

Electrical-transport measurements of KC_{60}

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We have measured the temperature-dependent electrical resistivity ρ of polymerized KC_{60} from 410 to 1.9 K. $\rho(T)$ shows evidence for a metal-to-semiconductor phase transition near 50 K, and increases dramatically above 400 K. Between 400 and 50 K, ρ is metal-like, decreasing smoothly with decreasing temperature. Under applied hydrostatic pressure, ρ decreases, and the 50-K transition is suppressed. No anomalous magnetoresistance is observed up to 7 T, and we find no evidence of superconductivity above 1.9 K.

Alkali-metal-intercalated C_{60} has been widely studied, especially the superconducting A_3C_{60} ($A=K, Rb, Cs$) phases. Yet it was only recently discovered that AC_{60} compounds form conducting polymers which are air and toluene stable.¹⁻⁷ When slowly cooled, these materials undergo a structural phase transition from an fcc rocksalt phase to an orthorhombic polymerized phase, $o-AC_{60}$, at 400 K. This phase transition has been observed in optical⁷⁻¹¹ and electron spin resonance^{1,3,9} (ESR) measurements; the low- and high-temperature structures have been confirmed by x-ray diffraction.^{3,4,6} Infrared and ESR studies^{1,3,7-11} show that the $o-AC_{60}$ phase is conducting, and give evidence for a quasi-one-dimensional electronic structure; a transition near 50 K to a magnetically ordered state (possibly a spin-density wave) has been reported in RbC_{60} .³

In this paper we present direct electrical-transport measurements of polymerized KC_{60} . We have measured dc resistivity of KC_{60} samples from 420 to 1.9 K, and find a metallic temperature dependence, as well as evidence for two phase transitions, including a previously unreported low-temperature transition. We have investigated the pressure- and magnetic-field dependence of the resistivity, and find that applied hydrostatic pressure significantly affects both the resistivity and the low-temperature phase transition, while application of a magnetic field has little effect.

The KC_{60} samples were prepared using a method motivated by the procedure described by Pekker *et al.*¹ for the synthesis of crystalline KC_{60} . Pristine C_{60} crystals were grown by the vapor transport method,¹² and then sealed in an evacuated quartz tube with a stoichiometric amount of potassium. The tube was heated to 400 °C for 5 days and cooled to room temperature over 10 h. It has previously been shown that polymeric $o-KC_{60}$ is the only phase of K-doped C_{60} that is insoluble in toluene after exposure to air.^{1,5} Therefore, the doped crystals were exposed to air and immersed in toluene. The toluene turned magenta from dissolved C_{60} , but part of the material remained insoluble; after a few days, the insoluble pieces were removed. X-ray diffraction studies of these samples yielded patterns closely matching previously published spectra for polymerized KC_{60} (Ref. 10) and RbC_{60} ,^{3,6} confirming that the samples are composed of polymerized KC_{60} .

The samples used in this study are metallic gray, and smaller than the original pristine C_{60} crystals. They are elec-

trically conducting, and highly stable in air: they still conduct after six months of exposure to air. Considering the rapidity with which other phases of alkali-doped C_{60} degrade in air, the stability of this material is extraordinary. dc electrical resistivity was measured by the standard four-probe in-line technique. The best contacts were obtained by cleaving the samples to expose a fresh surface and evaporating gold pads onto that surface. Gold wires were then attached to the pads using conductive silver paint.

Figure 1 shows the resistivity ρ vs temperature of a representative KC_{60} sample. ρ shows a metallic temperature dependence between 400 and 50 K. A total of seven samples were measured; all show an identical temperature dependence between 300 and 80 K, when normalized to their room-temperature value. An empirical function of the form

$$\rho(T) \approx a + bT + cT^2 \quad (1)$$

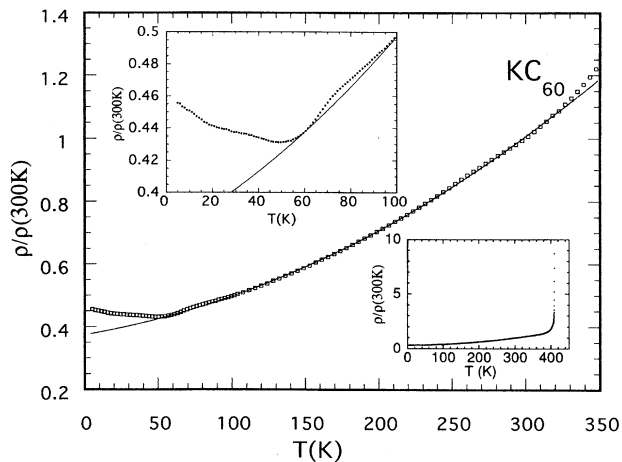


FIG. 1. Normalized dc electrical resistivity $\rho(T)$ for KC_{60} . The solid line is the empirical form $\rho(T) = a + bT + cT^2$, fitted to the data between 300 and 100 K and extended throughout the range of the data. The bottom inset shows resistivity data over an extended temperature range. The upper inset shows the low-temperature resistivity: the material shows a transition from a metallic to a semiconducting phase near 50 K.

provides the best fit to the measured resistivity in this temperature region. The solid line in Fig. 1 is Eq. (1) with fitting parameters $a = 0.375$, $b = 7.84 \times 10^{-4}$, and $c = 4.41 \times 10^{-6}$. The $\rho(T)$ behavior is similar to that of K_3C_{60} in the normal state,¹² which exhibits a temperature dependence of the resistivity of the form

$$\rho(T) \approx a + bT^2. \quad (2)$$

The marked difference, however, is in the presence of a substantial linear term ($bT \approx cT^2$ at 190 K) for KC_{60} . The T^2 dependence of the resistivity in the A_3C_{60} system has been explained as an artifact of the high coefficient of thermal expansion of the A_3C_{60} system: the constant-volume resistivity (as opposed to the more conventionally measured constant-pressure resistivity) is linearly temperature dependent.¹³ Polymerized KC_{60} would presumably undergo less expansion along the polymerized direction, and would therefore retain more of the linear temperature dependence in a constant-pressure measurement.

The KC_{60} samples measured all show no significant change in resistivity at 260 K, where pristine C_{60} undergoes a structural phase transition. In underdoped A_3C_{60} samples, this transition produces a sharp change in resistivity due to the stress induced in the crystal; its absence here indicates at most a small proportion of pristine C_{60} .

The lower inset of Fig. 1 shows that, upon heating above 400 K, KC_{60} exhibits a rapid increase in resistivity; this is in agreement with previous work^{1,3-11} which gives evidence that KC_{60} undergoes a decomposition from a polymerized structure to a rocksalt structure at this temperature. The large increase in resistivity is not found to be reversible, and is probably due to cracking of the sample as the material depolymerizes. The difference in volume between the low-temperature polymerized state of KC_{60} and the high-temperature rocksalt phase is on the order of 9%.⁶

The upper inset of Fig. 1 shows the low-temperature resistivity of KC_{60} . A second phase transition is observed, in which the resistance smoothly changes from metallic to semiconductinglike behavior. The minimum resistivity occurs in the neighborhood of 50 K, but varies somewhat among samples. ESR measurements³ give evidence for a phase transition at 50 K in RbC_{60} , but no transition has been observed in KC_{60} . It remains to be seen whether the same mechanism is responsible for the transition in both systems. Although all of our KC_{60} samples studied show evidence of the 50-K transition, the increase in resistance below 50 K varies among samples; the largest increase was 10%. Below the transition, ρ increases gradually with decreasing temperature, with a roughly linear temperature dependence between 40 and 20 K, and a slightly steeper linear dependence between 20 and 4 K. The solid line in the upper inset is a continuation of the $\rho(T) = a + bT + cT^2$ curve fit to the higher-temperature data. All samples measured exhibit the same qualitative features described above, although the quantitative behavior below 100 K is somewhat sample dependent.

Chauvet *et al.*³ have attributed the 50-K transition in RbC_{60} to the formation of a spin-density wave. Such a transition at temperature T_P would be accompanied by the formation of an energy gap at the Fermi surface, and a ther-

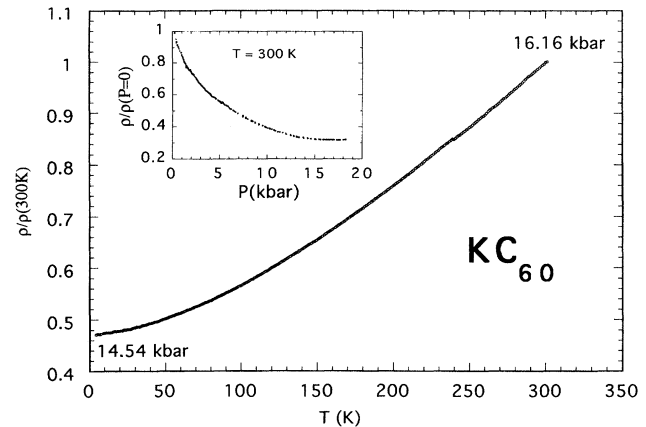


FIG. 2. Normalized resistivity of KC_{60} under hydrostatic pressure. The pressure increases as the sample warms; the average pressure is about 15 kbar. Note that the phase transition at 50 K has disappeared. The inset shows the pressure dependence of the resistivity at room temperature.

mally activated behavior below the transition.¹⁴ A high T_P [more than twice as high as in spin-density-wave organic linear-chain compounds such as $(DMET)_2Au(CN)_2$] implies a large gap; however, we observe neither an exponential dependence of resistivity on the temperature nor the drastic increase in resistivity expected with the opening of a large energy gap. This could be due to an incomplete nesting of the Fermi surface.

Figure 2 shows the behavior of the resistivity of a KC_{60} sample under externally applied hydrostatic pressure. The sample was mounted in a self-clamping pressure cell, where 16 kbar of hydrostatic pressure was locked in at room temperature. Fluorinert FC-75 was used as the pressure medium. The inset to Fig. 2 shows ρ measured as a function of applied pressure at room temperature. $\rho(P)$ saturates near 15 kbar to a value about 30% of the ambient pressure resistivity. The main body of Fig. 2 shows $\rho(P, T)$. The pressure inside the cell was continuously monitored using a calibrated manganin coil. Because the thermal contraction of the pressure medium is larger than that of the pressure cell, the pressure inside the cell continuously decreased from 16 kbar at 300 K to 14.5 kbar at 4.2 K. Under pressure, the 50-K phase transition is suppressed, and the resistivity continuously decreases with decreasing temperature. Investigations to determine the exact pressure dependence of the transition temperature are underway.

The low-temperature transition in RbC_{60} is observed at 34 K in IR transmission experiments,¹⁰ as opposed to 50 K in ESR,³ it has been suggested¹⁰ that the discrepancy is an effect of the magnetic field used in the ESR investigation. To clarify this issue, and to examine whether KC_{60} undergoes any type of magnetic-field-induced spin-density-wave transition, we have measured the resistivity of our samples in magnetic fields up to 7 T. We observe no change in the temperature dependence of the resistivity in high field, and the 50-K transition does not shift. We have performed field sweeps at 4.2 K. At that temperature, the resistance of the sample changes by less than 0.5% in the presence of fields up to 7 T.

The samples have been cooled to 1.9 K under ambient pressure, and no evidence of superconductivity has been found. This confirms that there is very little if any of the K_3C_{60} phase in any of the samples. It is perhaps interesting to estimate what the superconducting transition temperature for KC_{60} might be. A naive approach is to note that the A_3C_{60} materials exhibit a roughly linear dependence of T_c on lattice constant,¹⁵ and ask what the T_c of the A_3C_{60} phase would be if it were compressed to a volume equivalent to that of the A_1 phase. As mentioned above, the transition to the polymerized phase is accompanied by a 9% decrease in volume, which would imply a T_c of about 1 K. Formation of a spin-density wave, however, would reduce the critical temperature by removing some or all of the Fermi surface. In materials which exhibit both a charge-density-wave state and

a superconducting state, the superconducting transition temperature can be raised by suppressing the charge-density wave.¹⁶ It is possible that, if the spin-density wave were to be suppressed by a modest pressure, KC_{60} would superconduct at a low temperature.

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