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Metallic phase in potassium fulleride K_xC_{70}: Electrical, magnetic, and structural properties of K_4C_{70}

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The metallic phase in potassium fullerides K_xC_{70} was researched using electrical resistivity measurements in the case of film samples and magnetic susceptibility measurements in the case of powder samples. The K concentration dependence of the electrical resistivity of the K_xC_{70} film at 423 K showed two minima: namely, 1.0×10^{-1} and 6.1×10^{-3} Ω cm at $x=1.1$ and 4.1, respectively. The temperature dependence of the resistivity of the K_4C_{70} film showed a disordered-metallic behavior. Superconducting quantum interference device (SQUID) measurements for K_4C_{70} powder revealed a temperature-independent magnetic susceptibility contribution of 3.47×10^{-4} emu/mol. This contribution was attributed to Pauli paramagnetism, and it was also observed in electron spin resonance (ESR) measurements. Futhermore, ESR spectra for K_4C_{70} powder showed that the linewidth broadened with increasing temperature. It was clearly established that K_4C_{70} is a metallic phase in K_xC_{70}. The crystal structure of K_4C_{70} was found to be simple tetragonal with $a=1.266$ nm and $c=1.098$ nm. No superconductivity was observed in K_4C_{70} above 2 K.

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I. INTRODUCTION

Since the discovery of the superconductivity of K_3C_{60},[1] several fulleride superconductors have been found in alkali-, alkaline-earth- or lanthanide-doped C_{60}. However, no bulk fulleride superconductors originating from higher fullerenes have been confirmed so far, though a small degree of diamagnetic susceptibility has been observed below 12 K in rhombohedral K_xC_{70} with $x\approx3$.[2] According to the electronic structure calculated based on a local density approximation, the C_{70} cluster has a nondegenerated lowest unoccupied molecular orbital (LUMO) and a twofold-degenerated second LUMO.[3] On the basis of a rigid band model, it is possible that the doping of one, three, four, or five electrons per C_{70} molecule would realize 1/2 filling of the LUMO-derived band and 1/4, 1/2, or 3/4 filling of the second-LUMO-derived band, respectively. Therefore M_xC_{70} (M is a monovalent element) with $x=1$, 3, 4, and 5 are expected to be metallic.

In potassium-doped C_{70}, the stoichiometric phases KC_{70}, K_3C_{70}, K_4C_{70}, K_6C_{70}, and K_9C_{70} have been identified.[2,4] Imaeda *et al.* have measured the doping-time dependence of electron spin resonance (ESR) spectra for K_xC_{70} powder.[5] They observed a sudden broadening of the ESR linewidth and Pauli paramagnetic behavior in the ESR intensity. They concluded that the sudden broadening of the ESR linewidth corresponded to the phase change from insulating K_3C_{70} to metallic K_4C_{70}. It should be noted that their ESR results were obtained for nonstoichiometric samples. Wang *et al.* have reported that the conductivity of K_xC_{70} films increased up to 600 S/cm and the temperature dependence of the conductivity of the K_xC_{70} film with the maximum conductivity was characterized as a disordered-metallic system.[6] The composition of the most conductive K_xC_{70} film has not been confirmed, though they have assumed it to be K_4C_{70} by considering the ESR results of Imaeda *et al.* in Ref. 5. These ESR and conductivity results suggested that the K_4C_{70} phase was possibly metallic. However, Knupfer *et al.* have reported that they found no metallic character in the photoemission spectra for K_xC_{70} up to $x=6$.[7] The metallic phase in K_xC_{70} remained unresolved. We have recently reported preliminary results of resistivity and superconducting quantum interference device (SQUID) measurements and suggested that K_4C_{70} was metallic.[4]

In the present paper, we report electrical resistivity data for K_xC_{70} film samples as a function of K concentration and temperature in order to reveal possible metallic phases. SQUID and ESR measurements were performed on stoichiometric K_4C_{70} powder samples to confirm the contribution of Pauli paramagnetism. X-ray diffraction results for K_4C_{70} are presented also.

II. EXPERIMENTAL DETAILS

Toluene-extracted C_{70} powder of over 99% purity (MER Corp.) and K metal of 99.95% purity (Soekawa Chemical Co. Ltd.) were used.

Electrical resistivity measurements were carried out for K_xC_{70} film samples. Pristine C_{70} films of 100 nm thickness were deposited on glass substrates at 423 K under high vacuum of the order of 10^{-4} Pa. The glass substrate had four predeposited gold stripes as electrodes for a resistivity measurement. Resistivity measurements were performed by either a two- or four-probe method depending on the resistance of the sample.

K concentration dependences of the resistivity of K_xC_{70} films were obtained by monitoring the resistance change of the film during K deposition. The C_{70} film was maintained at 373, 423, or 523 K throughout the K deposition process. K metal was deposited onto the film in an evaporation chamber under high vacuum of the order of 10^{-5} Pa. The composition of the K_xC_{70} film was estimated from the thickness ratio of K to C_{70}, which was measured by a quartz oscillator thickness monitor. In order to examine the uniformity of the K_xC_{70} film with regard to the doping process, we compared the results from two K deposition runs: a continuous deposition run and an intermittent run at 10-min intervals per K increment $\Delta x = 0.5$. The K deposition rate was 0.01 nm/s in both cases.

K_xC_{70} films for temperature dependence measurements were prepared in a Pyrex glass tube with electrical feedthroughs. The pristine C_{70} film and K metal were set in the middle and bottom of the Pyrex tube, respectively. The Pyrex tube was evacuated to a high vacuum of 10^{-4} Pa and heated at 383 K in an electric furnace. When the resistivity of the film reached the expected doping level, the Pyrex tube was transferred from the furnace into a liquid nitrogen reservoir in order to stop the reaction. The temperature dependence of the resistivity was measured between 90 and 200 K as the temperature was raised.

SQUID and ESR measurements were performed on K_4C_{70} powder samples. Stoichiometric K_4C_{70} powder samples were synthesized by thermal treatment of a mixture of K_9C_{70} and C_{70}. Starting C_{70} powder was washed with tetrahydrofuran in an ultrasonic cleaner and heated at 573 K overnight under vacuum to remove the solvent. To prepare K_9C_{70}, a K-saturated phase of K_xC_{70}, the pristine C_{70} powder and excess K metal were sealed into each end of a Pyrex glass tube after evacuating, and heated at 573 K for a week. The formation of K_9C_{70} was confirmed by x-ray powder diffraction with Mo $K\alpha$ radiation and by weight measurement. The stoichiometric mixture of the K_9C_{70} and the pristine C_{70} ($K_9C_{70}:C_{70} = 1:1.25$ molar ratio) was sealed into a Pyrex glass tube after evacuating and heated at 723 K for a week. The product was confirmed to be K_4C_{70} single phase by x-ray powder diffraction using synchrotron radiation (SR) at the Photon Factory (KEK-PF, BL-1B) and an imaging plate as detector. For SQUID measurements the K_4C_{70} powder was sealed, together with He gas at about 6×10^3 Pa for thermal exchange, into a quartz tube that had a partition in the center. SQUID measurements were performed between 2 and 300 K under an applied field of up to 5 T using a Quantum Design MPMS-5SH SQUID magnetometer. For ESR measurements, the K_4C_{70} powder was sealed into a commercial ESR quartz tube together with He gas at about 6×10^3 Pa to allow thermal exchange. ESR were measured between 4 and 300 K using a JEOL JES-RE2X ESR spectrometer operating at 9.1 GHz with a field modulation frequency of 100 kHz with a JEOL ES-LTR5X cryostat. Mn^{2+} was used as a marker of a reference for ESR intensity and 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL) was used for the estimation of spin concentration.

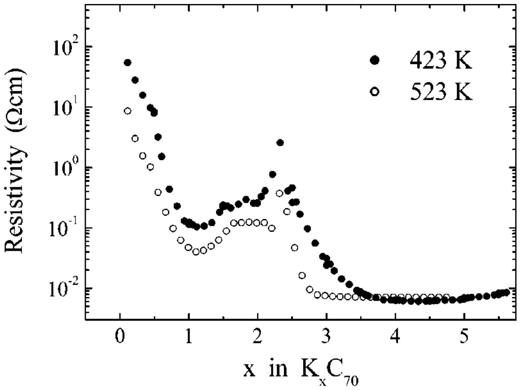

FIG. 1. K concentration dependence of the electrical resistivity of K_xC_{70} films. Solid and open circles show the results of K deposition at 423 and 523 K, respectively.

III. RESULTS AND DISCUSSION

K concentration dependences of the resistivity of K_xC_{70} films at 423 and 523 K are shown in Fig. 1. The result at 373 K was similar to that at 423 K. No essential difference was found between the results of the continuous and intermittent K deposition. In the case of intermittent deposition, the resistance change ceased within a minute after interrupting K deposition. This suggests that deposited K atoms could easily diffuse into the film above 373 K and that the K concentration in the film rapidly reached its equilibrium state. Therefore we assume that the K_xC_{70} film composition estimated from the thickness ratio is sufficiently representative of the bulk composition. At 423 K, the resistivity decreased with K doping and showed two minima: namely, 1.0×10^{-1} Ω cm at $x=1.1$ and 6.1×10^{-3} Ω cm at $x=4.1$. We believe that these minima signal the formation of the KC_{70} and K_4C_{70} phases, respectively. The lowest resistivity value, 6.1×10^{-3} Ω cm at $x=4.1$, is the same order of magnitude as the resistivity for the metallic K_3C_{60} film.[8] The resistivity peak of 12 Ω cm at $x=2.3$ can be assigned to the formation of K_2C_{70}, which is supposed to be an insulator if two doped electrons per C_{70} molecule fully occupy the LUMO-derived band of C_{70}. However, the existence of a stable K_2C_{70} phase has not been confirmed yet. For the K deposition at 523 K, the lowest resistivity minimum occurred at $x=3.2$, while the resistivity behavior below $x\approx2.3$ was similar to that at 423 K. The resistivity minimum at $x=3.2$ corresponds to the formation of a K_3C_{70} phase at 523 K. The discrepancy between the results at 423 K and 523 K is attributed to the phase stability of K_3C_{70}. In case of the preparation of K_xC_{70} powders, we could synthesize K_3C_{70} single phase only by rapid cooling from 700 K to 77 K, whereas K_4C_{70} powder could be obtained easily under any cooling condition. This suggests that K_3C_{70} is stable only at high temperatures. The resistivity of the K_3C_{70} film was roughly on the same order as that of the K_4C_{70} film.

Temperature dependences of the resistivity for K_xC_{70} films at the first and second minima are shown in Figs. 2(a)

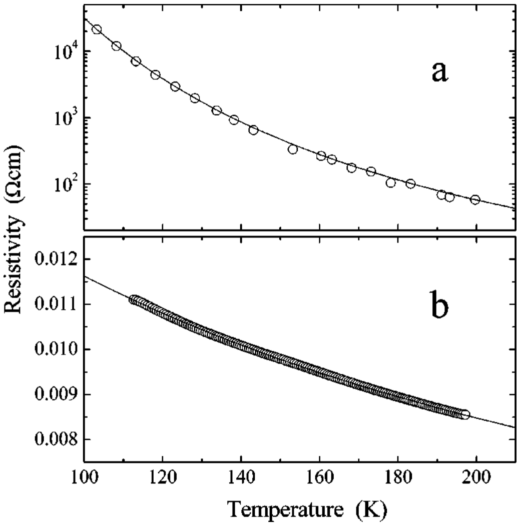

FIG. 2. Temperature dependence of the electrical resistivity of KC_{70} (a) and K_4C_{70} (b) films. Solid lines show the fitting curves with Eq. (1) for KC_{70} and Eq. (2) for K_4C_{70}, respectively.

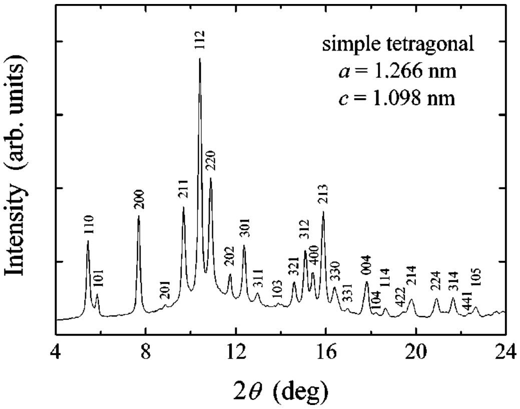

FIG. 3. X-ray powder diffraction profile of K_4C_{70} at 298 K. The data were measured by using SR ($\lambda = 0.08500$ nm). Here 311 and 331 reflections are observed on a simple tetragonal structure, not on a bct structure.

and 2(b), respectively. From the resistivity behavior up to each minimum and the resistivity values, the compositions of the films in Figs. 2(a) and 2(b) were estimated to be KC_{70} and K_4C_{70}, respectively. The temperature dependence of the resistivity of the KC_{70} film in Fig. 2(a) follows a simple thermal activation behavior and can be expressed as

$$\rho = \rho_0 \exp\left(\frac{E_g}{2k_BT}\right), \tag{1}$$

where E_g is the energy gap and k_B is the Boltzmann constant. For this KC_{70} film, ρ_0 and E_g were found be 0.10 Ω cm and 0.21 eV, respectively. As its resistivity was higher than the usual metallic fulleride films by two orders of magnitude, and also based on Eq. (1), we characterized the KC_{70} film to be a semiconductor. The temperature dependence of the resistivity of the K_4C_{70} film in Fig. 2(b) can be described using the fluctuation-induced tunneling (FIT) model.[9]

$$\rho = \rho_0 \exp\left(\frac{T_1}{T+T_0}\right). \tag{2}$$

Fitting parameters ρ_0, T_1, and T_0 are 1.90×10^{-3} Ω cm, 856 K, and 373 K, respectively. Other models describing the relationship between ρ and T, such as the variable-range hopping model or the weak-localization model, could not trace the data in Fig. 2(b). We conclude that this K_4C_{70} film has a disordered-metallic character. Wang *et al.* have reported that the K_xC_{70} film with the highest conductivity exhibited the characteristics of a disordered-metallic system using the FIT model with fitting parameters T_1 and T_0 equal to 35.5 K and 27.5 K, respectively.[6] They also reported that these fitting parameters were highly sample dependent. Our parameters T_1 and T_0 were about one order of magnitude larger than those of Wang *et al.* In the FIT model, the parameter T_1 is given by

$$T_1 = \frac{a\mathcal{E}_0^2}{k_B}, \tag{3}$$

where a and $\mathcal{E}_0$ are a measure of the junction volume and the normalized thermal fluctuating field, respectively. The parameter T_0 varied in proportion to the parameter T_1. Our large T_1 and T_0 could have arisen from a large a value which might indicate a large junction volume. We used a film of 100 nm thickness, while they used one of 250 nm thickness. The geometry or quality of the film may be related to the junction volume.

The x-ray powder diffraction profile of a typical K_4C_{70} powder sample for SQUID and ESR measurements is shown in Fig. 3. The data were obtained using SR ($\lambda = 0.085\,000$ nm) at 298 K. The composition of this specimen was confirmed to be $K_{4.0}C_{70}$ by weight measurement. All peaks were indexed to the simple tetragonal structure with $a = 1.266$ nm and $c = 1.098$ nm. We previously assigned a powder diffraction profile of K_4C_{70} using Mo $K\alpha$ radiation to the body-centered tetragonal (bct) structure with $a = 1.263$ nm and $c = 1.095$ nm, though the profile had an unidentified peak near $2\theta \approx 11°$.[4] The peak can now be assigned to the 311 reflection from the simple tetragonal structure. For the bct structure, C_{70} molecules on the vertices and the body center of the unit cell were considered to be equivalent by orientational (perhaps merohedral) disorder. The simple tetragonal structure suggests that this tetragonal unit cell accommodates two C_{70} molecules that are not equivalent to each other by orientational order.

Figure 4 shows the temperature dependence of the magnetic susceptibility of the K_4C_{70} powder determined by SQUID. The net SQUID response signal for the K_4C_{70} powder was extracted by subtracting the response for a blank quartz cell from the combined (K_4C_{70} powder and quartz cell) response. The magnetization value was estimated based on this net response signal. In a M-H curve, a small contribution due to ferromagnetic impurities was observed and it was saturated entirely below 1 T. In order to eliminate the ferromagnetic contribution, the magnetic susceptibility was obtained using the formula

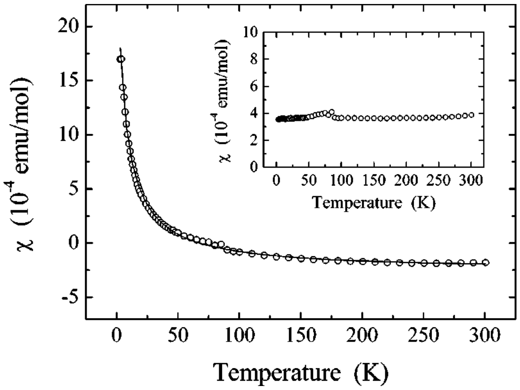

FIG. 4. Temperature dependence of the magnetic susceptibility of K_4C_{70} powder, as revealed by SQUID measurements. Solid line shows the fitting curve given in Eq. (5). Inset shows the data after subtracting the contributions of the Curie component and core diamagnetism.

$$\chi = \frac{M(5\ \mathrm{T}) - M(2\ \mathrm{T})}{3\ \mathrm{T}}, \tag{4}$$

where $M(5\ \mathrm{T})$ and $M(2\ \mathrm{T})$ are the magnetization measured under 5 T and 2 T, respectively. The fitting curve shown in Fig. 4 is given by the expression

$$\chi = \frac{C}{T+\theta} + \chi_0, \tag{5}$$

where C is the Curie constant, θ is the Weiss temperature, and χ_0 is the temperature-independent component in the susceptibility. The spin concentration estimated from C is 0.035 spins per one C_{70} molecule. This small spin concentration suggests that the temperature-dependent term in Eq. (5) is attributable to impurities and/or defects in the sample. The χ_0 comprises the contributions of the core diamagnetism, orbital paramagnetism, and moreover Landau diamagnetism and Pauli paramagnetism if the specimen has conduction electrons. As the core susceptibility contribution, we adopted susceptibilities of -5.68×10^{-4} emu/mol for the C_{70} core (this value was obtained from SQUID measurements on sublimed C_{70} powder) and -1.49×10^{-5} emu/mol for the K^+ cation. Upon subtracting the core contributions from χ_0, we obtained a residual paramagnetic susceptibility contribution of 3.47×10^{-4} emu/mol, which we believe is due to Pauli paramagnetism. In case of alkali-doped C_{60}, it is considered that Landau diamagnetism is quenched by molecular rotational disorder.[10] We treated the Landau diamagnetic contribution as negligible for K_4C_{70} following the precedent of alkali-doped C_{60}. No indication of the significant orbital (Van Vleck) paramagnetism was found at low temperature in the inset of Fig. 4. (The kink around 80 K is not intrinsic. It is attributed to the enhancement of the unreliability of raw data because of the rather feeble SQUID response in this temperature area.) Based on a Pauli paramagnetic susceptibility of 3.47×10^{-4} emu/mol, the density of states at the Fermi level was estimated to be 5.4 states/(eV spin C_{70}). This is about one-third that of the value for K_3C_{60}.[10]

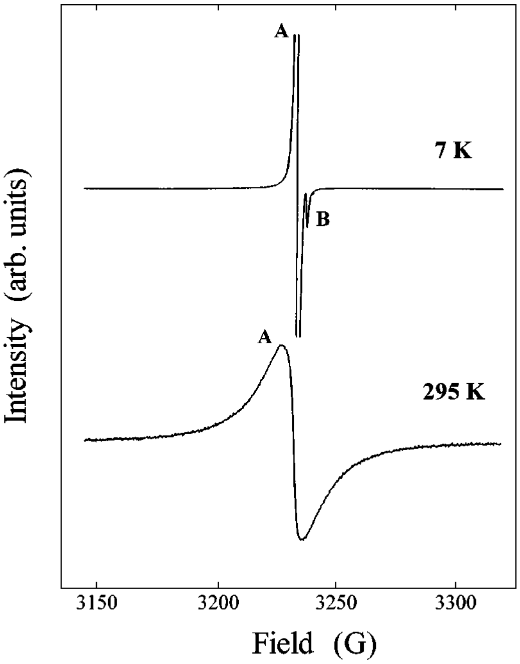

FIG. 5. ESR spectra of K_4C_{70} powder at 7 and 295 K. Peaks *A* and *B* correspond to the Pauli paramagnetic and Curie components, respectively, as described in the text.

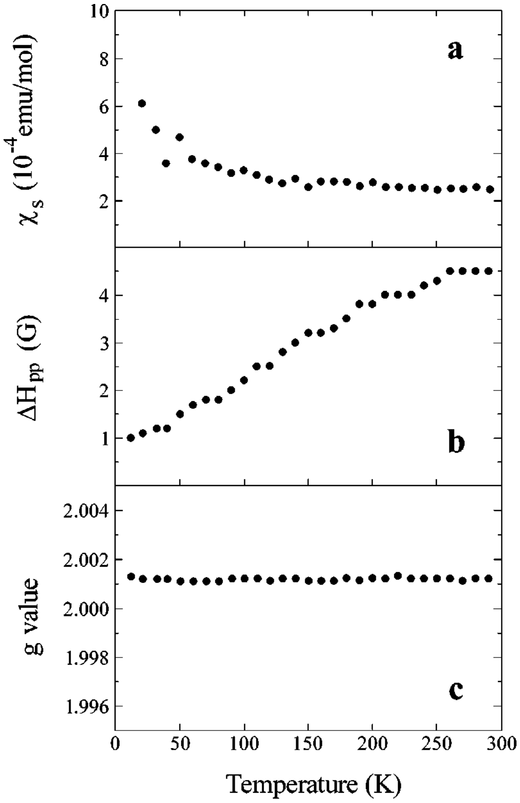

FIG. 6. Temperature dependence of the spin susceptibility estimated from the integrated ESR intensity (a), the peak-to-peak linewidth (b), and the *g* value (c) for peak *A* in Fig. 5.

ESR spectra of K_4C_{70} powder at 7 and 295 K are shown in Fig. 5. Two sharp peaks, labeled *A* and *B*, were observed at low temperatures. The *g* values of peaks *A* and *B* at 7 K are $g_A = 2.0012$ and $g_B = 1.9993$, respectively. Peak *A* broadened with increasing temperature and showed Pauli paramagnetic behavior. By contrast, peak *B* showed Curie paramagnetic behavior and disappeared above 150 K. Figure 6 shows the temperature dependence of the spin susceptibility estimated from the integrated ESR intensity (a), the peak-to-peak linewidth (b), and the *g* value (c) for the peak *A*. The enhancement in the spin susceptibility below 100 K was attributed to the residual contribution of peak *B*, owing to the incomplete subtraction of peak *B* from the ESR spectrum. Pauli paramagnetic behavior was observed above 100 K in Fig. 6(a). The spin susceptibility of the K_4C_{70} powder at 296 K was estimated to be 2.5×10^{-4} emu/mol. This Pauli paramagnetic susceptibility is approximately consistent with that derived from the SQUID measurement. The broadening of the ESR linewidth with increasing temperature is explained by Elliot's expression, which describes the relaxation mechanism of a typical conduction electron in a metal.

Low resistivity and disordered metallic behavior were observed in the case of the K_4C_{70} film. Pauli paramagnetic susceptibility was detected by SQUID and ESR measurements on the K_4C_{70} powder. From these results, we conclude that K_4C_{70} is a metallic phase in K_xC_{70}. The metallic character of K_4C_{70} is in sharp contrast to the insulating character of K_4C_{60} despite the fact that the two have nominally identical ionic charge numbers. In the case of K_4C_{60}, the combination of electron correlations and Jahn-Teller effects appear to stabilize the insulating correlated ground state.[11] In K_4C_{70}, the Jahn-Teller effect is probably not observed because of the lower molecular symmetry of C_{70} (D_{5h}) as compared to C_{60} (I_h). No superconductivity was observed for K_4C_{70} powder above 2 K by SQUID measurements under 0.5 mT.

IV. CONCLUSION

The K concentration dependence of the resistivity of the K_xC_{70} film measured at 423 K showed two minima at $x = 1.1$ and 4.1 and a maximum at $x = 2.3$. These points correspond to the formation of the KC_{70}, K_4C_{70}, and K_2C_{70} phases, respectively. The resistivity at $x = 4.1$ $(6.1 \times 10^{-3}\ \Omega\,\mathrm{cm})$ is on the same order as that for metallic K_3C_{60} film. The K concentration dependence of the resistivity at 523 K suggested the formation of a K_3C_{70} film. Temperature dependence of the resistivity of the KC_{70} film showed a semiconducting behavior with an energy gap of 0.21 eV. Temperature dependence of the resistivity of the K_4C_{70} film well fitted the FIT model expressing a disordered-metallic character. A Pauli paramagnetic contribution of 3.47×10^{-4} emu/mol was observed for K_4C_{70} powder by SQUID measurements. This result was confirmed by ESR. The x-ray powder diffraction profile of K_4C_{70} was assigned to the simple tetragonal structure with $a = 1.266$ nm and $c = 1.098$ nm. K_4C_{70} was concluded to be a metallic phase in K_xC_{70}. No superconductivity was observed for K_4C_{70} powder above 2 K.

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