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THE ENERGY GAP OF THE M_3C_{60} SUPERCONDUCTORS

ZHE ZHANG and CHARLES M. LIEBER
Department of Chemistry and Division of Applied Sciences,
Harvard University, Cambridge, MA 02138, USA

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We briefly review tunneling spectroscopy studies of the new fullerene-based superconductors, K_3C_{60} and $Rb_{30}C_{60}$ from our laboratory. At low temperature the reduced energy gap, $2\Delta/kT_c$, has a value of 5.3 ± 0.2 and 5.2 ± 0.3 for K_3C_{60} and Rb_3C_{60}, respectively. The magnitude of the reduced gap for these materials is significantly larger than the value of 3.53 predicted by BCS theory. These results demonstrate that the energy gap scales with T_c and show that the pair coupling interaction is strong in the M_3C_{60} superconductors, and thus they provide information essential to understanding superconductivity in the M_3C_{60} materials.

The discovery of superconductivity in potassium-doped[1] C_{60} has been followed by an intense effort to understand the physics and chemistry of metal-doped fullerene solids.[2–10] Experimental studies have elucidated several important properties of the superconducting phase, including the face-centered cubic (fcc) structure,[5,6] the coherence length,[7] the penetration depth,[7,8] and the lower and upper critical fields.[7] In addition, investigations of the dependence of the transition temperature (T_c) on the fcc lattice constant[6] and on pressure[8,9] have led to the proposal that changes in T_c can be explained solely through variations in the density of electronic states (DOS) at the Fermi-level (E_f). That is, using the BCS expression for the transition temperature, $T_c \alpha h\omega \exp(-1/NV)$, [where, $h\omega$ is the excitation energy relevant to electron pairing, N is the DOS at E_f, and V is the electron-phonon coupling strength] variations in T_c can be explained by variations in N, while V and $h\omega$ are essentially constant.[2,6,9]

This analysis is based on the assumption of weak coupling. Recent theoretical and experimental results have, however, suggested that the coupling may be quite strong.[10–12] For example, Zhang *et al.* have claimed that superconductivity arises from strong coupling between the potassium-ion optical phonon and carriers on the C_{60} molecules.[12] Erwin and Pickett have also concluded that the coupling may be exceptionally strong in this system.[11] from first principles calculations. Both of these calculations gave the strong coupling results. The superconducting energy gap (Δ) provides a measure of the coupling strength and can therefore address this

issue especially. In particular, weak-coupling BCS theory predicts that there is a universal value for the reduced energy gap, $2\Delta/kT_c$, of 3.53,[13] and thus we have sought to address this key issue by determining Δ in the new C_{60}-based superconductors. This review discusses recent tunneling measurements on the M_3C_{60} materials made in our laboratory using a scanning tunneling microscope.[11]

Tunneling spectroscopy has been one of the most successful techniques used to probe conventional metal and alloy superconductors.[14] In particular, tunneling spectra can provide values for both the energy gap Δ and the electron-phonon spectral function $\alpha^2F(\omega)$, where α^2 is a measure of the coupling and $F(\omega)$ is the phonon density of states. To obtain an unambiguous value of Δ by tunneling, it is essential to prepare a uniform insulating barrier between the superconductor and metal junction. Because the C_{60} superconductors have short coherence lengths and the polycrystalline samples exhibit some inhomogeneity, we expect that planar junctions might show broadened gap features (even for the ideal BCS case). We have therefore used a low temperature scanning tunneling microscope (STM) to make point junctions with a sharpened metal tip.

The M_3C_{60} samples were prepared by reaction of alkali-metal alloy or alkali-metal with C_{60}.[4] Briefly, a 3:1 mixture of MHg or M (M = K, Rb) and C_{60} were sealed under vacuum in a quartz tube and then heated at 200°C. When the shielding fraction of M_3C_{60} superconducting phase reached ca 40%, the tube was opened and the polycrystalline powder was pressed into 3 mm diameter pellets within an inert atmosphere glove box. The pellets were then sintered at 200°C until the shielding fraction approached 100%. Magnetization versus temperature curves typical of the K_3C_{60} and Rb_3C_{60} samples used in this study are shown in Fig. 1. The transition temperatures of these K- and Rb-doped materials are 19 and 28.6 K, respectively, and the low temperature shielding fractions are near to 100% for both samples.

Magnetically characterized M_3C_{60} sintered pellets were mounted on the STM sample holder using silver paint in an inert atmosphere glove box ($[O_2] \approx [H_2O] \approx$ 1 ppm). The sample holder was then transferred to the STM which is contained within a vacuum can. After mounting the sample, the evacuated STM assembly was placed in a mechanically and acoustically isolated helium dewar. The metal (tip)-insulator-superconductor (N-I-S) junction was made by mechanically stepping the tip to the sample and then adjusting the junction resistance and position using the piezo tube-scanner of the STM. Tunneling measurement were made either through vacuum when the surfaces were metallic ($T > T_c$) or in point contact. In the latter case we believe that a partially oxidized sample surface functions as the insulating barrier. The data obtained from these two distinct types of junctions were similar. I–V curves were recorded digitally using custom-built electronics under computer control; the sample temperature is actively controlled for temperatures greater than 4.2 K.

Typical I–V curves recorded on K_3C_{60} and Rb_3C_{60} samples at 4.2 K are shown in Figs. 2(a) and 2(b), respectively. These curves exhibit features characteristics of the superconducting energy gap, including: (1) a distinct zero current regime about

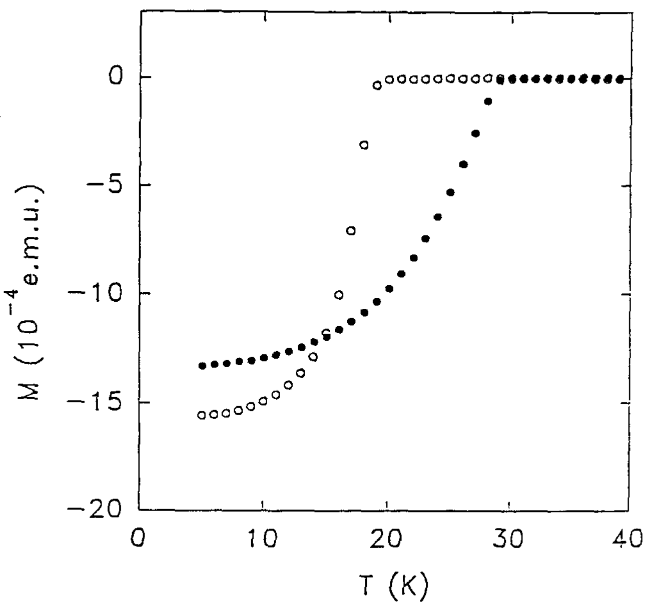

Fig. 1. Temperature dependence of the magnetization obtained for K_3C_{60} (open circles) and Rb_3C_{60} sintered pellets (filled circles). The T_c's of the K_3C_{60} and Rb_3C_{60} samples are 19.0 and 28.6 K, respectively. The curves were recorded by cooling in zero field to 5 K and subsequent warming in a 10 Oe field.

$V = 0$ and (2) conductance onset at $V = \pm 4$ mV for K_3C_{60} and $V = \pm 6$ mV for Rb_3C_{60}. We believe that these features, which are observed in most of the I–V curves recorded at 4.2 K, reflect the modulation in current due to the gap (2Δ) in the DOS of the M_3C_{60} superconductors probed in the N-I-S tunneling geometry.

Other possible explanations for this structure in the I–V curves are a coulomb blockade or superconductor-insulator-superconductor (SIS) tunneling. We believe, however, that both of these possibilities are unlikely. First, we do not find that $I \alpha V^2$ for small V as predicted and previously observed for coulomb-charging.[15,16] Furthermore, we find that the magnitude of the zero current region of $V \approx O$ is smaller in K_3C_{60} than in Rb_3C_{60} (Fig. 2) and for both materials this gap-like structure disappears for $T > T_c$.[10] Neither of these observations are consistent with the coulomb blockade. For S-I-S tunneling there should be a sharp current jump at $V = 2\Delta$,[14] and not the smooth increase observed in our data. In addition, it is unlikely that the same S-I-S tunneling would be observed for vacuum and point contact tunneling, and thus the conductance onsets have been assigned to $\pm\Delta$.[10] Lastly, we note that a small number of I–V curves recorded at 4.2 K exhibit large gaps which may be interpreted as S-I-S tunneling.

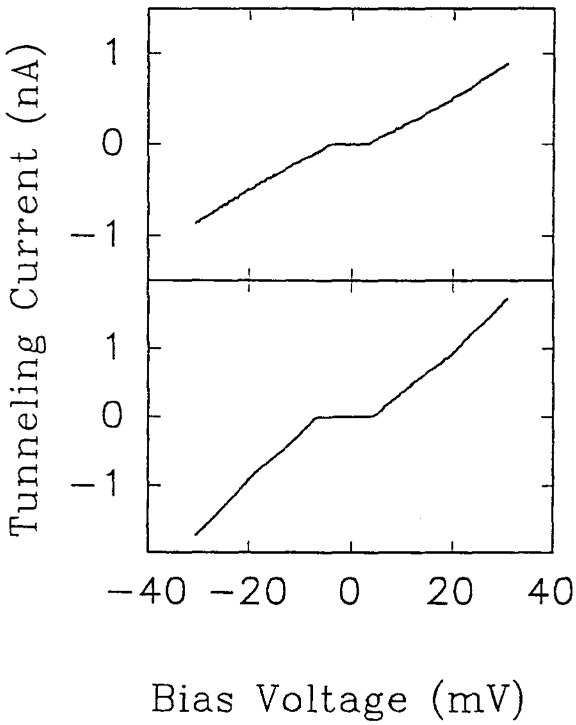

Fig. 2. Current versus voltage (*I–V*) curves recorded at K_3C_{60} and Rb_3C_{60} samples at 4.2 K. Typically, five subsequential *I–V* measurements at a specific sample location were averaged to produce a single curve.

An important point evident upon examination of the 4.2 K I-V curves is that the gap-structure for K_3C_{60} is significantly smaller than for Rb_3C_{60}. These results indicate qualitatively that Δ scales with T_c. To quantitatively assess the magnitude of Δ and the reduced energy-gap we have calculated the normalized conductance, dI/dV (Fig. 3). Since dI/dV is proportional to the superconducting DOS, N_s, the value of Δ can be determined from a fit of the conductance to a model for the DOS. We find that good fits of the experimental data are obtained using the broadened BCS function proposed by Dynes and co-workers, $N_s = \mathrm{Re}[|E - i\Gamma|/((E - i\Gamma)^2 - \Delta^2)^{1/2}]$. where E is the energy of the tunneling electron and Γ is a broadening function.[18] Dynes *et al.*[17] introduced Γ specifically to account for shortened quasi-particle lifetime, however, here we use Γ as a phenomenological parameter since the mechanism of broadening is not known. For example, inelastic scattering or strong coupling could broaden N_s relative to the ideal BCS model. The essential result obtained from the fits to the 4.2 K K_3C_{60} data is that the experimental value of Δ4.4 meV, is significantly larger than the $T \to 0$ BCS theory prediction of 2.73 meV. Furthermore, the average value of Δ (4.2 K) determined from these

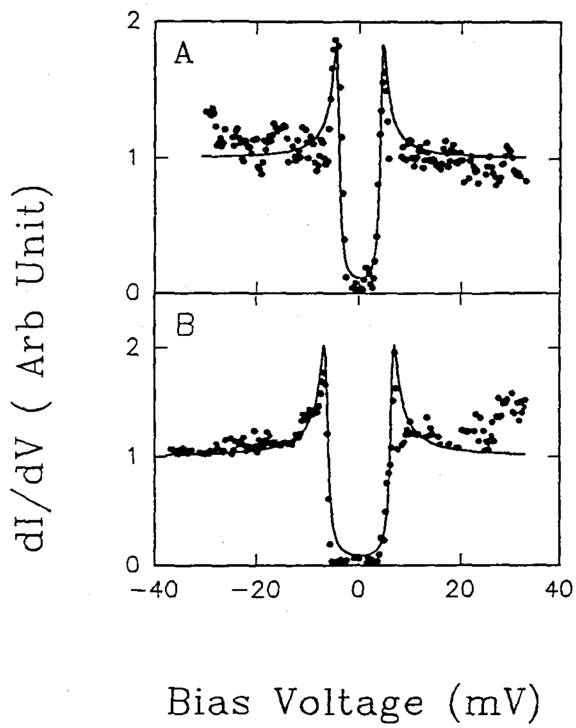

Fig. 3. Conductance versus voltage dI/dV curves for K_3C_{60} and Rb_3C_{60} at 4.2 K. The experimental data (filled circles) were obtained by numerically differentiating the I–V data. The solid lines correspond to the best fits of this data to the expression $dI/dV = \mathrm{Re}[|E - i\Gamma|/((E - i\Gamma)^2 - \Delta^2)^{1/2}]$. The values of the energy gap Δ and broadening function Γ in meV are $\Delta = 4.4$, $\Gamma = 0.5$ and $\Delta = 6.6$, $\Gamma = 0.6$ for K_3C_{60} and Rb_3C_{60}, respectively.

experiments yield a reduced energy gap $2\Delta/kT_c \pm 1SD$, of 5.3 ± 0.2 for K_3C_{60}. The value of the reduced energy gap at 4.2 K for Rb_3C_{60}, 5.2 ± 0.3, is the same within experimental error, and therefore we conclude that Δ scales with T_c in these materials. Importantly, the large value of $2\Delta/kT_c$ for the M_3C_{60} superconductors shows that the coupling in these materials is strong.

It is interesting to consider the implications of strong-coupling. Within the context of phonon-mediated pairing, theoretical work has shown that a large-value of Δ can arise from strong coupling to low-frequency modes. In the M_3C_{60} solids C_{60}–C_{60} intermolecular vibrations and C_{60} rotations are low frequency (≤ 60 cm^{-1}).[11] In fact, the C_{60}–C_{60} mode has a frequency close to 2Δ and could therefore couple very strongly to the electrons. Alternatively, it has been suggested that the M^+ optical phonon could lead to strong coupling.[12] High frequency intramolecular C_{60} modes, which have been implicated in weak-coupling analyses,[2,6] are unlikely to yield the large value of $2\Delta/kT_c$ determined experimentally, however, a high-frequency mode could be responsible for the relative high T_c's observed in these materials. Although

additional work is needed to define whether the electron-phonon interaction is the operative coupling mechanism and if so the mode relevant to pairing, our finding of strong coupling should be accounted for in models of superconductivity in these materials.

In conclusion, tunneling spectroscopy has been used to define the energy gap in the M_3C_{60} superconductors. These experimental results have shown that the pair coupling in these materials is strong, and that the energy gap scales with T_c. Regardless of the mechanism of pairing in the M_3C_{60} system, our results will serve as important constraints for any theoretical explanation of superconductivity in these materials.

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