Pressure dependence of the electronic density of states and T_c in superconducting Rb₃C₆₀

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The functional dependence of the superconducting transition temperature T_c on the electronic density of states $N(E_f)$ was determined for Rb₃C₆₀ by measuring the magnetic susceptibility under hydrostatic pressure to ~ 1 GPa in a commercial SQUID magnetometer. Both T_c and $N(E_f)$ decrease under pressure at the rates -31%/GPa and -14.5%/GPa, respectively, but lie above the corresponding values for K₃C₆₀ at the same lattice parameter. The present results are consistent with weak-coupling BCS theory with characteristic energy $E_{char}/k_B \approx 320-810$ K. [S0163-1829(96)51738-8]

To account for superconductivity at high temperatures (20-30 K) in the alkali-metal-doped fullerenes, such as $K_{3}C_{60}$ and $Rb_{3}C_{60}$, both electron-phonon¹ and purely electronic pairing interactions² have been proposed. The characteristic energy E_{char} of the intermediary boson in this pairing interaction is an important factor in determining whether weak- or strong-coupling theory is more appropriate. High frequency [400–1400 cm⁻¹ (Ref. 3)] intramolecular vibrational modes or electronic excitations would tend to favor weak-coupling theory, whereas intermolecular modes [15- 150 cm^{-1} (Ref. 3)] would normally require strong-coupling theory. The reported "universal increase" of T_c with lattice parameter in both high-pressure and alkali-substitution experiments has been invoked to support weak-coupling theory;⁴ however, recent high accuracy high-pressure experiments on Rb $_3C_{60}$ reveal a sizeable ($\sim 20\%$) deviation from such universal behavior.⁵ Attempts to estimate the coupling strength from the gap ratio $2\Delta_c/k_BT_c$ vary from the weakcoupling value ~ 3.6 in μ SR studies⁶ to strong-coupling values in SIS tunneling (4.3),⁷ optical reflectivity (3-5) (Ref. 8) and point-contact tunneling (5.3).⁹ On the other hand, weak-coupling theory has received support from analyses of specific heat and magnetic susceptibility data,¹⁰ NMR Knight shift¹¹ and isotope effect studies.¹²

A time-tested strategy to explore the nature of the superconducting state is to compare the relative changes in the superconducting and normal-state properties under the variation of parameters such as the carrier concentration or lattice parameter. Studies under hydrostatic pressure are of particular interest since they permit, from measurements on a single sample, a particularly clear-cut evaluation of competing theoretical models. In the present case, for example, the relative pressure dependences of T_c and $N(E_f)$ would be expected to be markedly different for weak or strong coupling. In addition, it would be of interest to apply sufficient high pressure to Rb₃C₆₀ to reduce its lattice parameter to that of $K_{3}C_{60}$ and compare $N(E_{f})$ and T_{c} . To our knowledge, no data on $N(E_f)$ under pressure exist for Rb₃C₆₀; NMR studies¹³ on K_3C_{60} indicate that $N(E_f)$ decreases under pressure at the rate $\sim -10\%/\text{GPa}$, but are of limited accuracy and do not include the parallel measurement of $T_c(P)$. In this paper we report the first accurate determination of the hydrostatic pressure dependence of both T_c and $N(E_f)$ on a single fullerene sample (Rb_3C_{60}). Our results lend strong support to a weak-coupling BCS description of the superconducting state.

The synthesis of high-purity powders of C_{60} and Rb_6C_{60} precursor is described in Ref. 5. Before insertion into the magnetometer, samples were placed into a quartz tube and sealed vacuum tight in a N₂ glove box. As seen in Fig. 1, the magnetic susceptibility of C_{60} is nearly temperature independent, except for a small 2.5% increase due to the rotational order-disorder transition as the sample heats through 260 K, in agreement with previous studies.¹⁴ The room temperature value of the magnetic susceptibility, $\chi(300 \text{ K}) \simeq -(2.45 \pm 0.05) \times 10^{-4} \text{ emu/mol C}_{60}$, is in excellent agreement with published values.¹⁴ The data for Rb_6C_{60} are seen to fit the expression $\chi \simeq [-7.92 + 222/(T + 222)/(T + 222)/(T$ + 16.5 K)] $\times 10^{-4}$ emu/mol, the Curie constant being consistent with < 1% spin- $\frac{1}{2}$ Rb⁺-ion vacancies (> 99% complete reaction). The large diamagnetic contribution confirms within 3% a prediction¹⁵ for the existence of exceptionally large ring currents in the C_{60}^{6-} ion.



FIG. 1. Measured magnetic susceptibility per mol C_{60} at 5 T versus temperature for powder samples of Rb_3C_{60} (\bullet) (41.2 mg), C_{60} (42 mg), and Rb_6C_{60} (57 mg). Solid line gives fit to Rb_6C_{60} data (see text); horizontal dashed line gives diamagnetism after subtraction of Curie-Weiss contribution. Open circles (o) give susceptibility data for a Rb_3C_{60} sample which was pelletized before reacting C_{60} with Rb_6C_{60} .

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FIG. 2. Cross section of CuBe pressure cell (length 21 cm) suitable for magnetization studies in a SQUID magnetometer.

C₆₀ and Rb₆C₆₀ powders were reacted in equal amounts at 250 °C for 3 days to yield stoichiometric Rb_3C_{60} which was homogenized at 350 °C for two weeks, yielding a Meissner fraction in 20 Oe field of 18%. The phase purity of the sample is estimated to be $\sim 95\%$ from neutron diffraction.⁵ The temperature-dependent susceptibility of $Rb_{3}C_{60}$ shown in Fig. 1 (Ref. 16) is notable by the absence of a Curie tail. Samples underdoped and overdoped by 5% Rb yielded within 3% an identical susceptibility dependence. Exposing a powder sample to a small concentration of air resulted in a susceptibility increase of $\sim 30\%$. For the highpressure measurement a portion of the Rb₃C₆₀ powder sample was pressed into pellets (3 mm diameter, 4 mm thick) with 92% density. To enhance their mechanical stability and oxidation resistance, the pellets were given a 2–4 μ m thick coating of polyvinyl toluene. All pellets were stored in the glove box inside vials containing K as getter. This pelletizing procedure, and one where the pellet is formed before the reaction, had no effect on the measured susceptibility (see Fig. 1).

From $\chi_{\text{total}}(T)$ we estimate the spin susceptibility of Rb₃C₆₀ using the relation $\chi_{\text{spin}}(T) = \chi_{\text{total}}(T) - \chi_{C_{60}}$ $-3\chi_{\text{Rb}^+}$, where the diamagnetic contributions, $\chi_{C_{60}}$ and χ_{Rb^+} , are taken to be temperature independent. Contributions from both Van Vleck paramagnetism (beyond that already contained in $\chi_{C_{60}}$) and Landau diamagnetism are expected to be small and are neglected. Substituting $\chi_{C_{60}} = -2.45 \times 10^{-4}$ emu/mol C₆₀ and $\chi_{\text{Rb}^+} = -0.22 \times 10^{-4}$ emu/mol Rb⁺,¹⁷ we obtain $\chi_{\text{spin}}(300 \text{ K}) \approx +9.4 \times 10^{-4}$ emu/mol Rb₃C₆₀ and $\chi_{\text{spin}}(50 \text{ K}) \approx +10.2 \times 10^{-4}$ emu/mol Rb₃C₆₀. $\chi_{\text{spin}}(T)$ in the present experiment agrees, within experimental error, with the uncorrected static susceptibility and ESR data of Jánossy *et al.*¹⁸ on a single sample, as well as with NMR studies by Kosaka *et al.*,¹⁹ but lie ~ 20% below those of Ramirez *et al.*¹⁰ Considering the phase purity of our sample and the small effect of nonstoichiometry on χ_{spin} , this difference is difficult to understand.

To permit the accurate determination of the pressure dependence of the spin susceptibility of Rb_3C_{60} in a commercial SQUID magnetometer (Quantum Design), a suitable hydrostatic pressure cell was constructed from hardened CuBe alloy (Berylco 25), as seen in Fig. 2. Fluorinert FC75 was used as pressure medium. The Rb_3C_{60} sample consisted of five stacked pellets with total length 1.5 cm, diameter 3 mm, and mass 198 mg. The design of the cell was such that the sample itself made the dominant contribution (60%) to the measured signal, suitable corrections being made for the quartz spacers and the pressure medium. The pressure at



FIG. 3. Measured magnetic susceptibility per mol of Rb_3C_{60} versus hydrostatic pressure at 50 K and 300 K for increasing/decreasing (closed/open symbols) pressure. The scale on the right gives $SN(E_f)$ (see text). Data for C_{60} at 300 K are also shown. Solid lines are guides to eye.

room temperature was determined either by measuring the change in length L of the cell to $\pm 1 \ \mu$ m using an optical microscope ($dL/dP \approx +42.2 \ \mu$ m/GPa), or from the value of T_c for a tiny Pb manometer located directly on top of the sample. A test measurement on pure C₆₀ reveals that its diamagnetism is essentially pressure independent, as seen in Fig. 3; this is not surprising, since the C₆₀ molecule is known to be highly incompressible.²⁰

The primary result of this paper is shown in Fig. 3, where we see that at both 50 K and 300 K the measured susceptibility, $\chi_{\text{total}}(T,P)$, of Rb₃C₆₀ decreases rapidly with increasing pressure. Since the change in $\chi_{C_{60}}$ and χ_{Rb^+} with pressure is negligible to 1 GPa, it follows that $\chi_{spin}(T,P)$ decreases rapidly under pressure. The electronic density of states can now be derived from $\chi_{\rm spin} = N_A \mu_B^2 SN(E_f)$, where N_A is Avogadro's number, μ_B the Bohr magneton, $S \equiv [1 - IN(E_f)]^{-1}$ the Stoner enhancement factor, and I the Coulomb interaction which we take to be pressure independent. From the above ambient-pressure value of χ_{total} at 50 K, we obtain $SN(E_f) = 31.5$ states/(eV C₆₀), as seen in Fig. 3. Band-structure calculations²¹ on Rb_3C_{60} yield values in the range $N(E_f) \approx 20-30$ states/(eV C₆₀), implying that the enhancement factor is in the range $S \approx 1-1.5$; unless otherwise specified, we use the value S = 1.3. Ramirez et al.¹⁰ estimated $S \approx 2$ from their higher value of χ_{spin} . From the data in Fig. 3, we find the average pressure and volume derivatives $d\ln N(E_f)/dP = S^{-1}d\ln[SN(E_f)]/dP$ $d\ln N(E_f)/d\ln V = B d\ln N(E_f)/dP$ $\simeq -14.5\%/\text{GPa}$ and $\approx +2.9$, where B = 20.2 GPa is the average bulk modulus at 50 K over the pressure range 0–0.66 GPa.⁵ This implies that the density of states scales as $N(E_f) \sim d^{2.7}$, where d is the



FIG. 4. Measured dependence of the superconducting transition temperature on hydrostatic pressure for Rb₃C₆₀ given by solid line through data points (\bullet) from Ref. 5. Calculated T_c values from the McMillan equation using $SN(E_f)$ from Fig. 3 are represented by open squares (\Box) for S = 1 and crosses (\times) for S = 2 (see text).

separation between closest carbon atoms on nearest-neighbor C_{60} molecules, in good agreement with theory.¹

At a pressure (0.72 GPa) sufficient to reduce the lattice parameter of Rb₃C₆₀ to that for K₃C₆₀ at ambient pressure,⁵ $\chi_{spin}(300 \text{ K})$ for Rb₃C₆₀ is reduced from +9.4×10⁻⁴ to +8.0×10⁻⁴ emu/mol C₆₀. Although measured values of χ_{spin} for K₃C₆₀ differ widely,^{10,11,19} there is agreement that the value of χ_{spin} for K₃C₆₀ is less than that for Rb₃C₆₀ at ambient pressure by the factor 1.32 ± 0.04, which gives $\chi_{spin}(300 \text{ K}, 1 \text{ bar}) \approx +(7.1 \pm 0.2)\times10^{-4} \text{ emu/mol C}_{60}$ for K₃C₆₀. We thus find that, in high-pressure and cation substitution experiments, $N(E_f)$ is not a universal function of lattice parameter, in analogy with the result reported by us earlier for T_c .⁵ The dependence of T_c on pressure for Rb₃C₆₀ from the present experiment is reproduced in Fig. 4 (Ref. 5) and is in good agreement with earlier studies.²²

Having determined in a single experiment the dependences of both T_c and $\chi_{spin} \propto SN(E_f)$ on pressure, we are now in a position to test expressions from theory which predict the functional dependence of T_c on $N(E_f)$. A particularly simple expression, valid for arbitrary values of the coupling parameter $\lambda \equiv \mathcal{V}N(E_f)$, where \mathcal{V} gives the pairing interaction, is given by²³

$$k_B T_c = \frac{0.26E_{\text{char}}}{\sqrt{e^{2/\lambda} - 1}}.$$
 (1)

Taking logarithmic derivatives with respect to pressure, we obtain

$$\frac{d\ln T_c}{dP} = \frac{d\ln E_{char}}{dP} + f \left[\frac{d\ln N(E_f)}{dP} + \frac{d\ln \mathcal{V}}{dP} \right], \quad (2)$$

where $f = f(\lambda) \equiv [\lambda(1 - e^{-2/\lambda})]^{-1}$. In the inset to Fig. 4, it is seen that for λ in the range 0 to 1, *f* decreases rapidly with λ . Since *f* is such a sensitive function of λ , the measurement of the various pressure derivatives in Eq. (2) should allow the accurate determination of *f*, λ and, from Eq. (1), E_{char} .

We first attempt an analysis of the present results using the weak-coupling model of Schlüter *et al.*,¹ where $N(E_f)$ is a sensitive function of the *intermolecular* separation and \mathcal{V} is an intramolecular interaction arising from "on-ball" vibrational modes on the C₆₀ molecule with high characteristic energy $E_{char} \approx 350-2400$ K (250-1700 cm⁻¹). Due to the extreme rigidity of the C_{60} molecule,²⁰ the pressure-induced changes in E_{char} and \mathcal{V} are negligible, i.e., $d\ln E_{char}/dP \simeq 0$ and $d\ln V/dP \simeq 0$. Inserting into Eq. (2) the average values of the pressure derivatives of T_c and $N(E_f)$ for a pressure change of 0.66 GPa, $d\ln T_c/dP \simeq -31\%$ /GPa (Ref. 5) and $d\ln N(E_f)/dP \simeq -14.5\%$ /GPa (assuming S = 1.3), we obtain $f \approx 2.13$, implying $\lambda \approx 0.48$. Inserting this value of λ and $T_c \simeq 29$ K into Eq. (1), we obtain $E_{char}/k_B \simeq 900$ K; a similar calculation for S = 1 and 2 yields $E_{char}/k_B \approx 520$ K and 2800 K, respectively. These values of E_{char} lie squarely in the energy range for intramolecular vibrations. The present experiments on $Rb_{3}C_{60}$ are thus clearly consistent with the above weak-coupling theory based on the electron-phonon interaction. However, theoretical approaches based on purely electronic pairing interactions on the C₆₀ molecule,² as long as E_{char}/k_B is less than 2800 K (0.25 eV), are also consistent with our data. It was recently pointed out that a nonadiabatic small polaron theory may be more appropriate if highfrequency phonons are involved.²⁴

We now attempt an analysis of the present experiments using Eqs. (1) and (2), but invoking intermolecular vibrational modes with $E_{\rm char}/k_B \approx 15-150$ K.³ Taking the average value $E_{\rm char}/k_B \approx 80$ K, we obtain from Eq. (1) the strong-coupling value $\lambda \simeq 4.8$; this yields $f \simeq 0.61$. Using the expression $\lambda = \eta / [M \langle \omega^2 \rangle]$ defined by Hopfield,²⁵ and setting $E_{char} \approx \langle \omega \rangle$, where $\langle \omega \rangle$ is a mean phonon frequency, we can rewrite Eq. (2) in the form $d \ln \eta/d \ln V \simeq -f^{-1}B(d \ln T_c/dP) - \gamma(2-f^{-1})$. Here $\gamma \equiv$ $-d\ln\langle\omega\rangle/d\ln V$ is the Grüneisen constant where typically $\gamma \approx +2$. We thus estimate solely from our experimental value $d \ln T_c / dP \simeq -31\%$ /GPa that $d \ln \eta / d \ln V \simeq +10.3 - 0.7 =$ +9.6. This value of $d\ln \eta/d\ln V$ differs grossly in both magnitude and sign from that typically found for conventional simple-metal (-1) or transition-metal (-3.5) superconducting elements, alloys, or compounds.^{25,26} A satisfactory description of superconductivity in the fullerenes in terms of the above strong-coupling approach thus appears highly unlikely.

A more quantitative analysis of our data can be obtained using the McMillan equation²⁷ $k_B T_c = E_{char} \exp[-1.04(1 + \lambda)]/[\lambda - \mu^* - 0.62\lambda \mu^*]$, which is valid for values of the electron-phonon coupling $\lambda \leq 1.5$. Here the effective Coulomb interaction is estimated to be $\mu^* \approx 0.2$.¹ Inserting the $N(E_f)$ high-pressure data from Fig. 3 into the McMillan equation, where $\lambda \equiv \mathcal{V}N(E_f)$, we vary the value of E_{char} to obtain the best fit to the $T_c(P)$ data in Fig. 4; \mathcal{V} is held constant at that value required to satisfy Eq. (1) at ambient pressure. It is seen that in the range S = 1 to 2 the quality of the fit is independent of the value of *S*. For S = 1, 1.3, and 2 we find $\lambda \approx 1.46$, 1.22, and 0.92 and $E_{char}/k_B \approx 320$ K, 430 K, and 810 K, respectively. To describe superconductivity in the doped fullerenes, the present experiments are thus clearly consistent with weak-coupling BCS theory involving high-frequency intramolecular phonons.

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