Measurement of the Energy Gap in an Organic Superconductor: Evidence for Extremely Strong Coupling

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Point-contact tunneling is used to make what we believe to be the first measurement of a superconducting energy gap (Δ) in an organic superconductor. For a β-[*bis*(ethylenedithio)tetrathiafulvalene]$_2AuI_2$ single crystal, Δ shows consistent field and temperature dependences, but is more than 4 times larger than weak-coupling BCS value, implying extremely strong coupling. We speculate that very low-frequency modes may be responsible.

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We describe a point-contact tunneling experiment which, we believe, provides the first measurement of a superconducting energy gap, Δ, in an organic superconductor. The organic superconductor is a single crystal of the S-based β-(BEDT-TTF)$_2AuI_2$, or β-(ET)$_2AuI_2$, with $T_c \sim 3.8$ K at ambient pressure, and the tunneling counterelectrode tip is nonsuperconducting gold. In this Letter, we denote BEDT-TTF, *bis*(ethylenedithio)tetrathiafulvalene, with chemical formula $C_{10}H_8S_8$ as ET. The current-voltage characteristics, $I(V)$, show reasonable agreement with the standard interpretation of normal-metal–superconductor (NS) tunneling using the BCS density of states. The magnitude of Δ obtained from this analysis is considerably higher than the weak-coupling limit ($1.76k_BT_c$ at $T=0$) when the tip movement is perpendicular to the low-conductivity c^* axis,[1] but the preliminary, though incomplete, temperature dependence is consistent with BCS theory. The one datum point obtained with the tip movement parallel to the c^* axis is considerably smaller. In addition to measuring the gap, we have demonstrated that its decrease in small magnetic fields is consistent with inductive measurements of critical fields in this material.[2]

The importance of such gap measurements stems from potential differences between organic superconductors and standard metal-containing systems. For example, the conduction electrons may exhibit a reduced dimensionality leading to an anisotropic band structure[3] and the electron-phonon coupling may include libration and/or intramolecular modes.[4] More *et al.*[5] have suggested a gap vlaue about 12 times the BCS weak-coupling value for (TMTSF)$_2PF_6$ under pressure, on the basis of Schottky tunneling. TMTSF is tetramethyltetraselenafulvalene, $C_{10}H_{12}Se_4$. More recent tunneling studies[6,7] of the ambient-pressure organic superconductor (TMTSF)$_2ClO_4$ have not confirmed this observation; however, only one study[6] included temperatures well below T_c, and in that case the large gap of the superconducting Pb counterelectrode could have obscured the determination of the gap in the organic metal. For example, no variation of gap with temperature nor magnetic field was reported.[6]

The apparatus used in the present experiment is our variation of the vacuum-tunneling devices in common use for scanning microscopy[8] and for spectroscopic analysis of superconductors.[9] An electrochemically polished gold tip is moved along a direction perpendicular to the sample surface by the combined action of a differential micrometer and a stack of piezoelectric crystals. These are placed in a suitably rigid assembly mounted in a liquid-helium cryostat which is isolated from external vibration by use of a sandbox mounted on an air-suspension system. The unit is operated in an acoustic, screened room in a quiet corner of our laboratory basement.

This system has been tested in a number of ways. With use of chemically inert samples, such as Au, the exponential dependence of current on tip movement demonstrated vacuum tunneling.[8] Spectrum analysis of such junctions indicated that vibrations could be virtually eliminated. In addition, vacuum-tunneling data on single crystals of $ErRh_4B_4$ were analyzed by the same method as used for the β-(ET)$_2AuI_2$ (below), and showed the expected[9] superconducting gap of 1.15 meV at ≈ 2 K. On the other hand, samples exhibiting an insulating surface layer (e.g., an oxide) required mechanical touching, but could be analyzed as point-contact tunneling.[10] Our tests included observations of the superconducting energy gap in Pb and Nb as well as the present study of β-(ET)$_2AuI_2$.

The β-(ET)$_2AuI_2$ crystals were grown[11] by electrochemical oxidation of ET at a constant current of 1.0 μA/cm^2 in the presence of anhydrous [(n-$C_4H_7)_4N$]AuI_2 as the supporting electrolyte at 23.3 °C. With tetrahydrofuran as the solvent, we obtained three different phases of the (ET)$_2AuI_2$ crystals. The majority are the "distorted hexagon shaped" β-phase crystals which have a characteristic room-temperature EPR peak-to-peak linewidth of 18–20 G, and they were used in this study. The two other phases, Γ- and Γ'-(ET)$_2AuI_2$, are both thin plates with EPR linewidths of

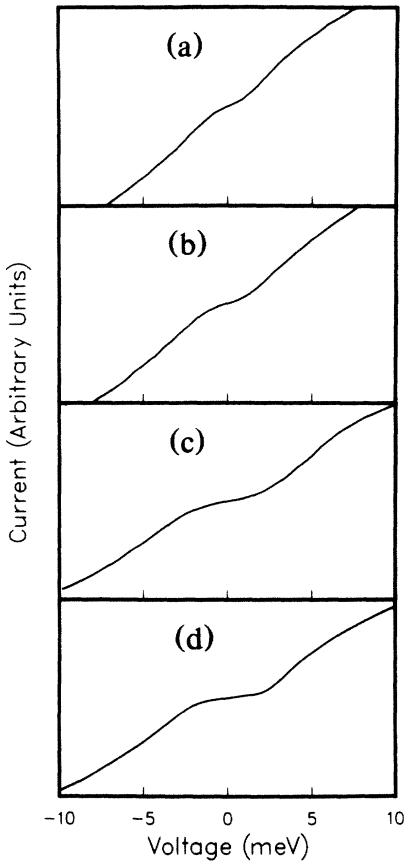

FIG. 1. The current-voltage characteristics for point-contact tunneling between β-$(ET)_2AuI_2$ and a nonsuperconducting Au tip: (a) tip movement parallel to the c^* axis at $T = 2.15$ K; (b)–(d) tip perpendicular to the c^* axis for $T = 3.25$, 2.5, and 2.4 K, respectively.

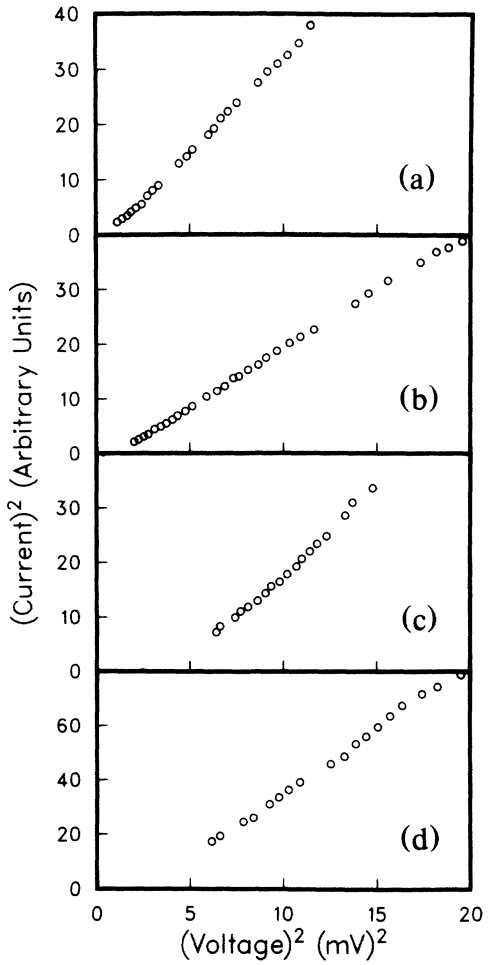

FIG. 2. Plots of I^2 vs V^2, showing agreement with the expectations of NS tunneling. The extrapolation to $I^2 = 0$ has an intercept at Δ^2. (a)–(c) Same data as Figs. 1(a)–1(c); (d) taken right after (c) in a field of 1 kOe.

27–35 and 10–15 G, respectively. The T_c was determined by a standard ac susceptibility technique.[12] The change in the real part of the susceptibility yielded an onset T_c of 3.8 K with a broad transition, ~ 1 K wide. The sample was mounted for tunneling by the attachment of 0.0005-in. Au wires to Au stripes evaporated on the crystal, by means of Ag-filled conductive paint. These Au wires also provided electrical contact and were looped before soldering to electrical posts to prevent strain on the crystal during thermal cycling.

Figure 1 shows a collection of $I(V)$ curves for a single sample under various experimental conditions. It should be noted that while such curves showing distinct gap structure were reproduced many times on different low-temperature runs, they could not be obtained routinely, nor maintained indefinitely. Thus a complete set of curves versus temperature was impossible with the present apparatus, since changing the bath temperature, and hence pressure, led to irreconcilable movements of the tip. It is also important to realize that several qualitatively different $I(V)$ curves could be obtained at different tip "positions" (caused by changes of the piezoelectric voltage and hence the force on the point contact). A variety of point-contact $I(V)$ curves have been nicely compiled and explained by Blonder and Tinkham,[10] and we have also observed the entire spectrum, from tunneling to microshorts, that is suggested by their theoretical and experimental analysis. In addition, we have observed a higher-resistance region for low voltages, but without the sharp rise at $V = \Delta$ and bending back at higher voltages that one expects for tunneling. We have no explanation for this, but it may be related to the nonsuperconducting behavior of β-$(ET)_2AuI_2$, since it was also seen above T_c.

We have analyzed only those data which are symmetric and show bending back of $I(V)$ at high voltage. We fit the $I(V)$, for $V > \Delta$, by the standard ($T = 0$) BCS expression $RI(V) = (V^2 - \Delta^2)^{1/2}$, where R is the high-voltage ($V >> \Delta$) junction resistance. By direct

calculation, we find that the effect of finite-temperature smearing leads to an overestimate of the actual Δ, but by no more than 7% in the worst case reported here. Since this is less than the "error bars," we report values of the intercept. This procedure avoids the weakness of assigning Δ to the peak in dI/dV, which could be incorrect because of gap smearing and possible leakage current, and even in ideal cases is 5%–10% larger than Δ as a result of finite temperature.[13] It is most convenient to make plots of I^2 against V^2, as shown in Fig. 2. In that case the slope is R^{-2} and the intercept is Δ^2. Deviations are to be expected for small currents because of finite temperature and possible leakage current.

A summary of the Δ values, with error bars reflecting the latitude of fitting the data of Fig. 2, are shown in Fig. 3. The data for zero field, with the tip movement perpendicular to the c^* axis but at an arbitrary azimuthal angle, are consistent with a BCS temperature dependence, but with a magnitude well in excess of the weak-coupling value at $T=0$ of $1.76k_BT_c \simeq 0.6$ meV. An additional datum point shows that application of a small magnetic field (~ 1 kOe) reduced the gap by about 10%–20%, which is reasonably consistent with expectations based on inductive measurements on this material.[2] The above measurements give a strong indication that we are measuring a BCS superconducting gap, in spite of its large value.

A very powerful potential of vacuum tunneling is to study the gap anisotropy in single-crystal samples since tunneling occurs preferentially along the direction perpendicular to the sample surface. The highly anisotropic band structure of these organic superconductors could certainly lead to a gap anisotropy. However, for the present case of point-contact tunneling, one cannot be sure of the tunneling direction. Thus, while we see a considerably smaller Δ (about 30% as big) for the tip movement parallel to the c^* axis, which is suggestive of large gap anisotropy, we can never be absolutely certain which direction is being probed. In addition, for the crystal face with the small gap, scanning electron microscopy (SEM) studies show some evidence of damage; however, it is impossible to determine whether the exact tunneling location coincided with any damaged region. To evaluate the anisotropy we would prefer having a method to clean the insulating surface layer, *in situ*, which leaves the superconductivity undisturbed, so that vacuum tunneling can be done.

The large gap value deserves further discussion, since experimental artifacts usually result in too small a gap value. Exceptions include an improper four-terminal measurement, which can lead to larger measured voltages ($V+IR_c$, where R_c is a series contact resistance). However, in our experiments the two contacts to the organic crystal were physically separated and the total resistance, including crystal, was

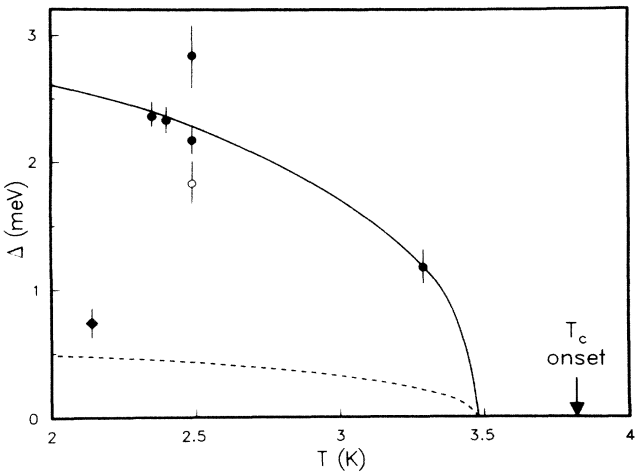

FIG. 3. The temperature dependence of Δ determined from plots like those of Fig. 2. Solid circles represent data taken with the tip movement perpendicular to the c^* axis. Also included are data (open circle) in a field of ~ 1 kOe and (lozenge) for the tip movement parallel to the c^* axis. The dashed curve represents the weak-coupling result of BCS theory for $T_c = 3.45$ K, and the solid curve is the BCS result, scaled vertically to match our data.

$\lesssim 100\ \Omega$ at low temperature. The estimated spreading resistance of the Au tip for a contact area of diameter 10 Å is likewise of the order of 100 Ω. Junction resistances for $V >> \Delta$ were always of order $10^6\ \Omega$, implying a negligible contribution for R_c. We can also consider whether tunneling may be occurring between two grains[14] of β-$(ET)_2AuI_2$, which would yield structure in $I(V)$ at 2Δ. Although a possibility, it seems unlikely for several reasons. First, the $I(V)$ for SS tunneling shows a sharp jump at $V=2\Delta$ rather than the smooth increase calculated for NS tunneling, with which our data agree quite well. Also, the similar values of Δ measured at ≈ 2.4 K were taken on three separate low-temperature runs for which the precise locations of the tunneling areas (of the order of 10 Å linear dimension), on both the tip and sample, must have been significantly different. It is unlikely that they all resulted in the unusual SS tunneling. After completion of the tunneling measurements, the tip was observed under an SEM and revealed no evidence for chips of β-$(ET)_2AuI_2$ nor damage. Finally, one can also consider whether the large Δ results from an enhanced T_c due to the pressure exerted by the point-contact tip. However, SEM studies reveal no evidence of damage by the tip for the surface on which the large gap was measured, and pressure studies[15] of β-$(ET)_2AuI_2$ show only decreases in T_c.

We offer a speculation on the origin of the large Δ. Strong-coupling superconductors are usually associated with very low-frequency phonons (e.g., Pb and Hg). Analysis of the Eliashberg equations by Bergmann and

Rainer[16] and Mitrovic, Leavens, and Carbotte[17] indicate that high phonon frequencies ($\omega \sim 8k_BT_c$) affect T_c most,[16] while $\Delta(0)$ and $\Delta(0)/k_BT_c$ are affected most by lower phonon frequencies ($\sim 4k_BT_c$ and $\sim 1.3k_BT_c$, respectively). Low-frequency libration and/or intramolecular (especially torsional and bending) modes may couple strongly to the conduction electrons in these organic superconductors, since the electron transmission probability from molecule to molecule may be strongly affected by such modes. Geilikman, Kresin, and Masharov[18] have solved the Eliashberg equations for an Einstein mode. They find that $\Delta(0)/k_BT_c$ can be significantly greater than that predicted by the weak-coupling BCS theory, but their solution is not valid for very low-frequency modes $\omega \lesssim \Delta(0)$. Experimental evidence for very low-frequency modes in organic superconductors is sparse; however, a 30-cm^{-1} mode (3.7 meV) has been seen[19] in $(TMTSF)_2PF_6$. Whether the above theories are appropriate for such large $\Delta(0)/k_BT_c$ values is unclear, but the first-order effect is in the right direction. Thus these experimental results establish the clear need for further experimental and theoretical work.

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