

ELECTRICAL TRANSPORT, THERMOELECTRIC, AND STRUCTURAL MEASUREMENTS OF POLYMERIZED AC_{60} (A=K,Rb) UNDER ZERO AND APPLIED PRESSURE

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We have performed a variety of experiments to elucidate the nature of the low- and high-temperature conduction mechanisms in the polymerized AC_{60} materials. Measurements at zero pressure include dc resistivity of pure and mixed-intercalant phases, and thermoelectric power. The constant-volume resistivity of KC_{60} and RbC_{60} can be calculated from high-pressure transport and structural measurements, and provides strong evidence for a common conduction mechanism in these materials.

1. Introduction

Many of the properties of the polymerized AC_{60} materials are still not well understood. In particular, the nature of the low-temperature phase transition observed in RbC_{60} and $CsC_{60}^{1,2,3}$ is not fully understood, nor is the difference between KC_{60} and the other two materials. To examine the high- and low-temperature phases of these materials, we have measured dc resistivity, magnetoresistance, and thermoelectric power. We have tried to interpolate between the behavior of KC_{60} and RbC_{60} by applying pressure to both materials and by synthesizing mixed-intercalant materials. Finally, we have performed structural studies under pressure and corrected our $\rho(T)$ data for conditions of constant volume.

2. Sample synthesis

Samples of the AC_{60} materials were synthesized by stoichiometric doping of pristine C_{60} crystals. After doping and annealing at $400^\circ C$ for 10 days, the crystals were slowly cooled, exposed to air, and immersed in toluene. In this way, all other phases are removed and we are left with pure-phase crystalline samples. Samples with mixed intercalants have been produced by the same method; initial characterization by SIMS and EDX suggests that they have an intimate mixture of alkali metals, but that the ratio of intercalants varies by approximately 10% over a given sample.

could be slightly different from 45° in one compound (which consistent with the X-ray diffraction data especially in the case one polymer could be disordered contrary to the other one. orbitals are very anisotropic, the overlap between neighboring orbitals is sensitive to their relative orientation. Strong overlap between the diagonal direction would lead to a 3D behavior. It is likely particular orientation of the ball, this overlap could be reduced giving rise to a low dimensional compound. In case of strong directionally to the chains (where two bonds "f-f" face each other),

to highlight the possible role of chain orientations in the differences of K_1C_{60} and $(Rb_1C_{60}$ and $Cs_1C_{60})$, which we believe to be in a different dimensionality of the electronic structure. We have seen quite a clear evidence from the MAS-NMR spectra that the chains modify the electronic structure of these materials between the chains are different in K_1C_{60} . This element might partially the overlap between the chains, so that it would be worth more details. Because of the rather complicated structure of the theoretical calculations are usually done by assuming orientations that allows a reduction of the unit cell. This may be a too this case. More experimental work is also needed to refine our the chain orientations in the different compounds. In addition, structure observed at low T in Cs_1C_{60} or Rb_1C_{60} would probably be to the orientational order of the C_{60} chains. Although a real develops in this phase, its structure is not clear at present. A real understanding of these materials (lengths of the polymerized distribution, domains etc.) would be helpful to go further.

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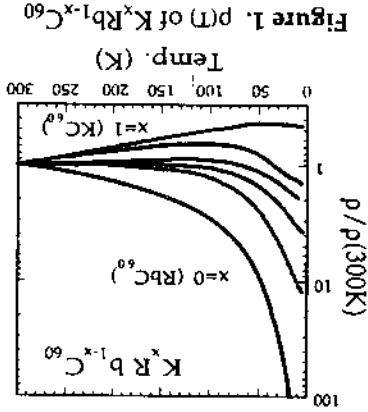


Figure 1. $p(T)$ of $K_xRb_{1-x}C_{60}$

Figure 1 shows the temperature dependence of the dc resistivity of KC_{60} and a series of samples with mixed intercalants. KC_{60} is metallic above 50 K and exhibits an upturn in resistivity below that temperature. As the K is mixed with higher concentrations of Rb, the upturn increases in temperature and becomes larger in magnitude. Finally, RbC_{60} displays non-metallic behavior at all temperatures. The continuity of the change in behavior from pure KC_{60} to pure RbC_{60} suggests that the same mechanism is responsible for the low-temperature upturn in KC_{60} and the behavior of RbC_{60} at all temperatures.

3. Zero-pressure measurements

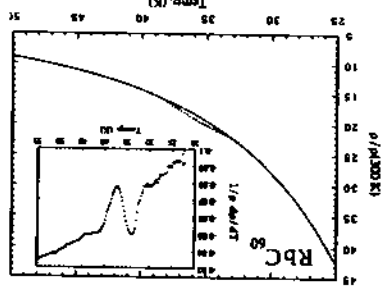


Figure 2. Anomaly in RbC_{60} $p(T)$

Figure 2 shows the $p(T)$ behavior of RbC_{60} . An anomaly is seen in all samples at this temperature, which coincides with the ordering temperature associated with the magnetic transition seen by other methods^{1,2}. This anomaly displays no hysteresis, and has a magnetoresistance of less than 0.1% in fields up to 8 Tesla. The $p(T)$ behavior of RbC_{60} may change slightly above and below the anomaly, as can be seen in the inset to figure 2, where the slope of the resistivity seems to jump to a larger value below the anomaly; the evidence is inconclusive, however.

Figure 3 shows the thermoelectric power of RbC_{60} and KC_{60} . The TEP of KC_{60} is linear and negative, indicating metallic, electron-like conduction. The opening of a gap at the Fermi surface causes a $(1/T)$ dependence in the TEP; this behavior is not observed in the TEP of KC_{60} below 50 K, indicating that the 50 K upturn in resistivity is not caused by a complete gapping of the Fermi surface.

Figure 3. TEP of KC_{60} and RbC_{60}

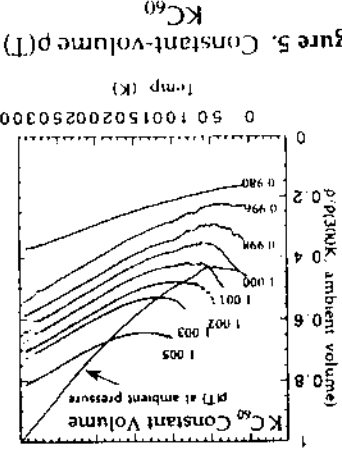
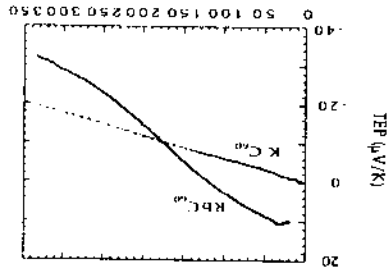


Figure 5. Constant-volume $p(T)$ of KC_{60}

It is difficult to extract meaningful information from the $p(T)$ behavior of molecular conductors such as the doped fullerenes. Their transport properties are highly sensitive to small changes in lattice constant; therefore, thermal expansion can dramatically alter the $p(T)$ behavior of these materials. It is, however, possible to correct for the effects of thermal expansion. This requires measurement of the thermal expansion coefficient, bulk modulus, and the pressure-dependence of $p(T)$. The thermal expansion coefficient of KC_{60} has been measured previously⁴. Below we will report measurements of the bulk moduli of RbC_{60} and

4. High-pressure measurements

The TEP of RbC_{60} displays a more complicated behavior, with a zero-crossing near 100 K, which may indicate that the Fermi level is near to a half-filled band, where a small change in Fermi energy (due to lattice contraction upon cooling) could cause the system to move from electron-like to hole-like conduction. Again, no $(1/T)$ behavior is observed for RbC_{60} , although our data are only reliable down to 20 K. Obviously, effort needs to be made to extend the range of this measurement. If we assume that KC_{60} is a 3-D free-electron-like metal, we can use the slope of the TEP to extract a Fermi energy of 0.22 eV.

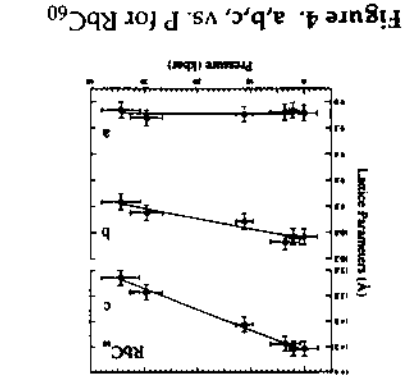


Figure 4. a,b,c, vs. P for RbC_{60}

KC_{60} . Finally, we have earlier⁵ reported a series of measurements of the $p(T)$ behavior of KC_{60} and RbC_{60} under pressure. Under pressure, the resistivity of both materials decreases dramatically, and upon cooling RbC_{60} undergoes a sharp transition to a better-conducting state. Using X-ray diffraction under pressure in a diamond anvil cell, we have been able to determine the pressure-dependence of the lattice parameters of KC_{60} and RbC_{60} . As the data for RbC_{60} are shown in figure 4. As expected, these materials are stiff in the polymer (a) direction and much more compressible in the b and c directions. We calculate values of 400 kbar and 580 kbar for

POLYMERIC GROUND STATE OF $\text{Na}_2\text{RbC}_{60}$: EFFECT OF CHARGE STATE ON BONDING GEOMETRY

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The story of polymerization of C_{60} and its derivatives is still full of surprises. Here, we present the derivation of the ground state structure of $\text{Na}_2\text{RbC}_{60}$ as a one-dimensional polymer of C_{60} molecules connected by a single carbon-carbon bond, in contrast to the RbC_{60} system. The question of why the former links fullerene molecules with a single bond, whereas the latter does so with two carbon-carbon bonds is of tremendous interest. We interpret our results to indicate that it is the charge state of the fullerene that drives the bonding mechanism, causing $(\text{C}_{60}^-)_n$ to favor cycloaddition and $(\text{C}_{60}^0)_n$ to favor single carbon-carbon bonds.

1 Introduction

The bonding of fullerene molecules has been reported in a variety of cases.¹⁻⁸ However, a systematic study of steric and electronic influences on the formation of fulleride polymers has not been possible to date, because the systems in which interfullerene bonds have been observed are very dissimilar. Calculations have found one-dimensional chains linked via $[2+2]$ cycloaddition (as found in the RbC_{60} ground state¹) to be the most stable configuration for C_{60} polymers.⁹⁻¹³ Recently, we have found that $\text{Na}_2\text{RbC}_{60}$ loses cubic symmetry when cooled slowly to temperatures below $T=230\text{ K}$ and suggested the formation of interfullerene bonds in this new phase.⁷ The C_{60} nearest-neighbor distance of 9.38 \AA made us suspect single bonds as interfullerene connection. We note here that the presence of K^+ or Rb^+ in the tetrahedral sites expands the cubic fulleride lattice relative to neutral C_{60} , locks the fullerenes into an orientationally disordered $Fm\bar{3}m$ structure and prevents polymerization, whereas the smaller Na^+ cation contracts the lattice relative to pure C_{60} , allows fullerene reorientation into the C_{60} $Fm\bar{3}m$ structure and does allow polymerization. Hence, we can explore the influence of the fullerene charge state

the bulk moduli of KC_{60} and RbC_{60} , respectively. Figure 5 shows the $p(T)$ behavior of KC_{60} , corrected for conditions of constant volume. Each curve represents $p(T)$ for KC_{60} at a different multiple of the material's unit cell volume at 4.2 K .

The curve labeled 1,000 represents the $p(T)$ behavior as the material is warmed at constant volume from 4.2 K , zero pressure. Under these conditions, the low-temperature upturn is enhanced, and the resistivity above that temperature is roughly linear. At higher volumes, the resistivity upturn increases in temperature, which is consistent with the measurements on mixed-intercalant materials. At lower volumes, the upturn is suppressed.

Figure 6 shows the $p(T)$ behavior of RbC_{60} under constant volume conditions. The constant-volume behavior of RbC_{60} shows clearly that there are two regimes of behavior for RbC_{60} . At high temperatures, the material is insulating. At temperatures between 150 K and 200 K , the material undergoes a metal-insulator transition. Below that transition, the material is a metal with a low-temperature upturn in resistivity; the temperature of that upturn increases with increasing volume. This behavior is qualitatively identical to that of KC_{60} , leading to the conclusion that, below the insulator-metal transition, these materials display a universal $p(T)$ behavior under constant-volume conditions. The key to understanding the differences between KC_{60} and RbC_{60} , then, may be to discover the nature of the pressure-induced phase transition.

5. References

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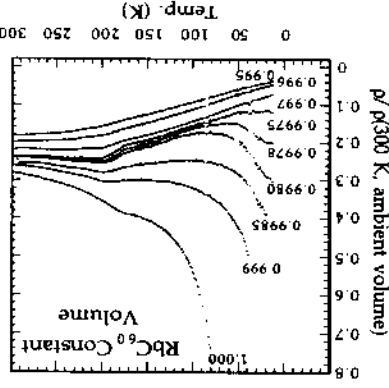


Figure 6. Constant volume $p(T)$ of RbC_{60}