

# Transport and structural properties of polymerized $AC_{60}$ ( $A = K, Rb$ ) under zero and high pressure conditions

K. Khazeni<sup>1</sup>, J. Hone<sup>1</sup>, Nasreen G. Chopra<sup>1</sup>, A. Zettl<sup>1</sup>, J. Nguyen<sup>2</sup>, R. Jeanloz<sup>3</sup>

<sup>1</sup> Department of Physics, University of California at Berkeley, and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA  
(Fax: +1-510/643-8497, E-mail: azettl@physics.berkeley.edu)

<sup>2</sup> Department of Physics, University of California at Berkeley, Berkeley, California 94720, USA

<sup>3</sup> Department of Geology and Geophysics, University of California at Berkeley, Berkeley, California 94720, USA

Received: 28 October 1996/Accepted: 13 December 1996

**Abstract.** Polymerized forms of alkali-doped  $C_{60}$  display transport properties vastly different from their unpolymerized counterparts. We here describe structural (X-ray diffraction and transmission electron microscopy) and dc resistivity measurements of polymerized  $AC_{60}$  ( $A = K, Rb$ ) at zero and high pressures. The structural and electronic properties are rich, and evidence is found for unusual phase transitions in both materials.

The recently-discovered [1] polymerized  $AC_{60}$  materials are the only air-stable alkali-doped  $C_{60}$  compounds. These materials have been characterized by many techniques, including structural analysis (XRD [2, 3], TFM [4]), magnetic probes (NMR [5–13] electron spin resonance [2, 14–19] and muon spin resonance [20–22]), optical spectroscopy (IR [14, 15, 23–27], Raman [1, 26, 28–30]), and electronic transport [25, 31]. Optical and magnetic measurements provide evidence that polymerized  $RbC_{60}$  and  $CsC_{60}$  undergo a transition to a magnetic ground state at a transition temperature of roughly 50 K. The same measurements have not detected any magnetic ground state in polymerized  $KC_{60}$ . The structure of these compounds is interesting in itself. It consists of covalently bonded  $C_{60}$  molecules which form linear chains. Such a geometry raises the possibility of one-dimensional conduction; however, there have been suggestions that the actual electronic transport is more complex [32]. The covalent bond between the  $C_{60}$  molecules is apparently a major obstacle to electronic conduction along the chains, and transport may actually follow a zig-zag path where electrons hop from one chain to a neighboring chain.

In this report we shall review structural and dc resistivity measurements of polymerized  $AC_{60}$  ( $A = K, Rb$ ) at zero and high pressures. In order to detect any anisotropy in transport, single crystal specimens would be desirable. Unfortunately, no method has yet been devised to synthesize true single crystals in which the direction of polymerization is uniform throughout the macroscopic sample. Therefore all measured resistivities

presented here represent an average over different crystal directions. Nevertheless, the results are illuminating and show a rich electronic structure.

## 1 Sample synthesis and structural characterization

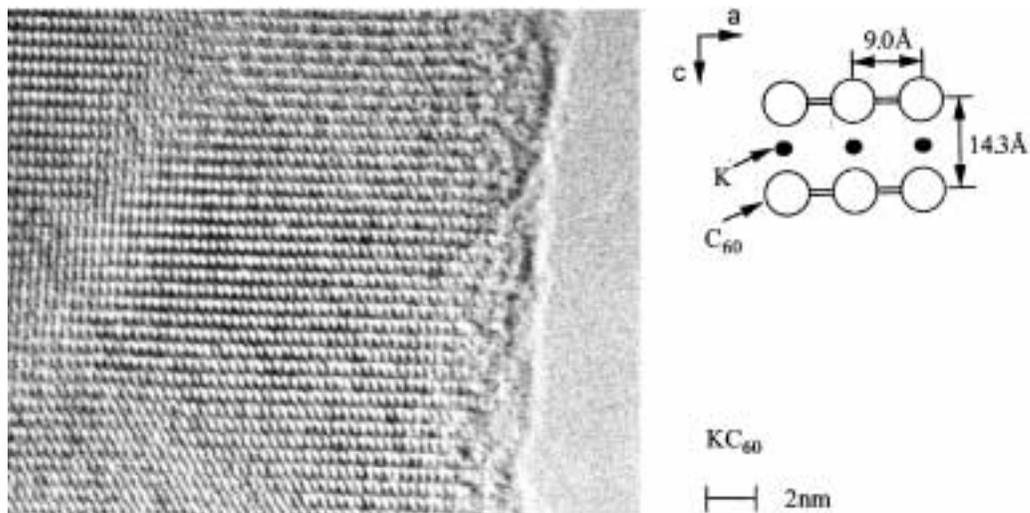
We have exploited the unique air-stability of the  $AC_{60}$  polymer phase to synthesize macroscopic samples of the material. Single crystals of pristine  $C_{60}$  are grown by vapor-phase transport, and then sealed in an evacuated Pyrex tube with a stoichiometric amount of alkali metal. The tube is heated to 400 °C for 10 days, and cooled slowly to room temperature. The doped crystals are then exposed to air and immersed in toluene for 10 more days, after which only the polymerized phase remains. While these samples are not truly single crystals, they have proved sufficient for a variety of measurements. The samples have been characterized by powder X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) [4].

Figure 1 shows a TEM image of a polymerized  $KC_{60}$ . The measured values of the lattice constants using the TEM image ( $a = 9.0 \text{ \AA}$ ,  $c = 14.3 \text{ \AA}$ ) are in good agreement with the previously published values of these parameters ( $a = 9.109 \text{ \AA}$ ,  $c = 14.321 \text{ \AA}$ ) [3].

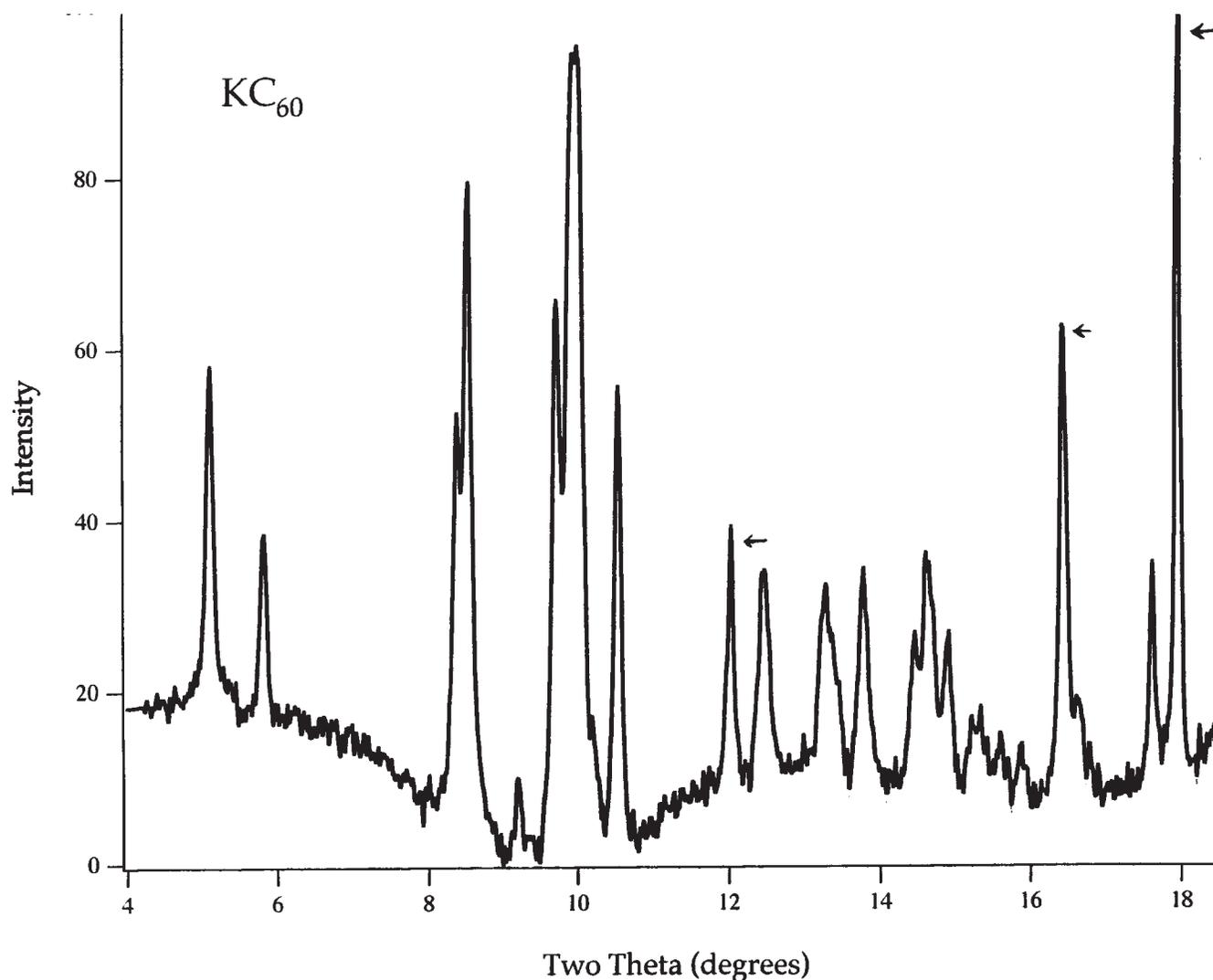
We have used XRD to confirm the composition of our samples and to study the room-temperature compressibility of polymerized  $KC_{60}$  and  $RbC_{60}$  at pressures up to 50 kbar. Samples were enclosed in a diamond anvil cell with 1 : 4 methanol-ethanol as a pressure medium, and aluminum and ruby as pressure calibrants. X-ray diffraction spectra were obtained using 17.038 keV synchrotron radiation at the Stanford Synchrotron Radiation Laboratory.

Figure 2 shows the X-ray diffraction spectrum of polymerized  $KC_{60}$  in the diamond anvil cell at ambient pressure. The arrows denote the diffraction lines due to aluminum and ruby. The spectrum closely matches previously-published spectra [2, 3], providing good confirmation of the phase-purity of the samples.

Figure 3 shows the preliminary results [33] of our study of polymerized  $RbC_{60}$ : it is highly compressible in the  $b$  and  $c$  directions, but very stiff in the  $a$  direction (the chain di-



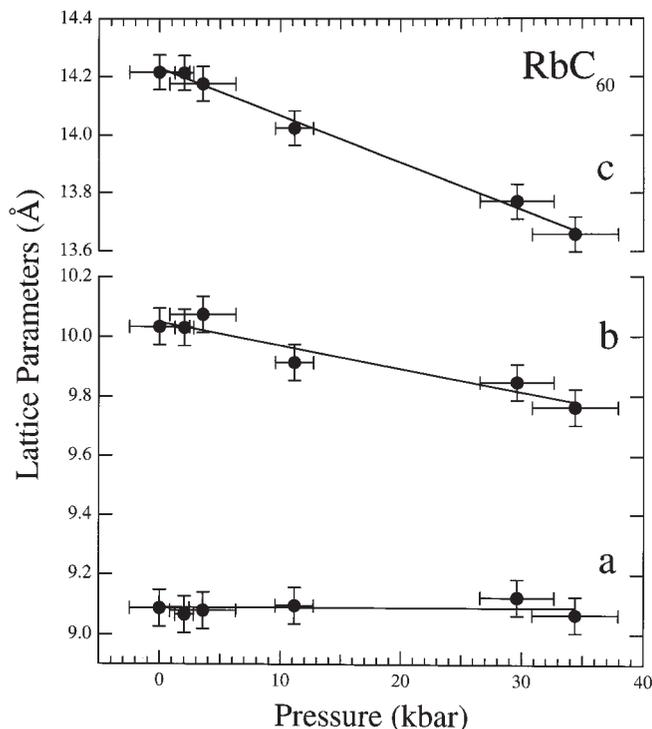
**Fig. 1.** TEM image of a sample of polymerized  $KC_{60}$ . The schematic drawing depicts the structure of the material in the direction perpendicular to the electron beam



**Fig. 2.** Powder X-ray diffraction spectrum of polymerized  $KC_{60}$ . The arrows indicate the diffraction lines due to aluminum and ruby, which were used as pressure calibrants

rection). Our high-pressure XRD study of polymerized  $KC_{60}$  also shows a very similar behavior [33]. These results are in

agreement with earlier thermal expansion studies [34], which show a similar anisotropy, and provides further confirmation



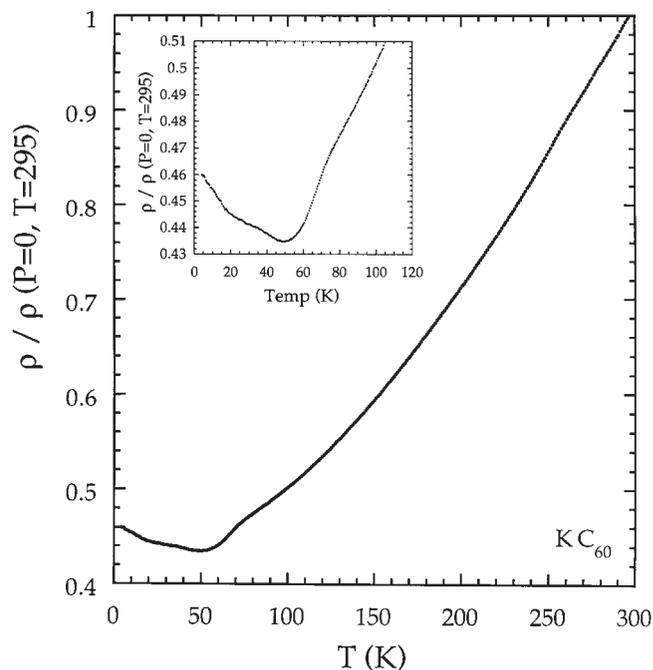
**Fig. 3.** Lattice constants of polymerized  $\text{RbC}_{60}$  vs. pressure, determined via synchrotron XRD in a diamond anvil cell. The solid lines are a least-squares linear fit to the data

of the polymerized nature of these materials. The preliminary calculated bulk moduli ( $B$ ) of polymerized  $\text{KC}_{60}$  and  $\text{RbC}_{60}$  from these measurements are 400 kbar and 580 kbar respectively. Compared to  $\text{A}_3\text{C}_{60}$  phases of the alkali-doped  $\text{C}_{60}$  with  $B \approx 250$  kbar [35], the polymerized  $\text{AC}_{60}$  fullerenes are much stiffer since they are very incompressible in the direction of polymerization which contains the covalently bonded  $\text{C}_{60}$  molecules.

## 2 dc resistivity of polymerized $\text{AC}_{60}$ at zero pressure

Four-probe resistivity measurements of polymerized  $\text{AC}_{60}$  samples were performed at temperatures from 400 K to 2 K. It was found that, in spite of the structural similarities between polymerized  $\text{KC}_{60}$  and  $\text{RbC}_{60}$ , they have greatly different transport properties at zero pressure [25, 31].

Figure 4 shows the normalized dc resistivity  $\rho$  of polymerized  $\text{KC}_{60}$  as a function of temperature. The resistivity is metallic, i.e.  $\rho$  decreases with decreasing temperature.  $\rho(T)$  does not follow any conventional form and displays a marked upward curvature, similar to that of the  $\text{A}_3\text{C}_{60}$  materials. The inset to Fig. 4 shows the resistivity of polymerized  $\text{KC}_{60}$  at low temperatures. Near 50 K, it displays a broad upturn, which may be the sign of a structural and/or electronic phase transition as in the case of the spin density wave (SDW) transition in the low-dimensional organic salt  $(\text{TMTSF})_2\text{PF}_6$  [36]. The low temperature resistivity in polymerized  $\text{KC}_{60}$  does not follow any activated form as might be expected with the opening of a gap at the Fermi energy. If the transition is indeed due to a SDW (or a charge density wave) then the Fermi surface is most likely only partially gapped. No superconductivity is observed to 4.2 K, nor does the material display any magne-



**Fig. 4.** Normalized resistivity of polymerized  $\text{KC}_{60}$ . The inset shows the low-temperature metallic-nonmetallic transition

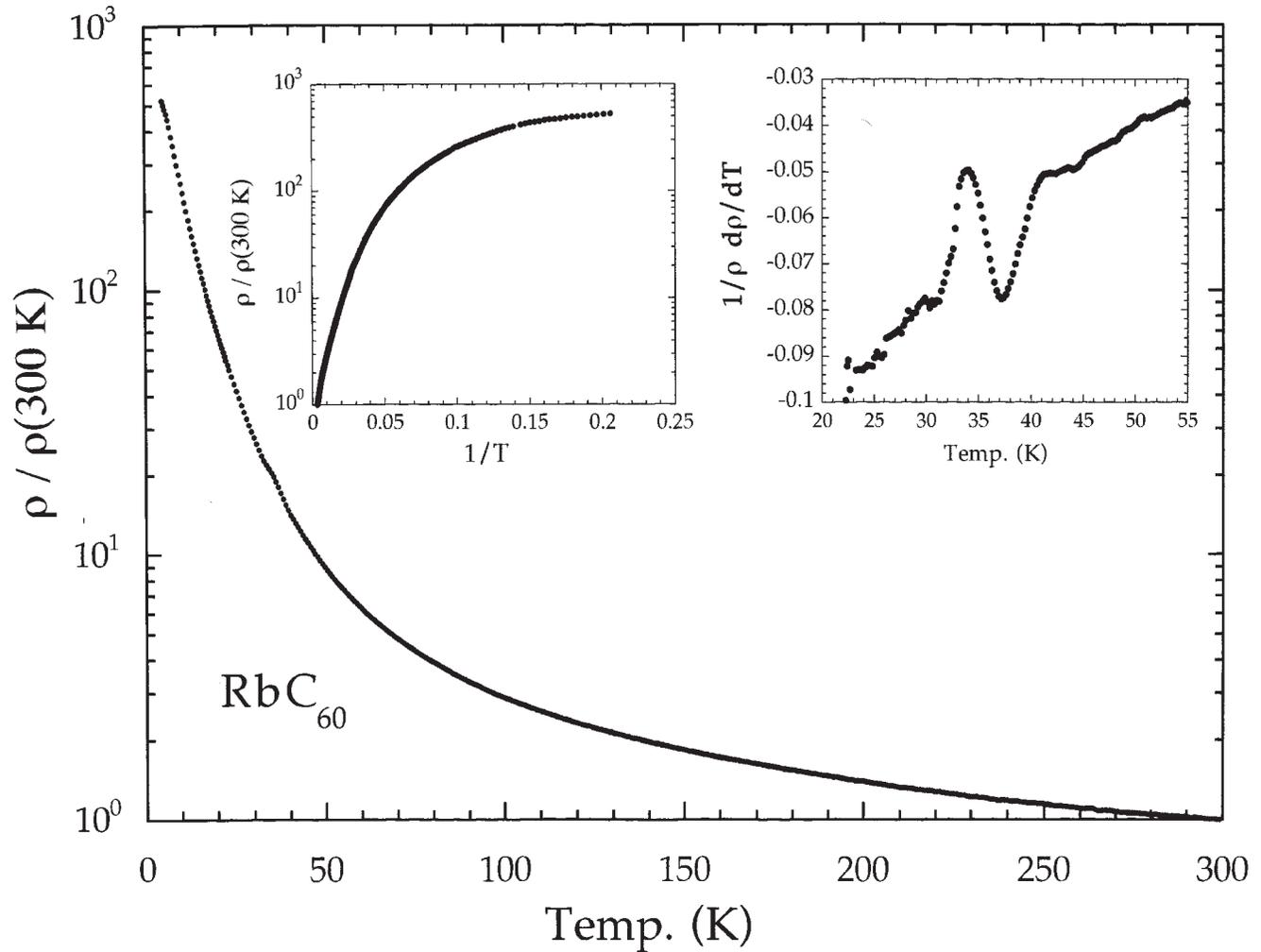
toresistance (within 0.10%) in fields up to 7 T from 4.2 K to 300 K.

Figure 5 shows the normalized resistivity of polymerized  $\text{RbC}_{60}$  as a function of temperature. In contrast to polymerized  $\text{KC}_{60}$ , this material has a semiconducting-like resistivity, and display no overall change in behavior at low temperatures. The upper left inset to Fig. 5 shows  $\log \rho$  vs.  $1/T$ . At high temperatures, the slope of this plot gives an activation energy of roughly 150 K, although clearly the behavior is not strictly semiconducting. However, an anomaly in the data is seen in all samples near 35 K, and may be related to the magnetic transition observed by other methods [2, 7, 20, 25]. This anomaly can easily be seen in the logarithmic derivative of  $\rho$  vs.  $T$  in the upper right inset of Fig. 5.

From our measurements and other published data [23, 25] it is clear that the electronic transport behavior of polymerized  $\text{KC}_{60}$  is significantly different from that of polymerized  $\text{RbC}_{60}$ . Polymerized  $\text{KC}_{60}$  shows metallic behavior between 300 K and 50 K and slightly increased resistivity below 50 K in dc as well as ac [25] conductivity measurements, but it shows no evidence of a magnetic phase transition at low temperatures. Polymerized  $\text{RbC}_{60}$  is somewhat more problematic: the above dc measurements show a continuous increase in resistivity with decreasing temperature, while optical and ac measurements [23, 25] display a more pronounced change in behavior at low temperatures. It remains to be seen how the dc and ac transport measurements correlate with the observed magnetic transition in  $\text{RbC}_{60}$ .

## 3 dc resistivity of polymerized $\text{AC}_{60}$ at high pressures

The resistivity of conductive phases of alkali-doped fullerenes is in general extremely pressure-dependent [35]. The polymerized alkali-doped fullerenes are no exception: at



**Fig. 5.** Normalized resistivity of polymerized  $\text{RbC}_{60}$ . The upper left inset is plot of  $\log \rho$  vs.  $1/T$ : its slope at high temperatures corresponds to an activation energy of roughly 150 K. The upper right inset is the logarithmic derivative of  $\rho$  vs.  $T$ . Notice the anomaly at  $\approx 35$  K

room temperature, an applied pressure of 15 kbar reduces the resistivity of polymerized  $\text{KC}_{60}$  by 70% [31]. This suggests that in a constant-pressure measurement the change in volume of the sample due to thermal expansion could result in a markedly different functional behavior of  $\rho(T)$  than if the measurement were to be done at constant sample volume. Since most transport model predictions assume constant sample volume, it is necessary to correct the measured resistivity data for constant sample volume in order to extract any meaningful parameters from the transport measurements.

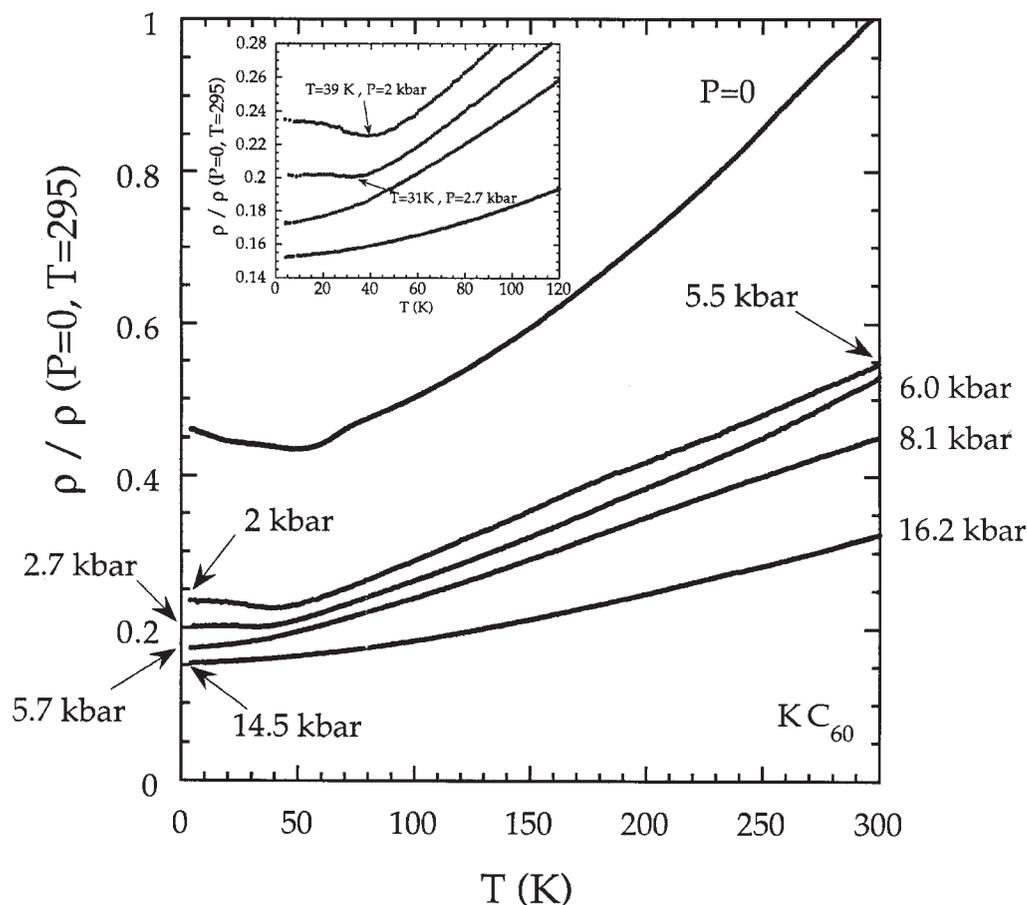
To obtain constant-volume resistivity data, the dc resistivities of polymerized  $\text{KC}_{60}$  and  $\text{RbC}_{60}$  samples were first measured at 0 pressure from 300 K to 4.2 K. The samples were then transferred into a self-clamping pressure cell, where hydrostatic pressure was locked in at room temperature. Fluorinert FC-75 was used as the pressure medium. The resistivity of the samples was again measured from 300 K to 4.2 K. The resistivity measurements under pressure are not isobaric; the pressure decreases monotonically as the temperature is lowered due to the difference in the thermal expansions of the pressure medium and the cell. The pressure was monitored as a function of temperature by a calibrated manganin coil. The

procedure was repeated for a range of initial room-temperature clamping pressures.

Figure 6 shows the normalized resistivity of polymerized  $\text{KC}_{60}$  at pressures up to 16.7 kbar, and temperatures from 300 K to 4.2 K. The inset to the figure shows the low-temperature behavior. Applied pressure greatly reduces the resistivity, and suppresses the low-temperature transition, as is shown more clearly in the inset. The minimum shifts downward in temperature, and disappears for applied pressures above  $\approx 4$  kbar. The suppression of the low-temperature resistive upturn with pressure is consistent with the picture of a transition to a state related to reduced dimensionality: applied pressure increases the dimensionality of the material and suppresses the transition.

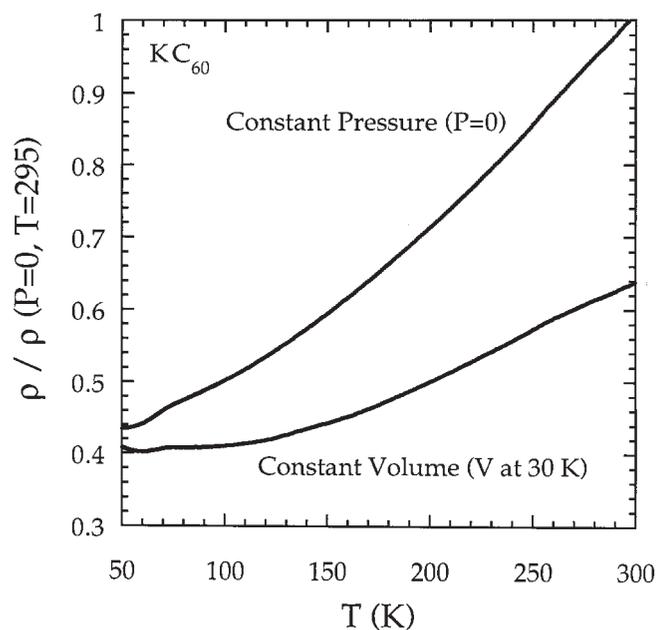
Figure 7 shows the resistivity of polymerized  $\text{KC}_{60}$  as measured at zero pressure and at constant volume, corrected using the measured values of the bulk modulus (400 kbar) and the volume thermal expansion coefficient ( $3.09 \times 10^{-5} \text{ 1/K}$ ).<sup>1</sup>

<sup>1</sup>In calculating the constant-volume  $\rho(T)$  it was assumed that the bulk modulus and the thermal expansion coefficient are both independent of temperature and pressure in the measured range of these parameters. It was also assumed that the thermal expansion coefficient is constant from 300 K down to 30 K, below which it is negligibly small.



**Fig. 6.** Normalized resistivity of polymerized  $\text{KC}_{60}$  at zero pressure and at pressures from 2 to 16.7 kbar. The labels indicate the pressures at 300 K and 4.2 K for each curve; the pressure is monitored continuously with a calibrated manganin coil. The inset shows the suppression of the low-temperature transition under pressure

It can be seen that neither the constant volume  $\rho(T)$  nor the measured constant-pressure  $\rho(T)$  follows any conventional behavior. However, the constant volume  $\rho(T)$  shows a markedly

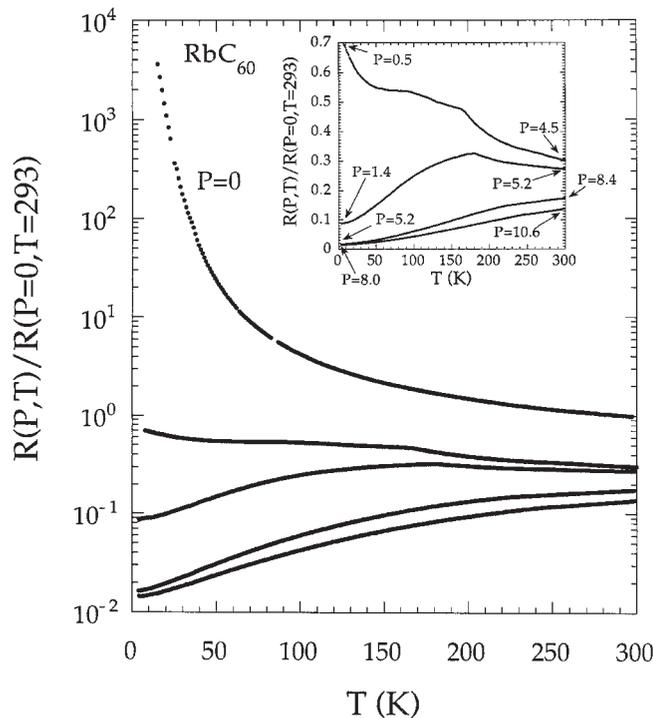


**Fig. 7.** Resistivity of polymerized  $\text{KC}_{60}$  at constant (zero) pressure and at constant volume

different smaller temperature coefficient justifying the concern for its calculation.

Figure 8 shows the normalized resistivity of polymerized  $\text{RbC}_{60}$  under high pressure conditions. As pressure is applied and the volume of the polymerized  $\text{RbC}_{60}$  unit cell is decreased, the material becomes metallic, behaving similarly to polymerized  $\text{KC}_{60}$  [37]. In fact, polymerized  $\text{RbC}_{60}$  is so close to the insulator-metal boundary that the application of 0.5 kbar at 4.2 K is sufficient to reduce the resistivity by over three orders of magnitude. Also significant is that polymerized  $\text{RbC}_{60}$  does not become metallic gradually, but instead undergoes a sharp transition to the metallic state. At higher pressures, the transition can be described as to a “better-conducting” state since the resistivity is metallic even above the transition temperature. This can be clearly seen in the inset to Fig. 8 as abrupt changes in the slope of  $\rho$  vs.  $T$ . The transition occurs regardless of whether the high- or the low- temperature phase is metallic or semiconducting. It is not seen at zero pressure, nor has it been observed by any other method.

Figure 9 shows this transition in polymerized  $\text{RbC}_{60}$  at 5 kbar upon cooling and warming. The hysteresis associated with the resistivity around the transition temperature  $T_{tr}$  gives strong evidence that the transition is first-order. This could mean that the material is undergoing a structural phase transition and that one should be able to measure the involved latent heat by calorimetric measurements. Unfortunately, such experiments are difficult to perform since the sample is immersed in a pressure medium inside a large metallic cell. A rough estimate of the latent heat may be obtained from the plot of  $P$  vs.



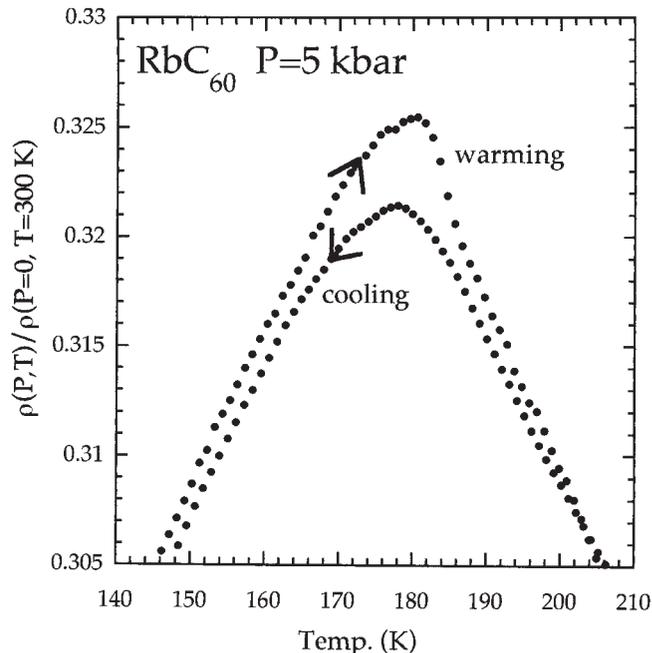
**Fig. 8.** Normalized resistivity of polymerized  $\text{RbC}_{60}$  at zero pressure and at pressures from 0.5 to 10.6 kbar. The resistivity decreases dramatically under pressure, and at higher pressures the material is completely metallic. The inset shows the sharp transition to a “better-conducting” state, which is manifested as a sharp change in the slope of the resistivity

$T_{tr}$  using the Clapeyron equation,  $P/T = \delta S_{tr}/\delta V_{tr}$ . Assuming the change in volume going from one phase to another is about  $1\% \approx 1 \text{ mJ/g}$ . This rather small value of  $L$  seems reasonable since the high-pressure phase has a smaller volume than the starting phase; hence, the change in volume across the transition dominates the change in entropy.

#### 4 Conclusions

We have synthesized samples of polymerized  $\text{AC}_{60}$  ( $A = \text{K, Rb}$ ) and performed a range of structural and transport measurements. TEM supports earlier XRD evidence of an orthorhombic structure. XRD studies under pressure show that these materials are highly incompressible in the  $a$  direction, providing further evidence that they are composed of covalently bonded chains. The dc resistivity of polymerized  $\text{AC}_{60}$ , determined at zero and at high pressures, has intriguing features. The zero-pressure resistivity of polymerized  $\text{KC}_{60}$  is metallic from room temperature down to  $\approx 50 \text{ K}$  below which it becomes non-metallic. Under applied hydrostatic pressure, resistivity of polymerized  $\text{KC}_{60}$  decreases and the low temperature transition to the non-metallic phase decreases in temperature and finally disappears near 4 kbar. The resistivity of polymerized  $\text{RbC}_{60}$  is semiconducting-like at zero pressure, but no activated behavior with a temperature-independent activation energy is observed. Under hydrostatic pressure,

<sup>2</sup>The 1% change in volume is motivated by the fact that polymerized  $\text{KC}_{60}$  is metallic and polymerized  $\text{RbC}_{60}$  is semi-conducting at zero pressure, and that their unit-cell volumes differ by about 1%.



**Fig. 9.** Hysteresis associated with the transition in polymerized  $\text{RbC}_{60}$

the resistivity of polymerized  $\text{RbC}_{60}$  decreases much more drastically than that of polymerized  $\text{KC}_{60}$ .

Only 0.5 kbar at  $\approx 4.2 \text{ K}$  changes the resistivity of polymerized  $\text{RbC}_{60}$  by 3 orders of magnitude. Another surprising feature is that polymerized  $\text{RbC}_{60}$  becomes metallic under pressure. The transition temperature to the “better-conducting” phase is hysteretic in temperature and suggests a first order phase transition, possibly structural, with a roughly estimated latent heat of  $\approx -1 \text{ mJ/g}$ .

**Acknowledgements.** This research was supported by National Science Foundation Grant No. DMR9501156 and by the Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of U.S. Department of Energy under Contract No. DE-AC03-765F00098. R. Jeanloz and J. Nguyen acknowledge support from ACS-PRF, NASA, and NSF. A. Zettl acknowledges support from the Miller Institute for Basic Research in Science. X-ray diffraction was performed at beamline 10-2 at the Stanford Synchrotron Radiation Laboratory.

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