Electronic Properties of Normal and Superconducting Alkali Fullerides Probed by ^{13}C Nuclear Magnetic Resonance

R. Tycko, G. Dabbagh, M. J. Rosseinsky, D. W. Murphy, A. P. Ramirez, and R. M. Fleming
AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974
(Received 6 November 1991)

We report the results of ^{13}C NMR measurements on K_3C_{60} and Rb_3C_{60} in the normal and superconducting states. Electronic densities of states at the Fermi energy in the normal state and energy gaps in the superconducting state are estimated from spin-lattice relaxation data. Implications of the relaxation and spectral data for the electronic properties of these materials are discussed.

PACS numbers: 74.30.Gn, 74.70.Ya, 76.60.−k

Current interest in the conducting [1] and superconducting [2-5] alkali fullerides A_3C_{60} (A=K, Rb, Cs) stems from the fact that their superconducting transition temperatures (T_c), at least as high as 32 K in the case of Rb_2CsC_{60} [6,7], are currently the highest known aside from those of the "high-T_c" ceramics, and from the fact that the alkali fullerides are three-dimensional, ionic, molecular solids and therefore appear qualitatively different in structure from other known superconductors. We and others have shown that ^{13}C nuclear magnetic resonance (NMR) measurements provide a wealth of information about the structure [8], molecular dynamics [9-12], phase diagrams [11,12], and electronic properties [12] of both pure C_{60} and the alkali fullerides. In this Letter, we present the results of ^{13}C NMR measurements on *both normal and superconducting* K_3C_{60} *and* Rb_3C_{60}. We obtain estimates of the electronic energy gap 2Δ in the superconducting state and of the density of electronic states at the Fermi energy $N(E_F)$ in the normal state. We discuss possible implications of the NMR data for the electronic properties in the normal and superconducting states.

Samples of Rb_3C_{60} and K_3C_{60} powder, roughly 60 mg each, were prepared as described previously [3,7,13,14] and shown to be single phase by x-ray diffraction and ^{13}C NMR. All natural-abundance ^{13}C nuclei in the samples contributed to the observed NMR signals, to within the accuracy of our calibration of the signal amplitudes (±10%). No significant attenuation of the signals was observed upon cooling below T_c. The magnetic shielding fractions were 40% and 13% and the zero-field T_c values were 29.4 and 19.4 K for the Rb_3C_{60} and K_3C_{60} samples, respectively, as determined from magnetization measurements. Samples were sealed in 5-mm Pyrex tubes with 0.5 atm He(g). NMR measurements were carried out in 9.39- and 2.37-T fields (100.5- and 25.4-MHz ^{13}C NMR frequencies) using a Chemagnetics CMX spectrometer. Low-temperature measurements were made using an NMR probe based on a modified Janis SuperTran-B cryostat [15]. For good thermal contact, the rf coil and sample were contained inside a sealed copper box that was filled with 1 atm He(g) and mounted on the cold finger. Low rf power levels (5 W peak, <0.1 mW average) were used at low temperatures. We estimate our temperature measurements to be accurate to within ±0.2 K.

^{13}C nuclear spin relaxation times T_1 were measured with the saturation-recovery technique, using a Carr-Purcell echo train to improve the sensitivity [16]. Because the recovery curves were slightly nonexponential, they were fitted to the "stretched exponential" form $S(\tau)=S_a-S_b\exp[-(\tau/T_1)^\beta]$, where τ is the recovery time and S is the peak height in the NMR spectrum, with $\beta=0.82$ for Rb_3C_{60} and $\beta=0.80$ for K_3C_{60}. The stretched exponential recovery curves reflect a distribution of spin-lattice relaxation rates [17], with a relative width that appears independent of the temperature. This distribution may arise from a dependence of the rate on the crystallite orientation, which would be possible if dipolar or orbital couplings contributed significantly to the relaxation rate [18], or from the fact that inequivalent carbon nuclei on a C_{60} molecule in the cubic A_3C_{60} structure may have different hyperfine couplings.

The relaxation data in Fig. 1, taken at 9.39 T, display three significant features. First, the product T_1T is nearly constant in the normal states of both K_3C_{60} and Rb_3C_{60}, as expected for a metal [18], with only a gradual increase with decreasing temperature from above 200 K to T_c. This increase may be a consequence of thermal contraction [19], which is expected to reduce $N(E_F)$. At the T_c determined from magnetization measurements, T_1T is 165 K s in K_3C_{60} and 100 K s in Rb_3C_{60}. Using the expression

$$\frac{1}{T_1T}=\frac{\pi k}{\hbar}A^2N(E_F)^2,$$

which applies to relaxation due to a contact hyperfine coupling between nuclear spins and noninteracting conduction electrons, and our previous estimate [12] of the hyperfine coupling constant $A=1.1\times10^{-20}$ erg (0.6 G for electron spins), we obtain $N^{K}(E_F)=17$ eV^{-1} and $N^{Rb}(E_F)=22$ eV^{-1} per C_{60} molecule (per spin state) just above T_c. These values are approximations, since our estimate of A may easily be in error by a factor of 2 and since there may be a distribution of hyperfine couplings. Similar values of $N(E_F)$ have been derived from static magnetic susceptibility [20] and critical field

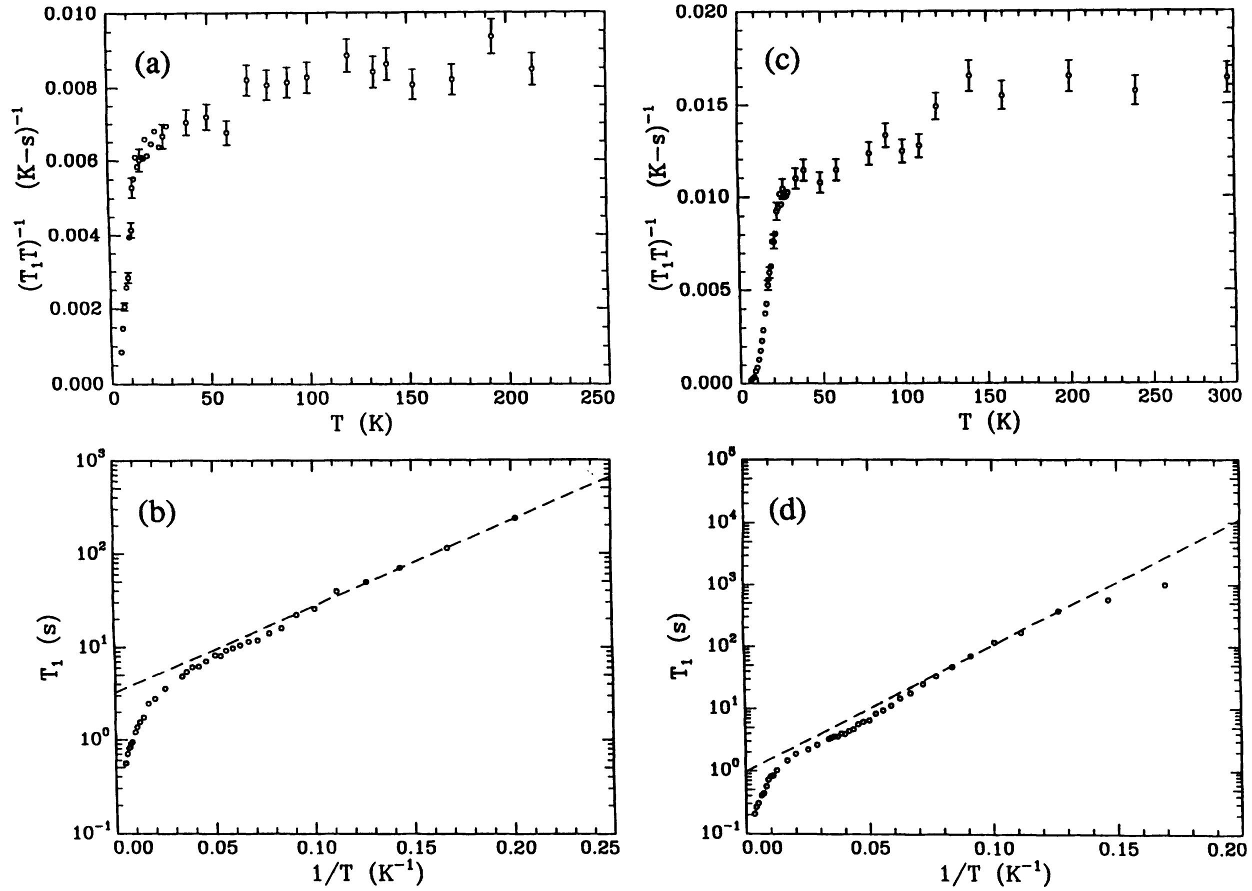

FIG. 1. Temperature dependence of the ^{13}C spin-lattice relaxation time T_1 in (a),(b) K_3C_{60} and (c),(d) Rb_3C_{60}, plotted as $(T_1T)^{-1}$ vs T [(a),(c)] and as $\log T_1$ vs T^{-1} [(b),(d)]. Error bars indicate 1 standard deviation. Dashed lines are fits of the data below 9 K [(b)] and from 8 to 12 K [(d)] by Arrhenius laws, leading to energy gaps $2\Delta^{K} \approx 42$ K and $2\Delta^{Rb} \approx 94$ K.

[20,21] measurements, while considerably smaller values have been obtained from electron spin resonance [22] and photoemission [23] measurements.

Second, $(T_1T)^{-1}$ decreases dramatically below an apparent superconducting transition temperature $T_c^{\rm NMR}$, which is 14 ± 1 K for K_3C_{60} and 23 ± 1 K for Rb_3C_{60}. Well below $T_c^{\rm NMR}$, the data can be fitted by the Arrhenius law $T_1^{-1} = We^{-\Delta/T}$, with $\Delta = 21.3$ K and $W = 0.31$ s^{-1} for K_3C_{60} and $\Delta = 46.8$ K and $W = 1.04$ s^{-1} for Rb_3C_{60}. Such a temperature dependence is expected if there is an energy gap 2Δ for electronic excitations in the superconducting state [24,25]. The values $2\Delta/T_c^{\rm NMR} = 3.0$ for K_3C_{60} and $2\Delta/T_c^{\rm NMR} = 4.1$ for Rb_3C_{60} are to be compared with the weak-coupling BCS result $2\Delta/T_c = 3.5$. Our result for Rb_3C_{60} differs from a recent determination by scanning tunneling microscopy [26] ($\Delta = 77$ K), possibly because NMR relaxation probes the minimum quasiparticle excitation energy, while tunneling probes the maximum in the quasiparticle density of states, or because of differences between surface and bulk properties. Our NMR relaxation data for Rb_3C_{60} clearly deviate from an Arrhenius law below 8 K. At these temperatures, ^{13}C spin-lattice relaxation is very slow ($T_1 \sim 1000$ s), so that any weak, extraneous relaxation mechanism may affect the observed T_1 values significantly. One such mechanism is provided by spin diffusion between ^{13}C nuclei in the bulk and the more rapidly relaxing ^{13}C nuclei in normal cores associated with a magnetic flux vortex lattice [27]. We estimate the spin diffusion constant for ^{13}C nuclei at natural abundance to be 1–10 Å^{2}s^{-1} and the distance between vortices to be 150 Å. Spin diffusion will then affect the observed relaxation rates strongly when $T_1 > 500$–5000 s. Vortex motion on the 1000-s time scale would also reduce the observed T_1 values.

Third, within the precision of our measurements, we see no Hebel-Slichter peak [24], which would appear as an *increase* in $(T_1T)^{-1}$ with decreasing temperature immediately below T_c. Our relaxation measurements on K_3C_{60} at 2.37 T (not shown) also do not show a Hebel-Slichter peak. The Hebel-Slichter peak has been observed experimentally in NMR measurements on some superconductors but not others [27,28]. The apparent suppression of $T_c^{\rm NMR}$ in both K_3C_{60} and Rb_3C_{60} by about

3 K below the values expected in a 9.39-T field ($dT_c/dH \approx -0.5$ K/T) may be the vestige of a broadened Hebel-Slichter peak. In other systems, the absence of a Hebel-Slichter peak has been attributed to pair-breaking interactions [27,29-31], gap anisotropy [27], or *d*-wave pairing [32].

Figure 2 shows the temperature dependence of the center of gravity of the ^{13}C NMR line for K_3C_{60} and Rb_3C_{60}, at 9.39 T, plotted as the frequency shift relative to a tetramethysilane signal (the standard reference for ^{13}C NMR shifts). Pure C_{60} resonates at 143 ppm. The difference between the ^{13}C NMR frequency in pure C_{60} and that in an alkali fulleride will have both chemical shift and Knight shift contributions. The chemical shift contribution will depend on the charge of the C_{60} anion. The Knight shift will only be present in conducting compounds, will be proportional to $N(E_F)$ in the normal state, and will vanish well below T_c. In K_3C_{60}, the shift is essentially independent of temperature in the normal state, lying between 185 and 190 ppm. In Rb_3C_{60}, the shift is more strongly temperature dependent, increasing from 171 ppm at 296 K to 192 ppm at 40 K. In both materials, there is a pronounced decrease in the shift below T_c, by 30-40 ppm. It is tempting to conclude that the Knight shifts in K_3C_{60} and Rb_3C_{60} are therefore positive (to higher frequency) and 30-40 ppm in magnitude. However, one must also take the diamagnetism of the sample below T_c into account [16]. An extrapolation of magnetization measurements on Rb_3C_{60} taken at fields up to 5 T indicates a magnetization $M \approx -2.0$ G at 9.39 T and 5 K. From the relation $B = H_0 + 4\pi M(1-n)$, we see that the average internal field B is reduced by roughly 20 G (200 ppm) from the applied field H_0, assuming a demagnetizing factor $n = \frac{1}{3}$. Thus, the observed decrease in the ^{13}C NMR shifts below T_c may easily result from the bulk diamagnetism alone. We have also measured shifts of 181 ± 2 ppm for Rb_4C_{60} and 154 ± 5 ppm for Rb_6C_{60} at 296 K. These compounds are neither conductors nor superconductors (T_1T is strongly temperature dependent for Rb_4C_{60}). The precise magnitudes and signs of the ^{13}C Knight shifts in the A_3C_{60} compounds are therefore uncertain, but the Knight shifts appear to be less than 100 ppm in magnitude. The Korringa relation [18] predicts Knights shifts of 160-260 ppm if T_1T is 60-165 Ks. The discrepancy may be due to a significant contribution to the relaxation rates from orbital or dipolar couplings, although this seems unlikely because the nonplanarity of the C_{60} molecule leads to a substantial carbon 2*s* orbital component in the conduction band wave functions [33]. An alternative is that the relaxation rates are enhanced relative to the Knight shifts by antiferromagnetic spin fluctuations or a short electron mean free path [34].

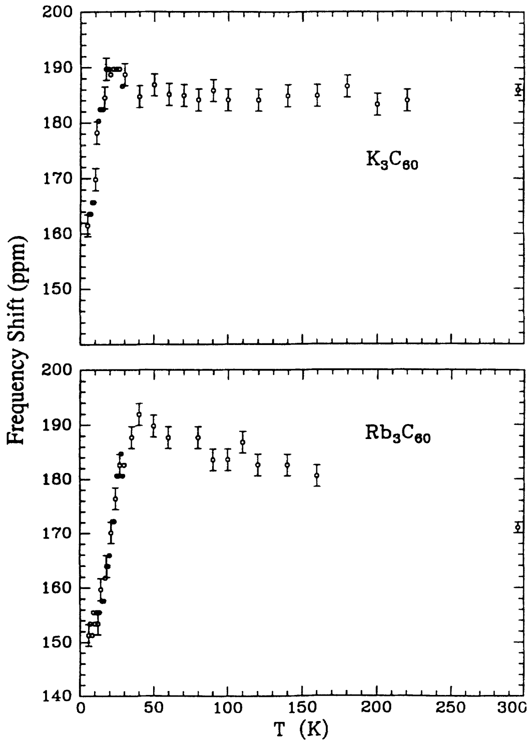

FIG. 2. Temperature dependence of the ^{13}C NMR frequency in K_3C_{60} and Rb_3C_{60}, reported as the shift relative to a tetramethylsilane reference signal.

Figure 3 shows examples of the spectra from which the data in Fig. 2 are taken. The line shapes in Fig. 3 are superpositions of shift anisotropy powder patterns from the crystallographically inequivalent sites. Above 270 K, the spectrum of K_3C_{60} is narrowed by large-amplitude reorientations of C_{60}^{3-} ions [9-12]. From just above to well below T_c, the lines broaden due to the inhomogeneity of B in the vortex lattice, by roughly 60 ppm in K_3C_{60} and 100 ppm in Rb_3C_{60} (FWHM, assuming Gaussian broadening). These values correspond [35,36] to magnetic penetration lengths $\lambda^K = 6000$ Å and $\lambda^{Rb} = 4600$ Å, in reasonable agreement with the value $\lambda^K = 4800$ Å deter-

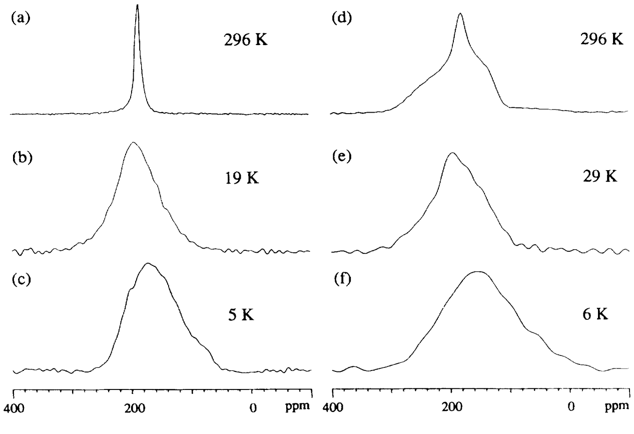

FIG. 3. ^{13}C NMR spectra of (a)-(c) K_3C_{60} and (d)-(f) Rb_3C_{60} at the indicated temperatures.

mined from muon spin relaxation measurements [36].

Our relaxation measurements in the normal state have possible implications for the mechanism of superconductivity. The ratio $R = N^{\mathrm{Rb}}(E_F)/N^{\mathrm{K}}(E_F)$ derived from the relaxation data should be more accurate than our estimates of $N(E_F)$, since A is expected to be the same in both materials. Using the BCS expression $T_c = \Omega \exp[-1/VN(E_F)]$, and assuming that the phonon frequency Ω and electron-phonon coupling constant V are the same in K_3C_{60} and Rb_3C_{60}, we obtain

$$\Omega = T_c^{\mathrm{K}} \exp\left[\frac{\ln T_c^{\mathrm{Rb}} - \ln T_c^{\mathrm{K}}}{1 - R^{-1}}\right].$$

Using $1.28 < R < 1.40$, the range dictated by the temperature dependence of the T_1T values in Fig. 1, this expression implies $60\ \mathrm{cm}^{-1} < \Omega < 94\ \mathrm{cm}^{-1}$ [and $VN^{\mathrm{K}}(E_F) \approx 0.6$]. Such a small value of Ω suggests that coupling between electrons and low-frequency phonons, i.e., "intermolecular" acoustic, alkali-C_{60} optic [37], or radial "intramolecular" phonons [38], rather than the high-frequency tangential intramolecular phonons [38–40], is important for superconductivity in A_3C_{60}. The same qualitative conclusion follows from the McMillan formula [41], which leads to $150\ \mathrm{cm}^{-1} < \Omega < 230\ \mathrm{cm}^{-1}$. Strong electron-electron interactions [34,42] would make this argument invalid, since then T_1T would not be proportional to $N(E_F)^{-2}$.

We thank B. S. Shastry and P. B. Littlewood for illuminating discussions, R. C. Haddon for the C_{60} starting material, and P. L. Gammel for experimental assistance.

---

[1] R. C. Haddon *et al.*, Nature (London) **350**, 320 (1991).
[2] A. F. Hebard *et al.*, Nature (London) **350**, 600 (1991).
[3] M. J. Rosseinsky *et al.*, Phys. Rev. Lett. **66**, 2830 (1991).
[4] K. Holczer *et al.*, Science **252**, 1154 (1991).
[5] S. P. Kelty, C. C. Chen, and C. M. Lieber, Nature (London) **352**, 223 (1991).
[6] K. Tanigaki *et al.*, Nature (London) **352**, 222 (1991).
[7] R. M. Fleming *et al.*, Nature (London) **352**, 787 (1991).
[8] C. S. Yannoni *et al.*, J. Am. Chem. Soc. **113**, 3190 (1991).
[9] C. S. Yannoni *et al.*, J. Phys. Chem. **95**, 9 (1991).
[10] R. Tycko *et al.*, J. Phys. Chem. **95**, 518 (1991).
[11] R. Tycko *et al.*, Phys. Rev. Lett. **67**, 1886 (1991).
[12] R. Tycko *et al.*, Science **253**, 884 (1991).
[13] W. Kratschmer *et al.*, Nature (London) **347**, 354 (1990).
[14] J. P. McCauley *et al.*, J. Am. Chem. Soc. **113**, 8537 (1991).
[15] K. Carduner, M. Villa, and D. White, Rev. Sci. Instrum. **55**, 68 (1984).
[16] S. E. Barrett *et al.*, Phys. Rev. B **41**, 6283 (1991).
[17] E. Helfand, J. Chem. Phys. **78**, 1931 (1983).
[18] J. Winter, *Magnetic Resonance in Metals* (Oxford Univ. Press, New York, 1971).
[19] P. W. Stephens (private communication). In K_3C_{60}, the lattice parameter determined by x-ray diffraction changes from 14.265 Å at 300 K to 14.168 Å at 11 K, corresponding to a reduction in the nearest-neighbor carbon-carbon distance of 0.07 Å.
[20] A. P. Ramirez *et al.* (to be published).
[21] K. Holczer *et al.*, Phys. Rev. Lett. **67**, 271 (1991).
[22] S. H. Glarum, S. J. Duclos, and R. C. Haddon (to be published).
[23] C. T. Chen *et al.*, Nature (London) **352**, 603 (1991).
[24] L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).
[25] Y. Masuda and A. G. Redfield, Phys. Rev. **125**, 159 (1962).
[26] Z. Zhang *et al.*, Nature (London) **353**, 333 (1991).
[27] D. E. MacLaughlin, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1976), Vol. 31, and references therein.
[28] P. C. Hammel *et al.*, Phys. Rev. Lett. **63**, 1992 (1989).
[29] L. Coffey, Phys. Rev. Lett. **64**, 1071 (1990).
[30] P. B. Allen and D. Rainer, Nature (London) **349**, 396 (1991).
[31] Y. Kuroda and C. M. Varma, Phys. Rev. B **42**, 8619 (1990).
[32] H. Monien and D. Pines, Phys. Rev. B **41**, 6297 (1990).
[33] R. C. Haddon, J. Am. Chem. Soc. **109**, 1676 (1987).
[34] B. S. Shastry (to be published).
[35] P. Pincus *et al.*, Phys. Lett. **13**, 21 (1964).
[36] Y. J. Uemura *et al.*, Nature (London) **352**, 605 (1991).
[37] F. C. Zhang, M. Ogata, and T. M. Rice, Phys. Rev. Lett. **67**, 3452 (1991).
[38] D. E. Weeks and W. G. Harter, J. Chem. Phys. **90**, 4744 (1989).
[39] C. M. Varma, J. Zaanen, and K. Raghavachari, Science **254**, 989 (1991).
[40] M. Schluter *et al.*, Phys. Rev. Lett. **68**, 526 (1992).
[41] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[42] T. Moriya, J. Phys. Soc. Jpn. **18**, 516 (1963).