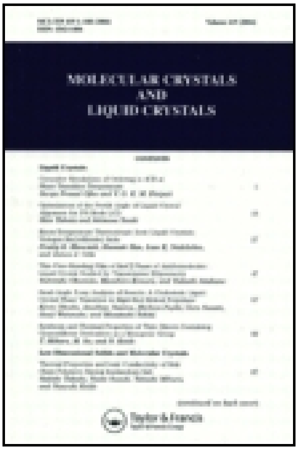

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Mototada Kobayashi [a], Toshifumi Hara [a], Kenichi Shiota [a], Yuichi Akahama [a], Haruki Kawamura [a] & Youichi Murakami [b]

[a] Department of Material Science, Himeji Institute of Technology, Kamigohri, 678-1297, Japan

[b] Photon Factory, Institute of Material Structure Science, High Energy Accelerator Research Organization, Tsukuba, 305-0801, Japan

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X-Ray Diffraction and Physical Properties of Potassium Fullerides K_xC_{70}

MOTOTADA KOBAYASHI[a], TOSHIFUMI HARA[a], KENICHI SHIOTA[a], YUICHI AKAHAMA[a], HARUKI KAWAMURA[a] and YOUICHI MURAKAMI[b]

[a]*Department of Material Science, Himeji Institute of Technology, Kamigohri 678–1297, Japan and* [b]*Photon Factory, Institute of Material Structure Science, High Energy Accelerator Research Organization, Tsukuba 305–0801, Japan*

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X-ray diffraction and magnetic-susceptibility measurements have been carried out for single phase K_xC_{70} (x=1, 3, 4, 6 and 9) compounds synthesized by heating stoichiometric amount of K_9C_{70} and C_{70}. The x-ray diffraction profiles show no structural transition down to 10K. The fairly large temperature-independent paramagnetic contribution was observed in x=3 and 4. The electrical resistivity has been measured for K evaporated C_{70} film with increasing K thickness. Two resistivity minima were observed at x=1 and 4.

Keywords: C_{70}; fulleride; x-ray diffraction; magnetic susceptibility; resistivity

INTRODUCTION

Since the discovery of superconductivity in K_3C_{60} by Hebard et al.[1], many attempts to dope a wide variety of atoms or molecules into fullerene have been made. As for K_xC_{70}, four doped phases, namely the fcc phase at x=3, the bct phase at x=4, the bcc phase at x=6 and the K-saturated fcc phase at x=9 were reported[2]. Wang et al. reported metallic behavior of K_xC_{70} film with x=4 by using FIT model[3]. Superconductivity in K_xC_{70} has not been reported except an appearance of a small diamagnetism in K_xC_{70} which resulted from C_{60} impurity by Imaeda et al.[4] and doped rhombohedral phase by the present authors[2].
In this paper, we report the x-ray diffraction and the magnetic-susceptibility measurements for K_xC_{70}(x=1, 3, 4, 6 and 9) together with the resistivity of K_xC_{70} film as a function of K concentration in order to search metallic phase.

EXPERIMENTS

The starting materials were sublimed C_{70} polycrystal(99% up purity, MER

Co.) and purified C_{70} powdered crystals extracted with toluene(99% purity, MER Co.). The toluene-extracted C_{70} was washed using THF(tetrahydrofuran) and heated at 300 ℃ for 6 h under a vacuum of the order of 10^{-1} Pa to remove the solvent. The fcc C_{70} was prepared by I_2 intercalation. After removing I_2, the fcc C_{70} with a=14.97 Å was obtained[5]. Figure 1 shows this process and the removal of I_2 was also checked by weight measurement.

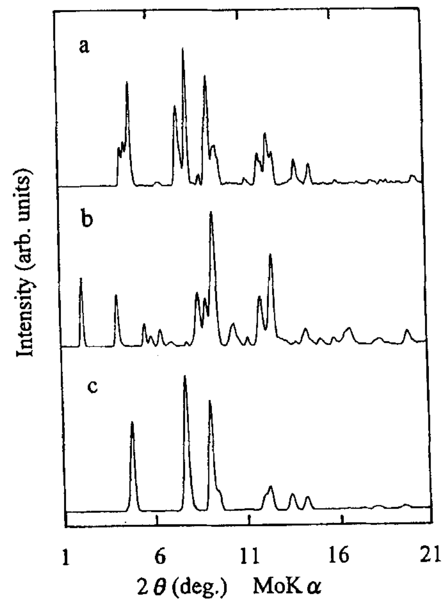

FIGURE 1 X-ray diffraction profiles for (a)sublimed C_{70}, (b)$C_{70}I_4$ and (c)fcc C_{70}(after I_2 de-intercalation).

Single-phase K_xC_{70}(x=1, 3, 4, 6 and 9) were synthesized by annealing stoichiometric amount of K_9C_{70} and C_{70}. For SQUID measurement, sample was transferred to a quartz tube with a partition in the center. For x-ray diffraction measurement, specimen was transferred to a capillary in a glove box.

The x-ray diffraction analysis was performed by a system equipped with an 18-kW rotating molybdenum anode as the x-ray generator and an imaging plate(IP, MAC Science, DIP100) as the detector. The synchrotron radiation(SR) at Photon Factory(KEK-PF, BL6C1 and BL1B) was also used. For resistivity measurement, about 1000 Å-thick C_{70} film was prepared on glass substrate at 150℃ after evaporating four gold strips as contacts. Base pressure was 10^{-4} Pa. K metal was evaporated onto C_{70} film at 150℃ and the resistance of the film was monitored continuously by means of four-terminal method. Composition was estimated from the thickness ratio of C_{70} to K. The temperature dependence measurement was performed in a liquid nitrogen reservoir. A SQUID magnetometer(Quantum Design, MPMS-5SH) was used for magnetic-susceptibility measurements.

RESULTS AND DISCUSSIONS

The x-ray diffraction profiles at room temperature(RT) for K_xC_{70}(x=1, 3, 4, 6 and 9) from fcc C_{70} using MoK α radiation are shown in Fig.2. K_1C_{70} and K_3C_{70} can be assigned to fcc structures with a=14.84 and 14.96 Å, respectively. K_4C_{70} can be assigned to a bct structure with a=12.63 Å and c=10.95 Å. K_6C_{70} has a bcc structure with a=12.00 Å. The K-saturated phase K_9C_{70} has an fcc structure with a=15.67 Å.

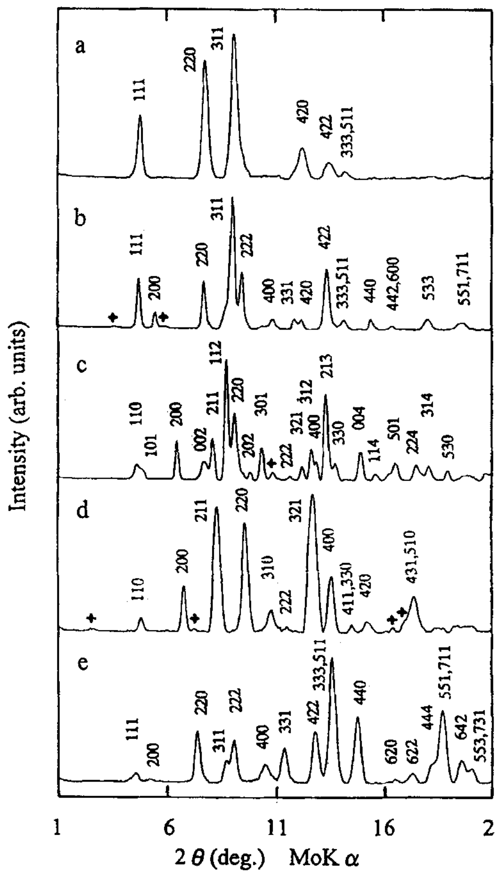

FIGURE 2 X-ray diffraction profile for K_xC_{70}: (a) x=1, (b) x=3, (c) x=4, (d) x=6 and (e) x=9. + symbols indicate unidentified peaks.

From the rough calculation using free rotation model, K_9C_{70} has eight K atoms in the O-site with a deformed cubic shape and the half of the T-sites is vacant[2]. These profiles were obtained under rapid cooling from RT to 77 K. A small amount of x=4 phase was mixed in x=3 compound under slow cooling from 450 ℃ to RT. The x=3 phase seems to be high temperature stable phase[6]. Structures for these phases at low temperatures were checked by using SR. There were no structural transition down to 10 K. Figure 3 shows the results for K_3C_{70} and K_4C_{70}. K_3C_{70} at RT and 10 K can be assigned as fcc structures with a=14.90 Å and a=14.88 Å, respectively. K_4C_{70} at RT has a bct structure with a=12.61 Å and c=10.97 Å. At 10 K those slightly decreased to a=12.60 Å and c=10.95 Å, respectively.

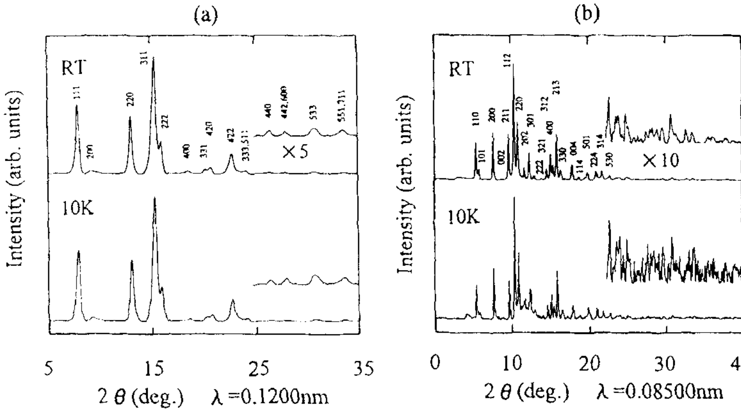

FIGURE 3 X-ray diffraction profiles for (a)K_3C_{70}(λ=0.1200 nm) and (b)K_4C_{70}(λ=0.08500 nm) using SR.

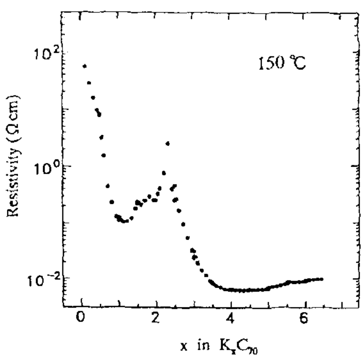

FIGURE 4 K concentration dependence of the electrical resistivity for K_xC_{70} film.

Figure 4 shows the electrical resistivity of K_xC_{70} film as a function of K concentration. It has two minima:1.0×10^{-1} ohmcm at x=1 and 6.1×10^{-3} ohmcm at about x=4. The latter value is about the same order to that for K_3C_{60} film[7]. The resistivity for x=4 film gradually increased with decreasing temperature down to 77K consistent with the result of Wang et al.[3]
The temperature dependence of the magnetic susceptibility χ for K_xC_{70}(x=1, 3, 4, 6 and 9) using a SQUID under 5T is shown in Fig.5.

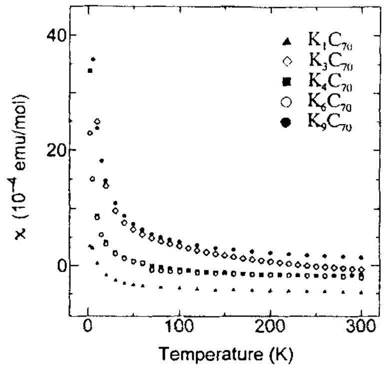

FIGURE 5 Temperature dependence of the magnetic susceptibility for K_xC_{70} (x=1, 3, 4, 6 and 9).

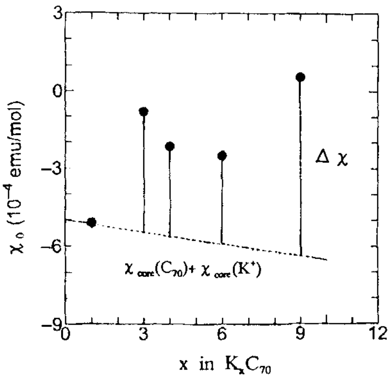

FIGURE 6 K concentration dependence of the temperature-independent magnetic susceptibility χ_0. Solid circles show χ_0. The dotted line shows the contribution from $\{\chi_{core}(C_{70}) + x \times \chi_{core}(K^+)\}$.

The temperature-independent term χ_0 was obtained by fitting the results to the formula $\chi = C/(T-\theta) + \chi_0$, where C is the Curie constant and θ is the Weiss temperature. The χ_0 values for K_1C_{70}, K_3C_{70}, K_4C_{70}, K_6C_{70} and K_9C_{70} are estimated to be -5.10, -0.80, -2.15, -2.50 and 0.57 (in $\times 10^{-4}$ emu/mol units), respectively, and depicted in Fig.6. The magnetic susceptibility shift $\Delta\chi$ for K_xC_{70} defines as $\Delta\chi = \chi_0 - \{\chi_{core}(C_{70}) + x \times \chi_{core}(K^+)\}$, where the $\chi_{core}(C_{70})$ and $\chi_{core}(K^+)$ are the core contributions from C_{70} and K^+, respectively. $\Delta\chi$ for each x is shown by vertical solid line in Fig.6. Paramagnetic $\Delta\chi$ of 4.7×10^{-4} emu/mol and 3.5×10^{-4} emu/mol were obtained for x=3 and x=4 phases, respectively. These paramagnetic contributions may result from Pauli paramagnetism and show the metallic character for x=3 and 4 phases. The x=6 and x=9 phases also have fairly large paramagnetic $\Delta\chi$. The core contributions for these two phases should be re-estimated because of the participation of t_{1g}-derived band. A small diamagnetism was observed in some samples with $x \fallingdotseq 3$ below 0.5 K, but has highly sample dependence.

SUMMARY

K_xC_{70} has a structure sequence of the doped fcc(x=1), the doped fcc(x=3), the bct(x=4), the bcc(x=6) and the K-saturated fcc(x=9) phases with increasing K concentration. The electrical resistivity of K_xC_{70} film shows two minima at x=1 and 4. The large temperature-independent paramagnetic contribution was observed in x=3 and 4. These results show the metallic character of x=3 and 4.

Acknowledgments

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