

## Linear Temperature Dependent Resistivity at Constant Volume in $\text{Rb}_3\text{C}_{60}$

W. A. Vareka and A. Zettl

*Department of Physics, University of California at Berkeley, Berkeley, California 94720  
and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720  
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The normal-state electrical resistivity  $\rho$  of the superconductor  $\text{Rb}_3\text{C}_{60}$  has been measured as a function of temperature and hydrostatic pressure. Under conditions of constant sample volume we find a *linear* temperature dependence,  $\rho \sim T$ , in sharp contrast to  $\rho \sim T^2$  observed under conditions of constant sample pressure. The pressure dependence of  $\rho$  at fixed temperature is exponential, with a reduction in  $\rho$  by more than 50% for 8 kbar at room temperature. Implications for the normal-state scattering mechanism are discussed.

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The discovery of superconductivity in the alkali-doped fullerenes [1,2] has resulted in materials with the highest  $T_c$ 's known for any three dimensional superconductors. Consequently, there has been an extensive theoretical and experimental effort to understand both the superconducting and normal-state properties of these compounds. As of yet, however, many fundamental questions about the nature of these materials remain unanswered. In particular, the role of electron-phonon scattering versus electron-electron correlation effects in determining the normal-state electrical transport behavior has not yet been resolved.

Previous studies [3-7] have shown that the temperature dependence of the resistivity for the doped fullerenes varies as

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

from  $T \approx 100$  K to well above room temperature. For a typical metal, the electron-phonon (el-ph) scattering mechanism is expected to dominate for temperatures  $T \gtrsim \theta_D$  (the Debye temperature) resulting in a linear temperature dependence of the resistivity. The presence of a  $T^2$ -like dependence could be evidence for some other scattering mechanism, e.g., electron-electron scattering. However, the combination of high and low frequency phonons may also mimic this behavior [8,9]. An important observation is that all measurements so far reported for the resistivity of doped fullerenes have been performed at constant sample pressure,  $\rho_p(T)$ , whereas most theoretical treatments assume constant sample volume,  $\rho_v(T)$ . Differences between  $\rho_p(T)$  and  $\rho_v(T)$  have been shown to be important in other compounds including the high  $T_c$  oxide superconductors [10,11] and organic conductors. Given that the compressibility  $\kappa$  of the representative material  $\text{Rb}_3\text{C}_{60}$  is comparable to the  $c$ -axis compressibility of graphite [12], one is naturally led to the question of how important the volume dependence of the resistivity in this material is.

In this Letter we show that external hydrostatic pressure has a significant influence on the normal-state resistivity of  $\text{Rb}_3\text{C}_{60}$ . At fixed temperature, the resistivity decreases

exponentially with increasing pressure. Remarkably, this sensitive lattice constant dependence leads to a constant-volume resistivity that varies *linearly* with temperature.

The single-crystal  $\text{Rb}_3\text{C}_{60}$  samples used in this study were prepared following the method outlined in Ref. [3]. Previous studies have demonstrated [5] that the overall normalized constant-pressure resistivity  $\rho_p(T)$  of  $\text{Rb}_3\text{C}_{60}$  crystals near optimal doping is very reproducible from sample to sample and represents intrinsic behavior. The samples used in this study displayed the characteristic  $\rho_p(T) \sim T^2$  temperature dependence. After ambient pressure measurements, the samples were transferred to a self-clamping pressure cell with Fluorinert FC-75 as the hydrostatic pressure medium. Contact resistances were unaffected by the transfer procedure. Two different measurement modes were used to determine  $\rho(T, P)$ . In the first, the pressure cell was maintained at constant temperature and the pressure was varied continuously. In the second, the pressure cell was clamped at a "fixed" pressure, and the temperature was varied continuously. However, as described in detail below, in the second mode the pressure inside the cell was not strictly constant, but was temperature dependent. The sample resistance was measured using a dc four-point configuration and the pressure was continuously and accurately monitored using a calibrated manganin pressure sensing coil.

Figure 1 shows the pressure dependence of the resistivity (normalized to the room-temperature  $P \approx 0$  value) of  $\text{Rb}_3\text{C}_{60}$ . The inset shows room-temperature data over a wide pressure range. Clearly the effect of pressure on the resistivity is quite large with a greater than 50% reduction in  $\rho$  at  $P = 8$  kbar. The main body of Fig. 1 shows  $\rho(P)$  for the same sample measured at three different fixed temperatures. All three sets of data are fit by the same functional form,

$$\rho(P) = \rho_0 + \rho_1 \exp(-P/P_0), \quad (2)$$

indicated by solid lines. The value of  $P_0$  is intrinsic to the material and is not dependent on doping quality. Samples with significantly different  $\rho$ 's (7 vs 30 m $\Omega$  cm at  $T \approx 290$  K) yielded roughly the same  $P_0$ . Given that

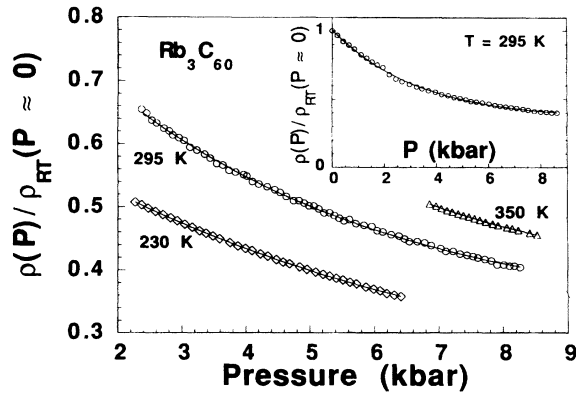


FIG. 1. Pressure dependence of the resistivity for fixed temperatures. The resistivity is normalized to the room-temperature,  $P \approx 0$ , value. For each temperature the data are fit by the form  $\rho(P) = \rho_0 + \rho_1 \exp(-P/P_0)$ . For  $T = 230$  K,  $\rho_0 = 0.18$ ,  $\rho_1 = 0.46$ ,  $P_0 = 6.7$ ; for  $T = 295$  K,  $\rho_0 = 0.31$ ,  $\rho_1 = 0.56$ ,  $P_0 = 4.4$ ; for  $T = 350$  K,  $\rho_0 = 0.36$ ,  $\rho_1 = 0.80$ ,  $P_0 = 4.0$ . Inset shows initial  $\rho(P, T = 295$  K) pressurization data with a curve fit by the same exponential function.

at room temperature a pressure of  $\sim 5.2$  kbar yields a reduction in the lattice constant of  $\text{Rb}_3\text{C}_{60}$  comparable to what occurs due to thermal contraction when the sample is cooled from room temperature to  $T_c$ , it is clear that the problem of constant volume vs constant pressure must be addressed if the theoretically relevant  $\rho(t)$  curve is to be experimentally determined.

In a typical temperature dependent run, the cell was initially pressurized and clamped at room temperature and then the sample resistivity was measured as a function of temperature. Because of differential thermal contractions between the pressure fluid and the pressure cell walls, the sample pressure dropped with decreasing temperature. The pressure dependence of the superconducting transition was determined to be  $dT_c/dP = -0.94 \pm 0.1$  K/kbar consistent with previous measurements [13]. The “residual” resistivity, which is quite large in this material, was found to be strongly pressure dependent. By comparing the  $\rho(T, P)$  data for different initial pressures, the pressure dependence of  $\rho$  at low temperatures was found to be consistent with Eq. (2) with  $P_0 \approx 3$ –6 kbar. Typical sources for residual resistivity, e.g., impurities ( $\text{C}_{60}$ ), defects, etc., are not expected to show such a strong and reversible pressure dependence. In addition the ratio  $\rho_p(T = 290$  K)/ $\rho_p(T \approx 0$  K) is roughly equal to 2 for nearly all  $\text{Rb}_3\text{C}_{60}$  samples, even though the magnitude of  $\rho_p$  can differ by a factor of 5 between samples. Therefore the ratio of the room-temperature resistivity to the “residual” resistivity is insensitive to the doping uniformity and yet shows a strong lattice constant dependence. Two possible explanations for the high residual resistivity are that it is related to the rotational disorder known to exist in this material or to a localization effect, both of which would be expected to show a pressure dependence.

To determine the constant-volume resistivity of the sample we exploited the natural pressure drop in the cell with decreasing temperature (which largely compensated for the thermal contraction of the sample). Additional corrections were made to the data as described below. The corrections require knowledge of the thermal expansion coefficient and the bulk modulus of  $\text{Rb}_3\text{C}_{60}$ . The thermal expansion coefficient has been measured [14] and it is  $d \ln(a)/dT = 3.05 \times 10^{-5} \text{ K}^{-1}$  and linear over the relevant temperature range. The room-temperature bulk modulus is  $B = 219$  kbar [12]. Unfortunately the temperature dependence of  $B$  has not been measured. For most materials the bulk modulus is relatively insensitive to temperature. However, data on the closely related Young’s modulus for pristine  $\text{C}_{60}$  do show [15, 16] a roughly linear temperature dependence with a negative slope of (7.5–11)% per 100 K. Therefore, we have used two different approximations for  $B$ . First we assume the bulk modulus is a constant,  $B_0$ , independent of temperature, and second we assume it has a linear temperature dependence  $B(T)$  with a slope of 11% per 100 K. In our cell, the combination of decreasing temperature and pressure gives rise to a net change in the lattice constant (for  $T = 295$  to 100 K) of  $-0.08\%$  for  $B(T)$  and  $-0.18\%$  for  $B_0$  compared to  $-0.6\%$  with no pressure compensation. We further correct for this small volume change error as follows: At all temperatures the pressure required to maintain a constant sample volume is known, along with the approximate form of  $\rho(P)$ . At each temperature point, we determine the additional pressure deviation (from the true experimental pressure cell pressure) necessary to reach the reference sample volume. This pressure deviation is converted to a resistance deviation which is used to correct the measured resistance.

Figure 2 shows the corrected and normalized constant-volume resistivity for  $\text{Rb}_3\text{C}_{60}$  assuming either a constant or a temperature dependent bulk modulus. For both cases the resistivity is clearly *linear* in temperature between  $\sim 100$  and 350 K. Hence, for constant sample volume, we find

$$\rho_v(T) = \alpha + \beta T, \quad (3)$$

in sharp contrast to Eq. (1),  $\rho_p(T) \approx a + bT^2$ , relevant to constant sample pressure. Depending on the initial sample pressure and the assumption used for the temperature dependence of the bulk modulus, the onset of the linearity can occur anywhere from  $\sim 100$  up to  $\sim 200$  K. Above 200 K, the corrections to the resistivity data are quite small and the assumption of the temperature dependence of the bulk modulus merely influences the slope of the resistivity; however, the data remain highly linear up to the highest temperature measured (350 K).

In the high temperature regime the slope of the  $\rho_v(T)$  curve,  $d\rho/dT$ , is related to the transport el-ph coupling constant,  $\lambda_{tr}$ . The Drude result for the resistivity is given by  $\rho(T) = m/(ne^2)\tau^{-1} = 4\pi\omega_p^{-2}\tau^{-1}$  where  $m$  is

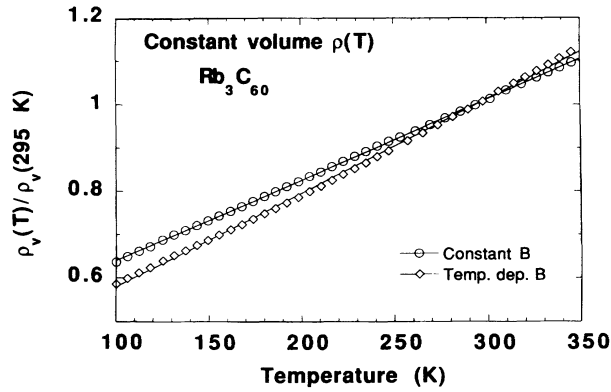


FIG. 2. Temperature dependence of the resistivity at constant volume for  $\text{Rb}_3\text{C}_{60}$ . The data are normalized to the room-temperature value. The bulk modulus is assumed to be either constant (open circles) or linearly temperature dependent (open diamonds). In both cases, a linear fit to the data is shown.

the electron mass,  $n$  is the number density,  $\omega_p$  is the plasma frequency, and  $\tau^{-1}$  is the el-ph scattering rate. For  $T \geq \theta_D$  the scattering rate can be expanded to yield  $\tau^{-1} = 2\pi\hbar^{-1}\lambda_{\text{tr}}k_B T$ . Hence,

$$\lambda_{\text{tr}} = \frac{\hbar\omega_p^2}{8\pi^2k_B} \frac{d\rho}{dT} = 0.246(\hbar\omega_p)^2 \frac{d\rho}{dT} \quad (4)$$

with units  $[d\rho/dT] = \mu\Omega \text{ cm/K}$ , and  $[\hbar\omega_p] = \text{eV}$ . To solve for  $\lambda_{\text{tr}}$ , it is necessary to determine the true value of the slope  $d\rho/dT$ . Stepniak *et al.* have shown [17] that the conductivity in  $\text{Rb}_3\text{C}_{60}$  is that of a granular metal conductor. The variation of the resistivity with doping concentration in  $\text{Rb}_x\text{C}_{60}$  is consistent with the picture that the  $\text{Rb}_3\text{C}_{60}$  phase is a line phase and that the typically doped material is a granular metal conductor with  $\text{Rb}_3\text{C}_{60}$  being the metallic phase and the pristine  $\text{C}_{60}$  being the insulating phase. It has also been shown that for granular metals [18,19] with a high volume fraction of metal the temperature dependence of the resistivity is essentially the same as that of the bulk metal. However, it differs in two important respects. First, the size of the resistivity can be larger than the pure bulk value by several orders of magnitude due to the electron scattering effects at the grain boundaries. This is commonly observed in  $\text{Rb}_3\text{C}_{60}$  where samples with similar sharp ( $< 1$  K) superconducting transition widths can have room-temperature resistivities that differ by a factor of 3. Second, the relative slope defined as  $\alpha_R = (1/\rho)^* d\rho/dT$  can be smaller than that in the pure bulk system. As the volume ratio of the metal approaches unity the value of  $\alpha_R$  should approach that of the pure metal. The relative slope for the best sample measured in this pressure study was  $\alpha_R \approx (1.9 - 2.2) \times 10^{-3} \text{ K}^{-1}$  depending on the assumption used for the temperature dependence of the bulk modulus. A sample which had a room-temperature resistivity 3 times larger than the best

sample had a relative slope only a few percent smaller, indicating that  $\alpha_R$  is saturating to the pure metal value. To extract  $\lambda_{\text{tr}}$  the slope  $d\rho/dT$  is needed and therefore this value of  $\alpha_R$  must be scaled by the true intrinsic value of the resistivity.

From both film and single-crystal studies, the best directly measured value for the room-temperature, ambient-pressure resistivity in  $\text{Rb}_3\text{C}_{60}$  is  $\sim 2.5 \text{ m}\Omega \text{ cm}$ . This value must then be reduced by an amount which depends on the initial starting pressure (see Fig. 1). For two different initial pressures (6.5 and 8 kbar) we find that the derived slopes agree to within  $\sim 3\%$ . Hence,  $d\rho/dT = 1.82 - 2.27 \mu\Omega \text{ cm/K}$ , where the range reflects the two different assumptions for the temperature dependence of the bulk modulus. The experimental value for the plasma frequency in  $\text{Rb}_3\text{C}_{60}$  is [20]  $\omega_p \approx 1.2 \text{ eV}$ . Using these values of  $d\rho/dT$  and  $\omega_p$  in Eq. (4) yields a range of values for the transport coupling constant of  $\lambda_{\text{tr}} \approx 0.65 - 0.80$ . It is important to realize that Eq. (4) determines  $\lambda_{\text{tr}}$  completely from experimentally measured quantities and yet the range of values obtained is characteristic of a typical superconductor.

In conclusion, the constant-volume normal-state resistivity  $\rho_v(T)$  of  $\text{Rb}_3\text{C}_{60}$  is found to vary linearly with temperature over a wide temperature range. This linearity is consistent with the picture that the scattering mechanism is simply of the electron-phonon type with a coupling constant  $\lambda_{\text{tr}} \approx 0.65 - 0.80$ . The resistivity of  $\text{Rb}_3\text{C}_{60}$  is found to vary strongly with pressure with an exponential dependence given by Eq. (2). This exponential dependence on pressure, or equivalently lattice constant, accounts for the significant difference between constant-volume and constant-pressure resistivity versus temperature.

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