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Electronic transport properties of K_xC_{70} thin films

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Transport properties of K_xC_{70} thin films doped to their maximum conductivity are studied. At this doping level, K_xC_{70} (nominally K_4C_{70}) is characteristic of a disordered metal with room-temperature conductivity close to 600 S/cm. The conduction bandwidth is estimated as 0.5–0.6 eV. The thermopower and magnetoconductance data are similar to those of K_3C_{60} and intercalated carbon materials. No superconducting transition is observed above 1.35 K.

Recently, fullerenes have attracted a great deal of attention in the scientific community following the discovery of superconducting phases in alkali-metal doped C_{60} samples.[1–6] A superconducting transition temperature of T_c=18–19 K for potassium-doped K_3C_{60} has been reported.[1] Transport studies on K_3C_{60} in the forms of single crystals[2,5] and thin films[3,4] have illustrated that the normal state of K_3C_{60} is a metallic state with a bandwidth of ~0.6 eV.[5] In single-crystal K_3C_{60}, the electron-phonon interaction dominates[2] the T dependence of the normal-state conductivity $\sigma(T)$, while weak localization (WL) phenomena and electron-electron (e-e) interactions are important for charge transport in thin-film samples.[4] Although K_3C_{60} has been extensively studied over the last two years, few studies have been reported on the physical properties of other doped fullerenes.

The extraction of C_{70} can now be made in sufficient quantities to allow experimental studies on this system.[6–8] While C_{70} is very interesting in its own right due to its relatively high molecular symmetry (D_{5h}), the study of doped C_{70} in comparison with C_{60} is also useful for understanding the mechanism of superconductivity in fullerenes. Based on its symmetry, C_{70} has two lowest unfilled levels: A_1'' and E_1'', which are singly and doubly degenerate, respectively.[7,9] One thus expects that K_1C_{70} and K_4C_{70} are metallic due to the half-filling of their lowest unoccupied molecular orbital (LUMO) bands. The K_4C_{70} compound is supposed to be more conducting owing to its higher density of states.[9]

Preliminary transport studies on alkali-metal doped C_{70} were reported by Haddon *et al.*,[6] who found that σ for K_xC_{70} initially increases with doping and reaches a maximum value ($\sigma \sim 2$ S/cm), but decreases with further doping.[6] Imaeda *et al.*[8] have performed EPR studies on K_xC_{70} and found that the spin concentration goes through two maxima as a function of doping. The susceptibility at the second maximum in the doping process showed Pauli-like behavior and the stoichiometry at this doping level was found to be K_4C_{70}, consistent with the band structure calculation,[8,9] but inconsistent with the results of Haddon *et al.*[6] who reported only one maximum in σ upon doping. Since the above studies on K_xC_{70} thin films were preliminary and contradictory, further transport studies are reported here to directly probe the electronic states of K_xC_{70} in the maximum-conductivity phase.

The room-temperature conductivity for our films is nearly as high as $\sim$ 600 S/cm with a typical T dependence characteristic of disordered metals[10] and $\sigma(T)$ can be fit by the fluctuation-induced-tunneling (FIT) model[11] over the range $4 < T < 300$ K. The thermopower (S) is negative (electronic conduction) and linear in T (metallic) with a deviation from linearity at approximately 100 K, similar to that of graphite intercalation compounds (GIC's).[12] The magnetoconductance (MC) is similar to that of disordered carbon fibers[13] and K_3C_{60} films[4] for which the T and H dependences are explained by weak localization (WL) and electron-electron (e-e) interaction effects.[14–16] We suggest that our K_xC_{70} thin films at the maximum-conductivity phase have a microstructure characteristic of a heterogeneous system in which small insulating barriers separate metallic regions. Within the metallic regions, electron states are weakly localized. We estimate the electronic conduction bandwidth as 0.5–0.6 eV, similar to that of K_3C_{60}. No superconducting transition occurs for $T > 1.35$ K.

Pristine C_{70} films, approximately 96% pure (with C_{60} as a major impurity) and 2500 Å thick, were deposited on glass substrates with precoated silver pads by thermal sublimation of C_{70} powder which was purified by liquid chromatography. The doping was carried out in a sealed Pyrex ampoule, with tungsten-wire feed-throughs attaching to the sample leads (copper) to monitor the conductivity. The films were baked overnight at 160–180 °C under a dynamic vacuum of 5×10^{-7} Torr, and approximately 10^{-2} Torr of He low-temperature exchange gas was introduced into the ampoule before sealing. The films, maintained at 100–120 °C, were slowly intercalated with K vapor at 90–100 °C over a period of one or two days. The temperature gradient prevented excess potassium from condensing on the K_xC_{70} film surface. Typically the conductivity σ initially increases to a maximum value of ~15 S/cm and the thermopower (S) of the sample at this doping level is positive with a room-temperature value of $S \sim 15$ μV/K. Upon further doping, σ decreases to a minimum value of ~5

S/cm, but increases again to another maximum value, $\sigma_{max} \sim 600$ S/cm. (We refer to this phase as the maximum-conductivity phase.) Doping at higher temperatures or faster rates results in a lower σ_{max}, presumably due to the disorder induced during the doping process.[4] We found that the σ_{max} of K_xC_{70} films, measured over a few samples, ranges between 10 and 600 S/cm, and σ_{max} is sensitively dependent on the doping conditions.

Figure 1 presents $\sigma(T)$ of a K_xC_{70} sample at the maximum-conductivity phase. The data in Fig. 1 can be fit over the whole T range (4–300 K) by the fluctuation-induced tunneling (FIT) model (solid line in Fig. 1),[11]

$$\sigma_{FIT} = \sigma_0 \exp[-T_1/(T+T_0)], \quad (1)$$

though the fitting parameters T_1 and T_0 vary from sample to sample. For the particular sample presented in Fig. 1, the fitting parameters are $T_1 = 35.5$ K and $T_0 = 27.5$ K, but for another sample (see inset) $T_1 = 29$ K and $T_0 = 9.7$ K when fitting these $\sigma(T)$ data above 5 K. The $\sigma(T)$ data for the inset to Fig. 1 extend to a lower T range and are taken on a less conducting sample (used also for magnetoresistance measurements). Below 5 K, σ decreases faster than what the FIT model predicts.[17] The $\sigma(T)$ data did not display a linear relation in the plots of ln $\sigma(T)$ vs $T^{-1/p}$ (p=1, 2, 3, 4) and $\sigma(T)$ vs $T^{1/2}$ or ln T, the relations for the variable-range-hopping[18] and the weak localization[14–16] (WL) models, respectively. To the lowest T(=1.35 K) reached in our experiment, we did not observe any sign of a superconducting transition.

In the thermopower measurements, the sample with two leads at the ends was mounted between two copper blocks between which a T difference of $\Delta T \sim 1$ K was maintained [ΔT is scanned up to 1 K to confirm the linearity of $S(T)$ prior to the measurement]. Thermal contact to the copper blocks was made using silver paint, and two junctions of a thermocouple were glued to the sample substrate near the electrical leads to measure the ΔT. The measured thermopower (S) at the maximum-conductivity phase is negative, with roughly a linear T dependence for $T < 100$ K (Fig. 2). In this T range, the slope $C = S(T)/T$ is approximately $-(0.12$ to $0.15)$ μV/K^2. A large change in slope is, however, found near $T \sim 100$ K. For $T > 100$ K, $S(T)$ deviates from the linear relation and only decreases slowly as T. The T dependence of $S(T)$ for different samples with very different room-temperature σ_{RT} values is qualitatively the same, as is shown in Fig. 2.

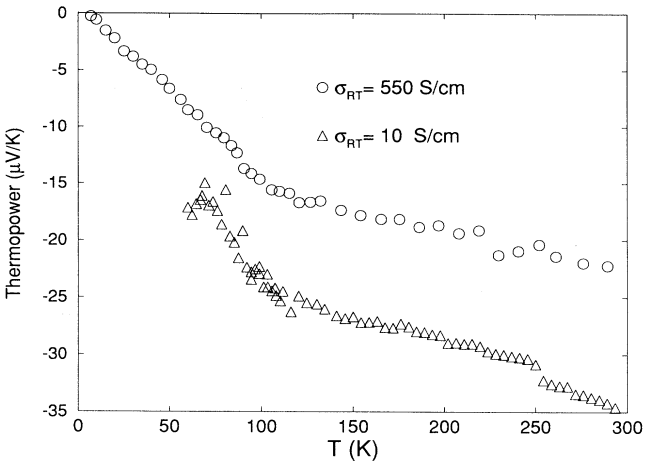

FIG. 2. The T dependence of the thermopower of K_xC_{70} at the stoichiometry of the maximum-conductivity phase ($x \approx 4$). The circles and triangles are for the data from samples with $\sigma_{RT} = 550$ S/cm and 10 S/cm, respectively.

The magnetoconductance (MC) data are presented in Fig. 3 as $\Delta\sigma(H)/\sigma$ vs magnetic field (H) at various temperatures T, where $\Delta\sigma(H) = \sigma(H) - \sigma(0)$. Note that $\Delta\sigma/\sigma$ is negative at low T and becomes positive for $T > 20$ K, qualitatively similar to that for K_3C_{60} thin films.[4] The solid lines are theoretical fits as discussed below.

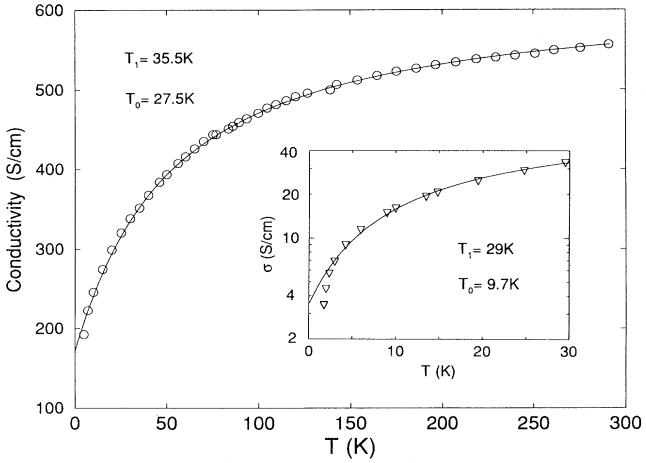

FIG. 1. T dependence of σ for a typical K_xC_{70} film at the stoichiometry of the maximum-conductivity phase ($x \approx 4$). The solid line is the theoretical fit of the FIT model to the data. The inset plots the data taken on a less conducting sample. The solid line in the inset is also a fit to the FIT model.

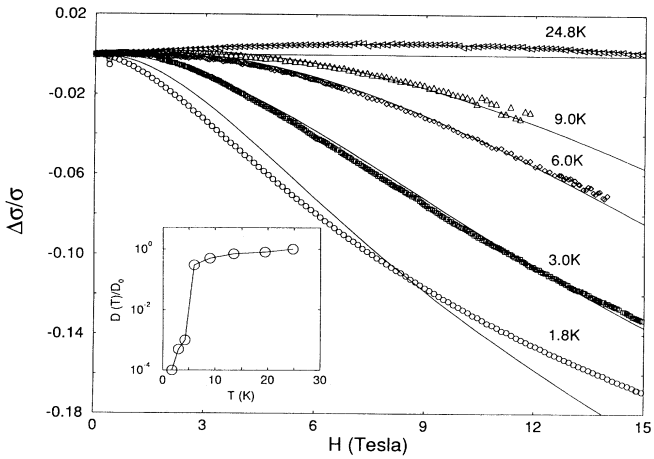

FIG. 3. Transverse magnetoconductance data plotted as $\Delta\sigma/\sigma$ vs H at various T. Solid lines are theoretical curves calculated according to the weak localization and e-e interaction model of Eq. (3). The inset shows a plot of D (plotted on a log scale and normalized to its 30 K value) as a function of temperature.

The stoichiometry of our samples at the maximum-conductivity phase is estimated to be K_4C_{70}, as inferred by comparing the variation of σ as a function of doping with the band structure calculations[7,9] and the EPR results of Imaeda *et al.*[8] A direct stoichiometry measurement has not been performed on these samples. For simplicity, we refer to our samples at the maximum-conductivity phase as K_4C_{70}.

Our room-temperature value for σ_{RT} and the T dependence of σ for K_4C_{70} are characteristic of disordered or heterogeneous metals. For disordered metals, a semiconductorlike T dependence of σ is often observed for samples with $\sigma_{RT} < 10^3$ S/cm.[10] Various models have been proposed to explain the $\sigma(T)$ for these disordered systems.[11,14–16,18] Our best fit to the measured $\sigma(T)$ over the T range of 4–300 K is the FIT model Eq. (1). This model assumes that the sample is heterogeneous, consisting of large metallic regions separated by thin insulating barriers. The charge transport is limited by tunneling across these barriers via thermal fluctuations. The model has been applied to a few disordered metallic systems and metal-insulator composites.[11] To apply this model to a system, the charging energy $E_c \sim e^2/d$ (where d is the dimension of a metallic grain) must be much smaller than the thermal energy k_BT (k_B is the Boltzmann constant).[11] Thus on the basis of the model, the size of the metallic regions in K_4C_{70} must be larger than several μm for the FIT model to fit the data at $T \sim 4$ K (see Fig. 1).

The thermopower $S(T)$ data of K_4C_{70} is similar to that of graphite intercalation compounds[12] (GIC's) and the negative sign of the $S(T)$ data indicates that the charge carriers are electronlike. In the case of GIC's, the flat plateau for $T > 100$ K is attributed to strong electron-phonon (e-p) interactions so that the phonon-drag thermopower S_g dominates. At low T (< 100 K), however, the diffusion thermopower S_d dominates.[12] Anomalies in S along the c axis are found in the range 50 to 100 K for K-intercalated GIC's,[12] similar to the behavior observed for K_4C_{70} (see Fig. 2). It has been suggested that the anomalies in the thermopower of GIC's are related to structural changes in the intercalate layers.[12,13] For K_4C_{70}, the large change in the slope of S vs T at ~ 100 K is perhaps also associated with a structural phase transition. A more recent study[19] shows a sign change in the Hall coefficient R_H for K_4C_{70} at approximately 100 K as well. However, by analogy to the importance of the S_g contribution to GIC's and disordered graphite[12,20] it is likely that S_g also contributes to the $S(T)$ of K_4C_{70}. As for the GIC's, we assume that S_d dominates the low T ($\ll 100$ K) behavior of $S(T)$ for K_4C_{70} so that[21]

$$S_d(T) = \frac{\pi^2 k_B^2 T}{3e}\left[\frac{3}{2E} + \frac{\partial \ln N(E)}{\partial E}\right]_{E_F}, \qquad (2)$$

where e is the electron charge, $N(E)$ the density of states, and E_F the Fermi energy. Because K_4C_{70} has a half-filled conduction band and this band is fairly symmetric,[9] we assume that $[\partial \ln N(E)/\partial E]_{E_F} \approx 0$. Comparing Eq. (2) to the measured slope $C = S(T)/T$ for $T < 100$ K, we find, in the same way as was previously done for K_3C_{60},[5] that $E_F \sim 0.25$–0.3 eV. Since the conduction band is half-filled, we obtain an estimate for the conduction bandwidth of ~ 0.5–0.6 eV. This value is similar to that deduced from $S(T)$ data for K_3C_{60} (~ 0.6 eV).[5]

The qualitative features of the magnetoconductance (MC) for K_4C_{70} are similar to those of K_3C_{60} thin films[4] and disordered carbon fibers.[12,13] For both K_3C_{60} thin films and disordered carbon fibers, weak localization and e-e interactions explain the observed charge transport phenomena. The $\Delta\sigma(H)/\sigma$ data for K_4C_{70} for $T > 5$ K appears to fit the three-dimensional WL and e-e interaction theory (see Fig. 3) although the T dependence of σ for K_4C_{70} does not follow the $T^{1/2}$ law as predicted by these theories.[14–16] One possible explanation for this discrepancy is as follows. As we mentioned previously, the FIT model fits the $\sigma(T)$ data. On the basis of the FIT model $\sigma(T)$ is limited by the thin insulating barriers which separate the metallic regions. Within the metallic regions, the electronic states appear to be weakly localized. As long as only the relative MC, $\Delta\sigma(H)/\sigma$, is considered, the formulas for the H-dependent part of $\Delta\sigma/\sigma$ (Refs. 14 and 15) can be applied to the system such as[19]

$$\Delta\sigma(H)/\sigma = \Delta\sigma_L(H)/\sigma + \Delta\sigma_I(H)/\sigma, \qquad (3)$$

where the weak localization contribution $\Delta\sigma_L(H)$ and the e-e interaction contribution $\Delta\sigma_I(H)$ are given by

$$\begin{aligned} \frac{\Delta\sigma_L(H)}{\sigma} &= k_1 \frac{e^2}{2\pi^2\hbar}\left(\frac{eH}{c\hbar}\right)^{1/2} f_3\left(\frac{4eD\tau H}{c\hbar}\right), \\ \frac{\Delta\sigma_I(H)}{\sigma} &= -k_2 \frac{e^2}{4\pi^2\hbar}\left(\frac{k_BT}{2\hbar D}\right)^{1/2} g_3\left(\frac{g\mu_B H}{k_BT}\right), \end{aligned} \qquad (4)$$

in which g is the Landé g factor, μ_B is the Bohr magneton, D is the diffusion constant, τ is the inelastic scattering time, f_3 and g_3 are two functions given by Kawabata[14] and Lee,[15] respectively, k_1 and k_2 are two weakly T-dependent coefficients, and D should be T independent for a simple metal.[14–16] Since the negative MC arises predominantly from the contribution from e-e interactions in GIC fibers and K_3C_{60} films, the dominance of the negative MC in the experimental results suggests a strong e-e interaction in K_4C_{70}. The solid lines in Fig. 3 are the calculated curves from Eq. (3), and while a good fit is obtained for the data at $T \geq 6$ K, deviations at low T are observed. To improve the fit, the diffusion constant D is assumed to be temperature dependent, and using the $D(T)$ dependence shown in the inset to Fig. 3, the fits to the MC data were made. The appearance of a discrepancy between the measured and the calculated $\Delta\sigma/\sigma$ at low T might be connected to the dramatic decreases in the diffusion constant $D(T)$ (see inset of Fig. 2) and in $\sigma(T)$ (see inset to Fig. 1 below 5 K). This low-temperature discrepancy might be caused by the charging energy of small metallic grains which be-

comes increasingly important at low T.

In conclusion, K_4C_{70} films are characteristic of disordered or heterogeneous metallic systems. The temperature dependence of the conductivity, thermoelectric power, and magnetoconductance are very similar to that observed for K_3C_{60} films and for intercalated carbon materials. We estimate the conduction bandwidth for K_4C_{70} to be 0.5–0.6 eV, similar to that of K_3C_{60}. No superconducting transition is observed above 1.35 K.

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[1] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, Nature (London) **350**, 600 (1991).

[2] Y. Maruyama, T. Inabe, H. Ogata, Y. Achiba, S. Suzuki, K. Kikuchi, and I. Ikemoto, Chem. Lett. **10**, 1849 (1991); X.-D. Xiang, J.-G. Hou, G. Briceno, W. A. Vareka, R. Mostovoy, A. Zettl, V. H. Crespi, and M. L. Cohen, Science **256**, 1190 (1992).

[3] G. P. Kochanski, A. F. Hebard, R. C. Haddon, and A. T. Fiory, Science **255**, 184 (1992); T. T. M. Palstra, R. C. Haddon, A. F. Hebard, and J. Zaanen, Phys. Rev. Lett. **68**, 1054 (1992).

[4] Z. H. Wang, A. W. P. Fung, G. Dresselhaus, M. S. Dresselhaus, K. A. Wang, P. Zhou, and P. C. Eklund, Phys. Rev. B **47**, 15 354 (1993).

[5] T. Inabe, H. Ogata, Y. Maruyama, Y. Achiba, S. Suzuki, K. Kikuchi, and I. Ikemoto, Phys. Rev. Lett. **69**, 3797 (1992).

[6] R. C. Haddon, A. F. Hebard, M. Rosseinsky, D. W. Murphy, S. J. Duclos, K. B. Lyons, B. Miller, J. M. Rosamilia, R. M. Fleming, A. R. Kortan, S. H. Glarum, A. V. Makhija, A. J. Muller, R. H. Eick, S. M. Zahurak, R. Tycko, G. Dabbagh, and F. A. Thiel, Nature (London) **350**, 320 (1991).

[7] P. J. Benning, D. M. Poirier, T. R. Ohno, Y. Chen, M. B. Jost, F. Stepniak, G. H. Kroll, J. H. Weaver, J. Fure, and R. E. Smalley, Phys. Rev. B **45**, 6899 (1992).

[8] K. Imaeda, K. Yakushi, H. Inokuchi, K. Kikuchi, I. Ikemoto, S. Suzuki, and Y. Achiba, Solid State Commun. **84**, 1019 (1992).

[9] S. Saito and A. Oshiyama, Phys. Rev. B **44**, 11 532 (1991).

[10] J. H. Mooij, Phys. Status Solidi A **17**, 521 (1973); A. B. Kaiser, in *Electronic Properties of Conjugated Polymers*, edited by H. Kuzmany *et al.* (Springer-Verlag, Berlin, 1987), p. 2.

[11] P. Sheng, Phys. Rev. B **21**, 2180 (1980).

[12] For reviews, see *Graphite Intercalation Compounds I and II*, edited by H. Zabel and S. A. Solin (Springer-Verlag, Berlin, 1992).

[13] M. S. Dresselhaus *et al.*, *Graphite Fibers and Filaments* (Springer-Verlag, Berlin, 1988).

[14] A. Kawabata, Solid State Commun. **34**, 431 (1980).

[15] P. A. Lee and T. V. Ramakrishnan, Phys. Rev. B **26**, 4009 (1982).

[16] B. L. Al'tshuler and A. G. Aronov, in *Electron-Electron Interactions in Disordered Systems*, edited by A. L. Efros and M. Pollack (North Holland, Amsterdam, 1985).

[17] The T at which the deviation from the FIT model occurs varies from sample to sample, depending on the disorder in the samples.

[18] N. F. Mott and E. Davis, *Electron Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979).

[19] Z. H. Wang *et al.* (unpublished).

[20] L. Y. Matzui, A. P. Naumenko, E. I. Kharkov, and L. L. Vovchenko, Mater. Sci. Forum **91**, 465 (1992).

[21] F. J. Blatt, P. A. Schroeder, L. Foiles, and D. Greig, *Thermoelectric Power of Metals* (Plenum, New York, 1976).