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Metal-insulator transition in AC_{60}: RbC_{60} and KC_{60}

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At zero pressure polymerized RbC_{60} is an insulator, whereas polymerized KC_{60} is a metal with a slight low-temperature resistive upturn. We report measurements of the resistivity of RbC_{60} under pressure, finding a hysteretic resistive transition in RbC_{60} near 200 K at 5 kbar, at which point the material transforms from insulator to metal. Correcting the resistivity to constant volume, both materials are metallic below the transition with a common low-temperature resistive upturn which is suppressed under compression. [S0163-1829(97)08636-0]

The interfullerene covalent bonds of AC_{60} (A=K,Rb) promise novel physics distinct from other alkali-doped fullerene materials. Slow cooling through 400 K converts AC_{60} from the rocksalt structure to a polymerized orthorhombic phase where each C_{60} molecule shares two covalent bonds with opposite neighbors.[1,2] One puzzle of the AC_{60} materials has been the qualitative difference in transport properties for only slight differences in structure, behavior which seems to contrast markedly with the uniform scaling in lattice constant observed in the A_3C_{60} phases.[3] Whereas at zero pressure KC_{60} is metallic between 400 K and 50 K, RbC_{60} and CsC_{60} are semiconducting.[4–6] The K and Rb materials differ only slightly in the interchain distance. In addition, infrared and electron spin resonance measurements[7–9] in the Rb and Cs compounds suggest a magnetic transition near 50 K which has not been observed in polymerized KC_{60}.[10] The sensitivity of transport properties to lattice constant in the A_3C_{60} compounds[3,11] motivates a pressure study of AC_{60} to search for the source of the qualitative differences between these uniquely polymerized doped fullerene materials.

C_{60} single crystals were doped to stoichiometry AC_{60} (A=K, Rb) at 670 K. The samples were then cooled slowly to room temperature and soaked in toluene for 10 days to remove possible minority phases. Details of the preparation are described elsewhere.[5] X-ray diffraction measurements for both materials closely matched previously published spectra.[2] Resistivity measurements used the standard four-probe technique with silver paint on gold pad contacts. The resistivity of each material was first measured at zero pressure from 300 to 4.2 K. The samples were then transferred to a self-clamping pressure cell where several kbar of hydrostatic pressure were locked in at room temperature using Fluorinert FC-75 as the pressure medium. The resistivity of each sample was again measured from 300 to 4.2 K. The pressure decreases as the temperature is lowered due to the difference in the thermal expansions of the pressure medium and the cell. Hence, the pressure was monitored as a function of temperature with a calibrated manganin coil. The procedure was repeated for larger clamping pressures.

As shown in Fig. 1, KC_{60} at zero pressure is metallic with a slight resistive upturn below 50 K. The upturn broadens and diminishes under hydrostatic pressure, disappearing under 6 kbar. The data for 8 kbar clamping pressure were extended down to 1.5 K without evidence of superconductivity.[12] External pressure strongly reduces the resistivity at all temperatures. This sensitivity to pressure motivates a conversion to constant volume to account for both thermal expansion and the variations in pressure during the temperature sweeps.

The correction to constant volume uses the measured pressure dependence of the resistivity, the thermal expansion coefficient of KC_{60} [$\Delta V/V = 3.1\times10^{-5}\ \mathrm{K}^{-1}$ (Ref. 13)] and the bulk modulus of KC_{60} (400 kbar) measured by x-ray

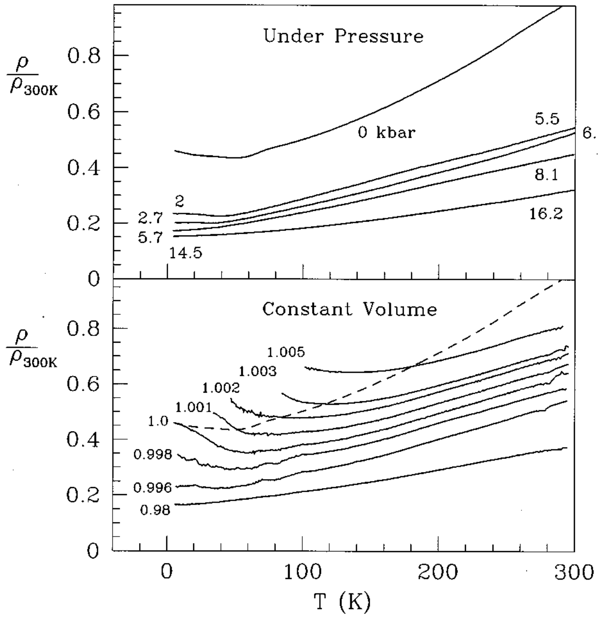

FIG. 1. Upper curves are the temperature-dependent resistivity of KC_{60} at zero pressure and four clamping pressures labeled by the pressure in kbar at 4.2 K and 300 K. The lower curves are the constant-volume resistivity labeled by the fraction of the $(P,T)=(0,0)$ volume occupied at $T=0$. The dashed line is the $P=0$ resistivity. Constant-volume results above this line extrapolate beyond the measured pressures. The jitter in the constant-volume resistivity is due to fluctuations in the fitting parameters and is not physical. $T=0$ is offset slightly for clarity.

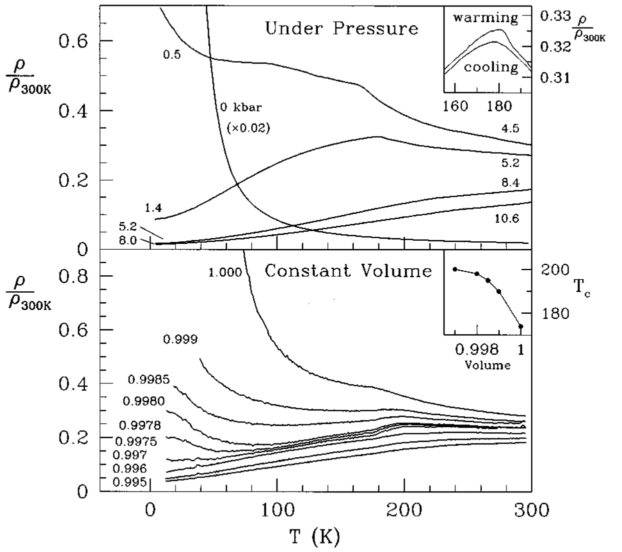

FIG. 2. Upper curves give the temperature-dependent resistivity of RbC_{60} at zero pressure and five clamping pressures. Numerical labels give the pressure in kbar at 4.2 K and 300 K. The inset shows the hysteresis in the 5.2 kbar clamping pressure data. The lower set of curves shows the constant-volume resistivity, labeled by the fraction of the $(P,T)=(0,0)$ volume occupied at $T=0$. The inset shows the variation in the resistive feature with volume.

diffraction at pressures up to 30 kbar.[14] The high-temperature thermal expansion coefficient is matched at 30 K to a T^3 form which smoothly flattens the low-temperature thermal expansion.[15] To derive the constant-volume resistivity, the five measured (R,P) points at each temperature are fit to a smoothly varying function which allows interpolation to the pressure required for the maintenance of a constant volume.[16] Many alternative interpolation techniques were tested to ensure that the results were not sensitive to the idiosyncracies of any particular fitting function.[17] The correction to constant volume shown in the lower curves of Fig. 1 accentuates the metal-insulating transition. Although data above the $P=0$ line extrapolate outside measured pressures, the results suggest a more pronounced resistive upturn occurring at higher temperatures in KC_{60} under lattice dilation.

A similar pressure study of RbC_{60} in Fig. 2 reveals a sharp resistive transition near 200 K and a strong suppression of the low-temperature resistivity. The transition bridges either two insulating phases, a metal and an insulator, or two metallic phases depending on the clamping pressure. These curves have been reproduced under both increasing and decreasing pressure. The transition is apparently first order, as evidenced by the resistive hysteresis shown in detail for the 5.2 kbar clamping pressure. Although the origin of the transition is at present unclear, it is well defined, reversible in temperature (with a slight hysteresis), and precisely reproduced in a second sample, results which betoken the discovery of a bulk phase transition. The detailed character of this transition towards metallic behavior is obscured by the variations in volume across the temperature range.

Once again we correct the data to reveal the constant volume resistivity. The correction uses the same techniques as for KC_{60} with our measured bulk modulus of 580 kbar (Ref. 14) for RbC_{60}. In the absence of a direct measurement, the thermal expansion coefficient is taken to be the same as for KC_{60}.[18] The correction to constant volume clarifies the character of the resistive transition. At large volumes the transition spans two semiconducting phases. Under compression the low-temperature phase gains metallic character until the material becomes metallic over the entire temperature range.

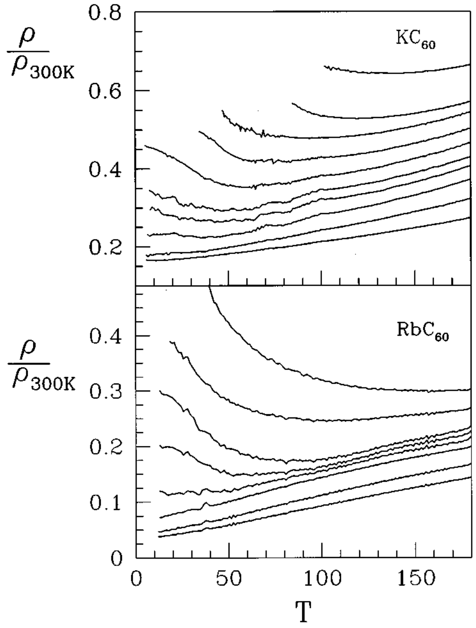

FIG. 3. Comparison of the low-temperature constant-volume resistivities of KC_{60} and RbC_{60}. Volumes in KC_{60} are 1.005, 1.003, 1.002, 1.001, 1.00, 0.998, 0.997, 0.996, 0.99, and 0.98 of the $(P,T)=(0,0)$ volume, respectively. Volumes in RbC_{60} are 0.999, 0.9985, 0.998, 0.9978, 0.9975, 0.997, 0.996, and 0.995 of the $(P,T)=(0,0)$ volume. The $(P,T)=(0,300)$ volume of RbC_{60} is roughly 1.01 times that of KC_{60} (Ref. 2).

Above the resistive transition RbC_{60} at constant volume is semiconducting for the larger volumes. Although the resistivity range is insufficient to unambiguously identify activated conduction, fits to such a form yield activation energies which collapse from roughly 200 K to zero as the $T=0$ volume decreases from 1.0 to roughly 0.996 times the volume at $(P,T)=(0,0)$. As volume increases, the high-temperature insulating behavior is stabilized. Since the transition occurs near 200 K for a constant volume equal to the $(P,T)=(0,0)$ volume and the transition temperature decreases with increasing volume, the zero pressure data should apparently span the transition at some temperature below 200 K.

The behavior of RbC_{60} below the transition is similar to that seen in KC_{60}. Figure 3 compares the low-temperature resistivities of both materials. At these volumes both materials show metallic behavior below 180 K with a low-temperature resistive upturn which is suppressed under compression. Although the two sets of curves differ in detail (for example, RbC_{60} exhibits a greater sensitivity to compression), one must keep in mind that the correction to constant volume is prone to detailed uncertainties due to differences in the anisotropies of the thermal expansion and the compressibility both within and between the two materials. The qualitative similarity of the low-temperature transport in these compounds suggests similar transport regimes in

(K,Rb)C_{60} once the Rb-doped material passes through the phase transition near 200 K.[21]

Geometric uncertainties complicate measurements of the absolute value of the resistivity. To our knowledge the smallest literature values for the room-temperature resistivities of KC_{60} (3 mΩ cm) (Ref. 19) and RbC_{60} (9 mΩ cm) (Ref. 9) imply a room-temperature resistivity of roughly 1 mΩ-cm for either material at its $(P,T)=(0,0)$ volume. This value is consistent with borderline metallic conduction, a regime associated with a strongly pressure-sensitive resistivity.

We now consider the origins of the two main resistive features: the sharp transition near 200 K in RbC_{60} and the smooth low-temperature resistive upturn in both materials. Although these complex materials have yet resisted a complete physical understanding, the dimensionality of the electronic structure, influence of domain walls, and the character of the interfullerene bonding all appear to be relevant to the interpretation of the transport. We first consider the low-temperature resistive upturn observed in both materials. No magnetic transition has been observed in KC_{60}. A pressure of 4 kbar in RbC_{60} eliminates the resistive upturn[20] but only slightly suppresses the magnetic transition. For these reasons, the low-temperature resistive upturn appears not to be associated with a magnetic transition. However, a puzzle remains in that a clear resistive feature of the magnetic transition cannot be seen in the dc resistivity under pressure.

The similarity of KC_{60} and RbC_{60} only below the 200 K transition suggests that perhaps this transition removes a salient periodic structural difference between the materials, the difference in either the covalent bonding between neighboring fullerenes or the ratios of the unit cell dimensions. In KC_{60} the two pairs of bonded atoms form a square whereas in RbC_{60} the interfullerene bonds between pairs are shorter than the intrapair bonds on either fullerene. Such a structural difference might affect transport through either a change in electronic bandwidth[22] or a strain-induced modulation of interdomain conduction. Alternatively, the transition may induce near-universal behavior by harmonizing the ratios of the three orthorhombic lattice constants in KC_{60} and RbC_{60}.

To better understand insulating behavior in (K,Rb)C_{60} we consider the initial process of polymerization. Before polymerization, the material is an essentially fcc lattice of C_{60} balls with interstitial alkali-metal atoms. Polymerization contracts the lattice along the a axis. This strain should eventually increase the distance to the next unpolymerized ball sufficiently to arrest the polymerization within that domain, yielding domains separated by well-defined boundaries.[7] An understanding of interdomain conduction then depends on the intradomain electronic dimensionality since the least resistive interdomain contacts would be less accessible in lower dimensional systems. The small axial bandwidth due to incompatible on-ball and interball bonding geometries implies a surprisingly three dimensional band structure at the KC_{60} lattice constant. A slight dilation in the lattice then suppresses interchain hopping and creates a nearly one-dimensional metal.[22] From this point of view the primary features of the pressure-dependent resistivity could arise from an interplay of interdomain conduction and intradomain structural and electronic properties, with the suppression of the low-temperature resistivity under pressure arising primarily from pressure-dependent interdomain conduction.[23]

Alkali-doped fullerenes are distinguished by a large thermal expansion and a narrow-band electronic structure which is sensitive to both lattice constant and the degree and character of interfullerene bonding. The transitions from metal to insulator in AC_{60} illustrate the necessity of accounting for thermal expansion in interpreting the transport properties of molecular metals. Under constant volume, similar resistive behavior in KC_{60} and Rb_{60} is uncovered, motivating further search for regularities in this unique family of doped crystalline polymers.

ACKNOWLEDGMENTS

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[14] J. Nguyen, J. Hone, R. Jeanloz, and A. Zettl (unpublished). The bulk moduli are nearly constant across the pressure range and corrections to constant volume using bulk moduli differing by 10–30 % do not change the essential results of this work.

[15] The crossover temperature is based on the linearity of the measured thermal expansion down to roughly 30 K and the expectation that low-frequency interchain phonons begin to freeze out at lower temperatures. Decreasing the crossover temperature accentuates slightly the low-temperature resistive upturn.

[16] Along the axis of polymerization both the thermal expansion and compressibility are essentially zero for our purposes. Perpendicular to this axis in KC_{60}, the ratio of the fractional thermal expansions in the b and c directions is 1.4 ± 0.3, whereas the ratio of the compressibilities is 0.9 ± 0.1, indicating that external pressure is an imperfect counterbalance to thermal expansion.

[17] Nonlinear least squares fits to forms $R=A+BP+Ce^{-DP}$ and $R=A+BP+Ce^{1/(D+P)}$ and interpolations using polynomials, rational functions, and cubic splines for full data sets and relevant subsets were compared to characterize the sensitivity to the interpolation technique used. The final correction to constant volume is semiquantitative.

[18] Variations of 30% in the thermal expansion alter the detailed form of the constant-volume curves but do not substantively alter the qualitative behavior.

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[21] Since the unit cell of RbC_{60} at room temperature is roughly 1.01 times larger than that of KC_{60}, the low-temperature upturn in RbC_{60} might occur at a slightly larger volume with a greater sensitivity to compression.

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[23] Although the zero-pressure resistivity in RbC_{60} can be fit to $\rho(T)=e^{T_0/(T_1+T)}$, which is appropriate for a granular metal, this fit must be treated with caution since there is a resistive transition near 40 K. Unfortunately, the correction to constant volume at high volume and low temperature is not sufficently reliable to allow detailed analysis.