Isotope Effect in Superconducting Rb_3C_{60}

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Measurements of the superconducting T_c and Raman spectra in isotopically modified Rb_3C_{60} are reported. A decrease in T_c of 0.65 ± 0.10 K in samples with $(75 \pm 5)\%$ substitution of ^{13}C for ^{12}C yields an exponent of $\alpha = 0.37 \pm 0.05$. This is interpreted as evidence for phonon-mediated pairing.

Superconductivity [1] in the alkali metal fullerides, A_3C_{60}, presents new opportunities for testing ideas about electron pairing. The observation of high T_c's, over 30 K, and the three dimensionality of these molecular materials set them apart from other families of superconductors. Among the models used to explain superconductivity in A_3C_{60} have been the traditional ones based on phonon-mediated pairing. These have employed either high-energy (1500 K) intramolecular modes [2,3] or low-energy (200 K) alkali-C_{60} optic intermolecular modes [4]. Alternatively, several workers have proposed models where pairing occurs via purely electronic means [5-7]. One of the cleanest ways of distinguishing between the two alternatives, phonon- or electron-mediated pairing, is the classical isotope experiment. For phonon-mediated pairing, $T_c \propto M^{-\alpha}$, where M is the ionic mass. The value $\alpha = 0.5$ is determined theoretically in the simple BCS model and experimentally for many simple materials [8]. There will be corrections due to Coulomb interactions and these will tend to depress α in the phonon-mediated case [9,10]. On the other hand, for purely electronic pairing there will be no mass dependence of T_c to first order [11]. In the high-T_c cuprates for example, the observation of $\alpha \ll 0.5$ has been argued to support the view of a predominantly electronic attractive interaction [12].

In this paper, we report the effect of isotopic substitution of ^{13}C for ^{12}C in Rb_3C_{60} on both T_c and the high-energy intramolecular phonon modes as probed by Raman scattering. We find that the Raman A_g and H_g modes near 1450 cm^{-1} shift by 85% of the expected amount, consistent with the mass spectrum of our samples. We also find T_c shifts by $(75 \pm 10)\%$ of that expected for $\alpha = 0.5$, i.e. $\alpha = 0.37 \pm 0.05$. This constitutes strong evidence that superconductivity in Rb_3C_{60} is driven primarily by phonon-mediated pairing involving carbon vibrations, but with significant Coulomb interaction effects.

The starting material for the $Rb_3{}^{13}C_{60}$ synthesis was 98.1% ^{13}C isotopically pure graphite powder. Rods were fabricated using 90% (universally ^{13}C labeled) D-glucose as a binder in a ratio of 3:1 graphite to binder. The rods were heated to 250 °C to polymerize the glucose to achieve mechanical hardness. They were then heated to 850 °C over a period of three days to drive out water completely and to anneal out stress. Finally they were graphitized at 2800 °C. Soot was produced from the rods in the usual manner, and the C_{60}-C_{70} mixture extracted. Column chromatography was used to separate the C_{60} which was then washed thoroughly in ether. From 10 g of rod material, 37 mg of C_{60} was obtained. Mass spectrometry was used to determine the ^{13}C concentration p. The main peak in the mass spectrum corresponded to a C_{60} molecule with $(90 \pm 5)\%$ substitution of ^{13}C for ^{12}C. However, a second peak, corresponding to 15% of the total mass, was centered at the $^{12}C_{60}$ position with resolution-limited width. From the specifications of the starting material, $p = 95\%$ was expected and we suspect some loss of ^{13}C occurred during the graphitization procedure due to CO_2 exchange with the walls of the graphite oven. We have no explanation as to the origin of the $^{12}C_{60}$ fraction. One $Rb_3{}^{12}C_{60}$ control sample and two $Rb_3{}^{13}C_{60}$ samples were prepared using identical heat treatments [13]. $Rb_{6.6}C_{60}$ was prepared by reaction of C_{60} with Rb metal in sealed, evacuated Pyrex ampoules (4 days at 250 °C, 4 days at 300 °C, followed by distillation of excess Rb metal away from the product). The $Rb_{6.6}C_{60}$ was then ground together with a stoichiometric amount of C_{60} in a dry box and heated in sealed Pyrex ampoules, containing 10^{-3} torr He for thermal contact, for 24 h at 250 °C and 24 h at 350 °C.

To characterize the change in phonon frequencies with isotopic substitution, a Raman spectrum of a film grown and remaining in vacuum was measured on the undoped $^{13}C_{60}$ between 1300 and 1600 cm^{-1} at room temperature. The unpolarized spectrum was excited by 50 W/cm^2 (15 mW incident power) of the 514.5-nm Ar-ion laser line in a backscattering geometry, and dispersed by a $\frac{3}{4}$-m Spex double spectrometer with 7-cm^{-1} spectral resolution. Details of film growth and Raman spectroscopy are given in Ref. [14]. The resulting spectrum is shown in Fig. 1, along with a spectrum of a $^{12}C_{60}$ film in vacuum. For $^{12}C_{60}$, the A_g mode is at 1458 cm^{-1} [14], and for the $^{13}C_{60}$ enriched material, this mode has shifted to 1410 cm^{-1}, with a full width at half maximum approximately twice that of the $^{12}C_{60}$ material. For pure $^{13}C_{60}$, this mode would be at $1458(\frac{12}{13})^{1/2} = 1401$ cm^{-1}.
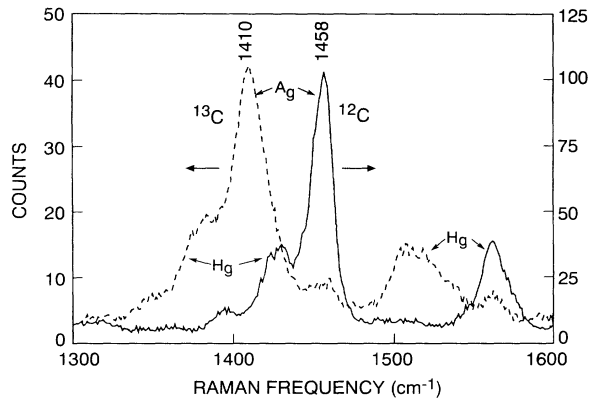
FIG. 1. Room-temperature unpolarized Raman spectra of $^{12}C_{60}$- (solid line) and $^{13}C_{60}$-enriched C_{60} (dashed line) films taken in vacuum. The laser power density is 50 W/cm^2 at 514.5 nm.

A similar shift is observed for the H_g modes indicated in the figure. The smaller than expected shift, 84% of that expected for pure $^{13}C_{60}$, is consistent with the centroid of the main peak in the mass spectrum, which is at $p = 90\%$. The larger width of the A_g mode in $^{13}C_{60}$ presumably reflects the width of the mass distribution. Note that a small A_g peak due to pure $^{12}C_{60}$ was observed along with the $^{13}C_{60}$ material, consistent with the mass spectrometry results.

The shielding signal in the dc magnetization $M(T)$ is shown in Fig. 2 for the $Rb_3^{13}C_{60}$ material as well as for several $Rb_3^{12}C_{60}$ samples in applied fields of either 5 or 10 Oe. Among the $Rb_3^{12}C_{60}$ samples is the control sample, as well as four others prepared with different batches of starting material. For all of the samples, normalization of the shielding data was made at 5 K. For the two $Rb_3^{13}C_{60}$ samples, the shielding fraction was determined to be 26% of the full exclusion, and similar values were found for the other $Rb_3^{12}C_{60}$ samples. Additional heat treatments did not alter these flux exclusion values. This incomplete shielding volume fraction is just as expected for powder samples with grain sizes not much larger than the penetration depth λ [15]. Here $\lambda \approx 4 \times 10^3$ Å [16] and typical grain sizes are 10^4 Å [17]. An additional effect of the small grain size is a rounding of the magnetization in the low-temperature tail of the transition (not shown). Thus, as the grain size and distribution vary from sample to sample, the shape of the transition will also vary. We presume this variation is the cause of the spreading of the $Rb_3^{12}C_{60}$ data among different samples well below T_c, seen towards the bottom of Fig. 2. Nevertheless, T_c, as defined by the temperature where $M(T)$ has the maximum curvature, is the same to within ± 0.1 K for all of these samples. If this variation in T_c is caused by having a small range of solid solution close to the A_3C_{60} stoichiometry, then the true T_c for $Rb_3^{12}C_{60}$ is the highest observed value. However, without a similarly large set of $Rb_3^{13}C_{60}$ samples, we must still ascribe an uncertainty of this magnitude to the observed shift. In

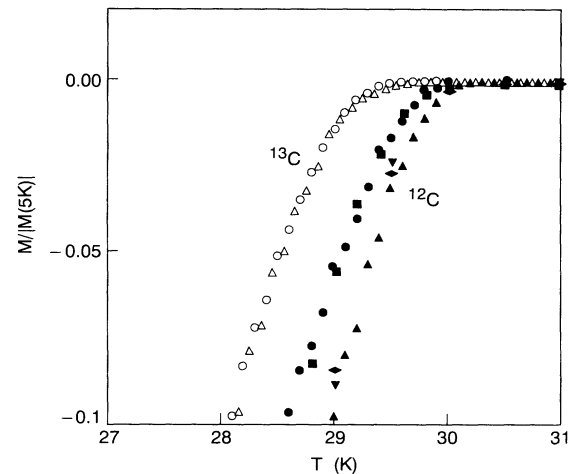FIG. 2. Magnetization data taken upon warming for the two Rb_3C_{60} samples in applied fields of either 5 or 10 Oe. The open symbols denote $Rb_3^{13}C_{60}$ data [$(75 \pm 5)\%$ ^{13}C content] and the closed symbols $Rb_3^{12}C_{60}$ data. The different symbol shapes denote different samples. The closed circles correspond to the $Rb_3^{12}C_{60}$ control sample.

the vicinity of the onset of diamagnetism, we therefore find the shift to be $\Delta T_c = 0.65 \pm 0.10$ K.

As noted above, 15% of the C_{60} molecules are pure ^{12}C, and the remainder contain $(90 \pm 5)\%$ ^{13}C enrichment. We believe this bimodality of the mass spectrum has only a marginal effect on the isotope shift for the following reasons. Although the origin of the $^{12}C_{60}$ fraction is unknown, we can be sure that it occurred prior to formation of the final solid-state product. In this process, all the $^{13}C_{60}$ and $^{12}C_{60}$ molecules are in molecular solution and the solid product is formed by evaporation of the solvent. Therefore, when the crystallites form in the precipitate, there will be homogeneous mixing of the two mass types on the molecular length scale. Since the phonon-oscillator mass responsible for superconducting pairing is obtained from a spatial average over a region the size of a mean free path, > 25 Å, there will be complete averaging of the isotopic distribution, and one expects a single sharp T_c, as observed.

For a ^{13}C concentration of $p = 75\%$, the expected shift for $\alpha = 0.5$ is 0.90 K. Thus, the observed shift of 0.65 ± 0.10 K leads to $\alpha = 0.37 \pm 0.05$. Deviations from the BCS phonon-only value of $\alpha = 0.5$ can be related to a finite Coulomb interaction strength in the following way. We use McMillan's two square-well expression, which holds for a wide range of coupling strengths [9],

$$T_c = \frac{\langle \Omega \rangle}{1.2} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right], \tag{1}$$

where $\langle \Omega \rangle$ is an average phonon frequency, λ is the electron-phonon coupling strength parameter, and μ^* is the phonon renormalized Coulomb interaction parameter. The ionic mass enters Eq. (1) also via $\mu^* = \mu/[1$

$+\mu \ln(\omega_c/\omega_{ph})]$, where ω_c is the Coulomb energy cutoff frequency, $\omega_{ph} \propto M^{-1/2}$ is the phonon cutoff frequency, and μ is the bare Coulomb interaction parameter. Thus [9],

$$\alpha \equiv -\frac{\partial \ln T_c}{\partial \ln M} = \frac{1}{2}\left[1 - \left\{\mu^* \ln\frac{\langle\Omega\rangle}{1.20 T_c}\right\}^2 \frac{1+0.62\lambda}{1+\lambda}\right]. \quad (2)$$

Together with Eq. (1), Eq. (2) allows us to determine λ and μ^* separately, assuming a particular value for $\langle\Omega\rangle$ and using the observed T_c. For high-energy carbon phonons, i.e. $\langle\Omega\rangle \simeq 1400$ K, as proposed in Refs. [2,3] for intramolecular modes, we find these equations are satisfied by $\lambda = 0.72$ and $\mu^* = 0.15$. Coupling constants of this magnitude are relatively common. Among the elements, for example, In, Tl, and Hg have λ of similar size [18]. On the other hand, for low-energy intermolecular carbon phonons, $\langle\Omega\rangle \lesssim 200$ K, we find $\lambda = 5.5$ and $\mu^* = 0.37$. Since this λ value exceeds the range of validity of Eqs. (1) and (2), we should consider the strong coupling ($\lambda \gg 1$) limit of the Eliashberg equations, derived by Kresin [19]:

$$T_c = 0.18 \lambda_{eff}^{1/2} \langle\Omega\rangle, \quad (3)$$

where $\lambda_{eff} \approx \lambda/(1+2.6\mu^*)$. We find

$$\alpha = \frac{1}{2}\left[1 - \frac{1.3\mu^{*2}}{1+2.6\mu^*}\right], \quad (4)$$

which yields, for $\alpha = 0.37$, $\mu^* = 0.78$ and $\lambda = (291/\langle\Omega\rangle)^2$, where $\langle\Omega\rangle$ is expressed in degrees Kelvin. If we assume $\langle\Omega\rangle = 200$ K as above, then $\lambda = 2.1$. These two limiting values for λ are, of course, very sensitive to the particular value of $\langle\Omega\rangle$—nevertheless an argument of this type implies that λ must be very large, 2-5, for pairing to proceed via low-energy intermolecular carbon phonons. If this is indeed the case, then alkali-doped C_{60} would be among the strongest coupled phonon superconductors.

For low-energy phonon modes involving mainly alkali vibrations, as proposed in Ref. [4], the carbon-mass dependence should be reduced by $M_{Rb}/M_{C_{60}}$, implying $\alpha \approx 0.05$. Clearly, the relatively large value of α rules out such a mechanism.

Finally, there is an additional dependence of T_c on ionic mass, independent of the nature of the coupling mechanism [11]. This is due to a modification of the electronic hopping parameters upon isotopic substitution. In the present case, $\lambda \propto N$ and $N \propto d^\nu$, where N is the density of states, $\nu \approx 3$, and d is the intermolecular distance which changes due to a change in zero-point motion for different mass values. Such an effect is expected to be small and should be investigated theoretically for this system. If present, there should then be a corresponding change in lattice constant. From the known dependence of T_c on lattice constant [20,21], a reduction in T_c of the measured value 0.65 K would require a reduction of the lattice constant of ≈ 0.01 Å, within the limits of observability.

In conclusion, we have observed a sizable isotope-induced shift in T_c in heavily ^{13}C-enriched Rb_3C_{60} samples. The size of the effect lends further support to a model of superconductivity involving pairing via high-energy carbon intramolecular phonons, but with sizable corrections from electron-electron interactions.

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