Carbon Isotope Effect in Single-Crystal Rb_3C_{60}

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The sharp resistive transitions in superconducting single crystals of natural abundance and 99% ^{13}C-enriched Rb_3C_{60} reveal the carbon isotope effect with unprecedented accuracy. The measured isotope exponent $\alpha_C = 0.21 \pm 0.012$ is outside the error bars of all previous reported values. Our precise value for α_C, combined with T_c, α_{Rb}, and an *ab initio* calculation of the frequency distribution of the electron-phonon coupling, allows a fully constrained determination of the coupling strength $\lambda = 0.9^{+0.15}_{-0.1}$ and the Coulomb repulsion $\mu^* = 0.22^{+0.03}_{-0.02}$. These new measurements reveal a phonon-mediated superconductor with moderate coupling to a wide range of phonons centered near ~1400 K.

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The high-temperature superconductivity [1] of alkali-metal-doped C_{60} (up to 40 K in Cs_3C_{60} [2]) has sparked much investigation into the mechanism of superconductivity and the nature of the normal state. Proximity to a Mott-Hubbard transition [3] could call into question the role of standard electron-phonon mechanisms. Theories of superconductivity in the fullerides have ranged from the conventional phonon-mediated electron pairing [4] to more unconventional electronic mechanisms [5]. The dependence of the superconducting transition temperature T_c on isotopic mass provides an important probe of the pairing mechanism. A precise measurement of α_C can place strong constraints on the role of electron-phonon coupling in this family of high-temperature superconductors.

Unfortunately, the many published reports of the carbon isotope effect in A_3C_{60} [6–12] are inconsistent. The isotope exponent α is defined by $T_c \propto M^{-\alpha}$, where M is the isotopic mass. Previously reported values for the carbon isotope effect exponent α_C range from 0.3 ± 0.05 to 2.1 ± 0.35 (Table I). The difficulties inherent in measuring T_c in powder samples of A_3C_{60} may play a role; the magnetization transitions for superconducting powder samples are very broad, often much wider than the isotope shift itself. In these cases, the indeterminant definition of T_c clouds the measurement of the isotope shift. Some measurements might also exhibit a possible anomalous isotope effect [11] at incomplete isotope substitution. Fortunately, resistive transitions in single-crystal samples of A_3C_{60} superconductors are narrow (~200 mK) and precisely reproducible [13]. Therefore, resistive measurements of isotopically pure A_3C_{60} single crystals are highly desirable for a precise determination of the isotope effect, which in turn allows a meaningful analysis of electron-phonon coupling in A_3C_{60}.

Commercially available 99% enriched-^{13}C powder was formed into rods using a method similar to that of Chen *et al.* [10]. After arcing the rods in a helium atmosphere, C_{60} was extracted from the resulting soot using high performance liquid chromatography. A similar batch of natural abundance C_{60} produced from graphite rods served as a control. As a natural abundance carbon is approximately 1.1% ^{13}C; both samples have similar (99%) isotopic enrichment. Time-of-flight mass spectrometry and secondary-ion mass spectrometry verified the purity and isotopic enrichment of the C_{60}.

Vapor transport from C_{60} powder using flowing argon yielded single crystals of natural abundance and ^{13}C-enriched C_{60}. After gold wires were affixed in the standard four-probe geometry using silver epoxy, the samples were sealed in a vacuum ampoule containing rubidium metal. Rubidium intercalation followed a previously reported method [14]. An electrical feed through in each ampoule allowed *in situ* measurement of the resistivity $\rho(T)$ during intercalation and at cryogenic temperatures.

The widths of the resistive transitions (Fig. 1) in all samples are much less than the isotope shift. The transitions for natural abundance and 99% ^{13}C-enriched samples are also nearly parallel, reducing the dependence of the measured isotope shift on the definition of T_c. We define T_c as the maximum of $d\rho/dT$, the definition which yields the most consistent results for different samples of the same isotopic composition.

Figure 2 shows the superconducting transition temperature as a function of the isotopic masses. The solid line is a best fit to $T_c \propto M^{-\alpha_C}$, giving $\alpha_C = 0.21 \pm 0.012$, corresponding to a shift in T_c of 505 ± 30 mK. The disagreement of our value of α_C for Rb_3C_{60} with those previously reported [6–13] (see Table I) is not surprising. All previous carbon isotope effect experiments measured the magnetic susceptibility of powder samples. Although Chen and Lieber [11] suggest that the large dispersion in measurements of α_C may in part arise from an anomalous isotope effect for nonhomogeneous partial carbon substitution, tests of this theory using inhomogenously

TABLE I. Published measurements of the superconducting isotope effects in A_3C_{60}.

Material	Technique	Enrichment (%)	α_C
Rb_3C_{60} (powder)	Magnet.	33	1.4 ± 0.50 [6]
Rb_3C_{60} (powder)	Magnet.	76	0.32 ± 0.05 [7]
K_3C_{60} (powder)	Magnet.	60	1.3 ± 0.30 [8]
Rb_3C_{60} (powder)	Magnet.	60	2.1 ± 0.35 [8]
Rb_3C_{60} (powder)	Magnet.	82	1.45 ± 0.30 [9]
K_3C_{60} (powder)	Magnet.	99	0.3 ± 0.06 [10]
Rb_3C_{60} (powder)	Magnet.	99	0.3 ± 0.05 [11]
Rb_3C_{60} (powder)	Magnet.	55[a]	0.3 [11]
Rb_3C_{60} (powder)	Magnet.	50[b]	0.8 [11]
Rb_3C_{60} (sngl. crys.)	Resist.	99	0.21 ± 0.012[c]
Material	Technique	Enrichment (%)	α_{Rb}
Rb_3C_{60} (powder)	Magnet.	99	<0.2 [12]
Rb_3C_{60} (sngl. crys.)	Resist.	99	−0.028 ± 0.036 [13]

[a] $Rb_3(^{12}C_{0.55}\,^{13}C_{0.45})_{60}$.
[b] $Rb_3(^{12}C_{60})_{0.5}(^{13}C_{60})_{0.5}$.
[c] This work.

isotopically disordered samples [11] could reproduce only a small fraction of the spread in isotope shifts shown in Table I.

More likely, the large isotope exponents reported in Table I indicate that in many cases the T_c's of ^{13}C-enriched samples were extrinsically depressed compared to the natural abundance samples, most probably due to reduced sample quality in the ^{13}C-enriched material, which is more difficult to prepare due to the unavailability of ^{13}C in graphite form. Previous isotope effect measurements then place lower bounds on T_c for isotopically enriched samples and hence place upper bounds on the isotope effect exponent relative to $Rb_3{}^{12}C_{60}$.

The fact that resistively measured single-crystal Rb_3C_{60} yields the smallest isotope effect is telling. The resistive transition measures the sharp onset of superconductivity and is less likely to be corrupted by sample inhomogeneities. Our transition temperature for natural abundance single-crystal Rb_3C_{60}, 30.82 K, agrees precisely with previous resistive measurements on samples derived from different starting materials [13]. We then trust this result within the ±90 mK calibration accuracy of both measurements. This transition temperature exceeds that of any reported magnetizations measurement. Although strictly speaking our measurement of T_c for

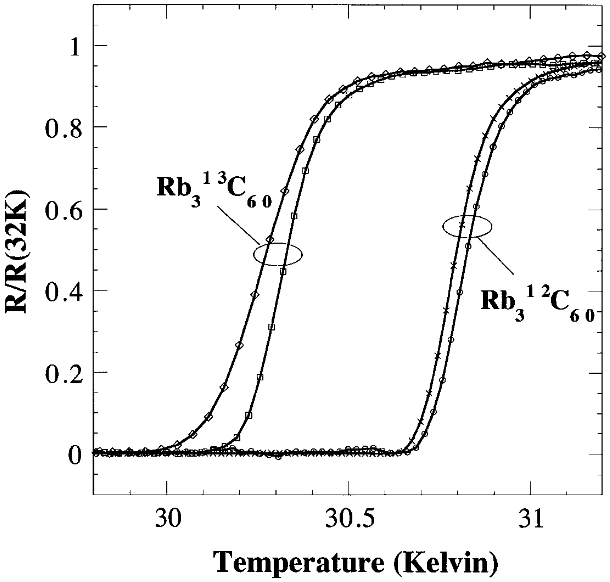

FIG. 1. The resistance (normalized to its value at 32 K) of two samples each of $Rb_3{}^{12}C_{60}$ and $Rb_3{}^{13}C_{60}$ versus temperature. Solid lines guide the eye.

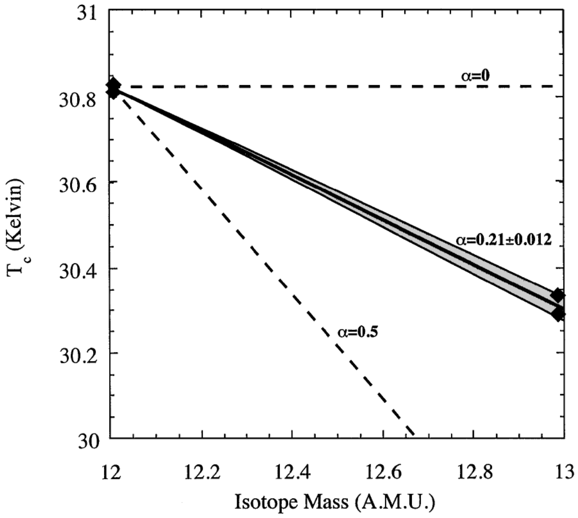

FIG. 2. The superconducting transition temperature, T_c, of two samples each of $Rb_3{}^{12}C_{60}$ and $Rb_3{}^{13}C_{60}$ versus isotropic mass. The solid line fits $T_c \propto M^{-\alpha}$, and gives $\alpha = 0.21 \pm 0.012$. Dotted lines show $\alpha_C = 0$ and $\alpha_C = 0.5$ for comparison. The shaded area represents the error bars for this measurement.

$Rb_3{}^{13}C_{60}$ is again a lower bound, the reduced sensitivity of the resistively measured T_c to inhomogeneities and our precisely reproducible T_c's give confidence that our result is correct within the stated error bars.

Precise values for α_C and T_c, together with other parameters, allow a stringent test of superconducting pairing mechanisms, in particular electron-phonon models. A naive picture with $T_c \propto \omega_{\text{phonon}} e^{-1/\lambda}$ and mass-independent electron-phonon coupling λ yields $\alpha = -d \ln T_c / d \ln M = 1/2$. A simple two-square-well model with a Coulomb repulsion $\mu^* = \mu/[1 + \ln(E_F/\omega_{\text{phonon}})]$ and renormalized electron-phonon interaction $\lambda^* = \lambda/(1 + \lambda)$ in which $T_c \propto \omega_{\text{phonon}} e^{-1/(\lambda^* - \mu^*)}$ yields an isotope effect exponent $\alpha < 0.5$ due to the mass dependence of μ^*.

The small carbon isotope exponent of 0.21 ± 0.012 implies a relatively large Coulomb repulsion; the high T_c in the face of this large Coulomb repulsion then implies a large λ. The most accurate scheme for calculating T_c is a direct solution of the strong-coupling Eliashberg equations. The McMillan equation [15] and its Allen-Dynes extension [16] are less desirable since they lose accuracy at strong coupling, and they use an approximate single-moment expression for the frequency dependence of the electron-phonon coupling spectrum.

We have solved the isotropic Eliashberg equations [17] wherein the frequency dependence of the electron-phonon interaction follows an *ab initio* local density approximation frozen phonon calculation for molecular C_{60} [18]. Many other earlier estimates of the coupling spectrum exist [4], but the broad variation among these predominantly semiempirical techniques motivates our use of recent *ab initio* results. This calculation reveals a broad frequency distribution of coupling to the H_g modes with a logarithmic average frequency of 1390 K. Although we will neglect the heavily screened A_g modes in the specific spectrum chosen, their inclusion causes only a slight change in average frequency (both theory [4] and experiment [2,19] yield at most a small A_g contribution). The overall scale of the coupling function $\alpha^2 F(\omega)$ depends on the less precisely known density of states in the vicinity of the Fermi level. But this uncertainty is irrelevant, since we will derive the overall coupling $\lambda = 2 \int [\alpha^2 F(\omega)]/\omega \, d\omega$ directly from the experimental results.

Together, $\alpha_C = 0.21 \pm 0.012$, $T_c = 30.82$ K, and the frequency distribution completely determine the coupling strength λ and the Coulomb repulsion μ^* within the Eliashberg theory. We obtain $\lambda = 0.90^{+0.15}_{-0.1}$ and $\mu^* = 0.22^{+0.03}_{-0.02}$ where the errors arise primarily from an assumed ~10% uncertainty in the centroid of the frequency spectrum. This value of λ is consistent with the value for $\lambda_{\text{transport}}$ obtained from normal-state resistivity data [20] and other sources [21].

The theoretical result [18] for $V = \lambda/N(0)$ can then be used to derive a density of states at the Fermi level of $N(0) \approx 13.5 \pm 2.5$ states per eV per C_{60}, in good agreement with independent experimental estimates [22]. The slightly lower values from the theoretical band structure calculations [22] may arise from quasiparticle effective mass renormalizations beyond the local density approximation due to the proximity to a metal-insulator transition. The moderately large $\mu^* = 0.22$ is consistent with a narrow-band material on the metallic side of a metal-insulator transition [3]. The reduction in μ^* from the bare μ arises from frequency-dependent screening taking into account the disparity between the conduction bandwidth, the plasma frequency, and the full width of the π complex [23]. Hence the λ and μ^* determined from our measurements in Rb_3C_{60} are well accounted for by conventional phonon-mediated electron pairing.

Tiny isotope-induced changes in bond length have been proposed as an alternate mechanism for an isotope effect in electronic models for fullerene superconductivity [24]. Although the wide range proposed for such isotope effects proposed encompasses the present experimental value, this extreme sensitivity to bond length begs the coincidential correspondence of the measured T_c with the results of standard electron-phonon models.

In summary, the resistive measurements of the superconducting transitions in high-quality single-crystal Rb_3C_{60} of 99% carbon isotopic purity has revealed the carbon isotope effect with unprecendented accuracy. When combined with an *ab initio* electron-phonon frequency spectrum, this precise measurement determines the superconducting coupling strength λ, Coulomb repulsion μ^*, and the density of states $N(0)$. The results are consistent with the independent experimental determination of λ and theoretical and experimental results for the density of states at the Fermi level. The relatively large $\mu^* = 0.22$ is consistent with a narrow-band material on the metallic side of a metal-insulator transition. Conventional electron-phonon mediated superconductivity theory provides a complete, self-consistent picture of Rb_3C_{60}.

We note that although the lack of a significant Rb isotope effect in Rb_3C_{60} [13] seems to rule out an alkali phonon contribution to λ, the small α_{Rb} could possibly be an artifact an anharmonic Rb potential in the intersitial sites. The possibility of a small negative α_{Rb} [13] may hint at a similarity with the inverse hydrogen isotope effect in strongly anharmonic palladium hydride [25]. This raises the possibility that alkali-metal C_{60} phonons contribute to λ, but the alkali-metal isotope effect is masked by an anharmonic potential. No measurements of the potassium isotope effect in K_3C_{60} have been reported; such an experiment could shed light on this possibility.

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