suggesting an irreversible conversion of the graphite superconductor by applying pressure.

3-4. Pressure dependence of the crystal structure of $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$.

The pressure dependence of the XRD pattern for $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ was investigated for pressures ranging from 0 to 24 GPa. The evolution of the intensity peak ascribable to the 004 reflection is shown in Figure 4a. Its shift to higher values of 2θ implies the shrinkage of c . The 004 peak then disappears at 16 GPa. The pressure dependence of the integrated intensity of this 004 peak for $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ is plotted in Figure 4b. The pressure medium was not used for the XRD measurements under high pressure (Figures 4a and b). The monotonous decrease, before vanishing at 16 GPa, suggests a structural change in KC_8 to a non-graphite structure because the 004 peak is characteristic of KC_8 -type graphite. Here, it is noteworthy that the KC_8 structure does not change to CaC_6 structure because no peaks ascribable to rhombohedral graphite (CaC_6 structure) satisfying $-h + k + l = 3n$ (n : integer) were observed in the entire pressure range. Namely, the superconducting $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ with KC_8 structure directly transferred to superconducting non-graphite at 15 GPa. Furthermore, the above graphite – non-graphite transition should be distinguished from the order-disorder transition described in section 3-3, because the 004 peak should be maintained in the latter transition; the space group is maintained in the order-disorder transition of CaC_6 [13].

Figure 4c plots d_{AA} as a function of p for $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$, exhibiting an exponential decay up to 14 GPa. The d_{AA} values were determined from both XRD measurements under high pressure with /

without pressure medium, and a continuous change of $d_{AA} - p$ plot shown in Figure 4c implies that presence or absence of pressure medium does not cause the significant difference in the characterization of GIC compounds under high pressure. As described in section 3-3, the maximum T_c ($= 11.6$ K) is observed at 3.3 GPa. There is a rapid decrease in d_{AA} up to ~ 3.3 GPa, which can be regarded as a cause of the increase in T_c , as suggested previously [6]. The in-plane phonon mode of the Ca/K atoms must be softened with pressure as in CaC_6 [9,12], which would enhance T_c .

The $T_c - p$ behavior below 15 GPa is similar to that of CaC_6 [9], *i.e.*, the dome-like superconductivity is observed. Above 15 GPa, the slow decrease in T_c must reflect the T_c of non-graphite superconductor because the structural change occurs at 15 GPa. The d_{AA} shown in Figure 4(c) slowly approaches the d_{AA} of CaC_6 (4.52 Å) with continuing the KC_8 structure when applying pressure up to 14 GPa, and when applying more pressure, the KC_8 graphite structure changes to non-graphite structure. This suggests that KC_8 structure can no longer be maintained when the d_{AA} reaches that of CaC_6 . In addition, as described previously, the KC_8 -type $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ did not transfer to CaC_6 structure.

Furthermore, we must comment on the metal-insulator transition observed in the $R - T$ plot (Figure 3b) above 30 GPa. The metal-insulator transition seems to occur in the non-graphite superconductor, because 30 GPa is much far from 15 GPa corresponding to graphite – non-graphite transition. As seen from Figure 3b, the clear superconducting drop is suppressed above 30 GPa in conjunction to the emergence of metal-insulator transition at low temperature. The $T_c - p$ behavior (Figure 3d) does not alter above 30 GPa, but the reason is unclear.

Based on previous work on non-doped graphite [18], we suggest that the non-graphite structure is hexagonal diamond, which may be substantially insulating. It is reasonable that C - C bonds between the graphene sheets should form above 10 - 15 GPa. As explained above, superconductivity correlates with metallic behavior, and therefore the insulating hexagonal diamond would not show superconductivity. However, non-graphite $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_y$ superconductor was still metallic at 15 – 30 GPa, and changed to an insulating state in the low temperature range above 30 GPa. The insulating behavior suppressed the superconductivity and finally the superconductivity disappeared at 43 GPa.

We must finally comment on the fact that the 004 peak does not recover when pressure is reduced from 24 GPa. This result implies that the structural change is irreversible and the

Fig. 4. (a) The 004-reflection peak of $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ at different pressures. (b) Normalized integrated peak intensity of this 004 peak as a function of pressure p . (c) Graphene-sheet plane spacing d_{AA} versus p for $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$.

graphite structure does not reappear, consistent with the fact that the T_c does not follow the $T_c - p$ plot (Figure 3d) when reducing pressure.

4. Conclusion

We successfully synthesized new types of graphite superconductors, consisting of binary elements intercalated in graphite, denoted $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($0 < x < 1$). These show a continuous change of T_c as a function of x . T_c values were intermediate between those of KC_8 ($T_c^{\text{onset}} = 136 \text{ mK}$ [3,4]) and CaC_6 ($T_c^{\text{onset}} = 11.5 \text{ K}$ [1,2]). Their crystal structure was identified as ‘ KC_8 type’, or orthorhombic lattice (space group: No. 70, $Fddd$), which differs from that of Ca-doped graphite (CaC_6 : No. 166, $R\bar{3}m$). This finding is interesting because the T_c values ($> 5 \text{ K}$) for $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ ($0 < x < 1$) are much higher than those of KC_8 ($T_c = 136 \text{ mK}$), which implies that the high- T_c graphite superconductors are not confined to the CaC_6 structure.

For an understanding of pressure-induced phase transformation of $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$, the $T - p$ phase diagram (Figure 5) was made based on the $T_c - p$ plot shown in Figure 3d. As seen from Figure 5, $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ has a graphite structure (KC_8 -type structure) below 15 GPa. The pressure dependence of superconductivity in $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ behaved similarly to CaC_6 . A rise in T_c was observed as pressure increased up to 3.3 GPa. Such a positive pressure dependence has often been observed in carbon-based superconductors such as metal-doped C_{60} [19,20] and metal-doped hydrocarbons [21-24]. The T_c of $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ reached a maximum of 11.6 K at 3.3 GPa, which was lower than that of CaC_6 , 15.1 K [9]. T_c decreased rapidly with increasing pressure between 3.3 and 15 GPa. We therefore suggest from the analogy with CaC_6 [9,13] that the order-disorder transition may occur below 10 GPa, which may be a trigger of T_c reduction.

Figure 5. $H - T$ phase diagram of $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$. M, I and SC refer to metallic, insulating and superconducting phases, respectively, and the pink and yellow areas indicate graphite and non-graphite structures, respectively. p_{OD} , p_{ST} and p_{MI} refer to the pressures relating to the order-disorder transition, the structural transition and the emergence of metal-insulator transition, respectively.

The pressure-dependent XRD patterns of $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ clarified that the KC_8 -type $\text{Ca}_{0.6}\text{K}_{0.4}\text{C}_8$ is converted to non-graphite structure at 15 GPa, which is also a superconductor. As seen from Figure 5, T_c slowly decreased with increasing pressure above 15 GPa. Metallic behavior was observed in the entire temperature range of 1.9 – 300 K at 0 – 20 GPa; the slight increase in R when decreasing temperature below 50 K was observed at 22 – 28 GPa, but the behavior can be recognized as almost metallic. Above 30 GPa, the clear insulating behavior in $R - T$ plot was observed below 100 K. The clear emergence of metal-insulator transition in the low temperature range at 30 GPa showed no anomaly in $T_c - p$ plot (Figure 5), but the drop in $R - T$ plot ascribable to superconducting transition was definitely suppressed above 30 GPa (see Figure 3b), implying that the superconductivity can be closely related to metallic behavior. It has been found that the structural change from KC_8 to a non-graphite (hexagonal diamond) structure is

irreversible, *i.e.*, when reducing pressure from 43 GPa, KC₈-type graphite superconductor has never been found. To sum up, the successful synthesis of superconductors based on binary element intercalation in graphite opens a fresh perspective for realizing new graphite superconductors through a combination of various metals.

Acknowledgements

The authors are very grateful to Dr. Masafumi Sakata of Osaka University for his valuable assistance in the experiments, and Dr. Ritsuko Eguchi and Ms. Shino Hamao for their valuable discussion. This study was partly supported by a Grant-in-aid (22244045, 24654305, 26105004) from MEXT, the LEMSUPER project (JST-EU Superconductor Project), the JST-ACTC project of the Japan Science and Technology Agency (JST), and the Program for Promoting the Enhancement of Research Universities. The synchrotron XRD measurements were performed at BL10XU of the SPring-8 under proposal (2015A1513).

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