Direct evidence for Cooper pairing without a spectral gap in a disordered superconductor above $T_c$

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The idea that preformed Cooper pairs could exist in a superconductor at temperatures higher than its zero-resistance critical temperature ($T_c$) has been explored for unconventional, interfacial, and disordered superconductors, but direct experimental evidence is lacking. We used scanning tunneling noise spectroscopy to show that preformed Cooper pairs exist up to temperatures much higher than $T_c$ in the disordered superconductor titanium nitride by observing an enhancement in the shot noise that is equivalent to a change of the effective charge from one to two electron charges. We further show that the spectroscopic gap fills up rather than closes with increasing temperature. Our results demonstrate the existence of a state above $T_c$ that, much like an ordinary metal, has no (pseudo)gap but carries charge through paired electrons.

The zero-resistance state of superconductivity emerges when electrons form Cooper pairs, which condense into a superfluid with long-range phase coherence. For conventional, elemental superconductors, pairing and condensation take place concurrently when cooling below the critical temperature ($T_c$). By contrast, disordered superconductors exhibit unusual normal state properties above $T_c$ ($1$–$9$), which, analogous to high-temperature ($10$–$14$), interface ($15$–$17$), and heavy fermion superconductors ($18$, $19$), were thought to be a consequence of preformed or fluctuating Cooper pairs that could exist above $T_c$. However, there is no direct experimental evidence of this.

There have been several theoretical descriptions for electron pairs without superconductivity, i.e., without phase coherence (Fig. 1A). The best-known models postulate a phase fluctuation–driven breakdown of coherence at $T_c$ ($1$, $20$). Although strictly speaking only valid for neutral superfluids, such a breakdown has a particularly intuitive picture in the Berezinskii-Kosterlitz-Thouless theory: Fluctuating vortex-antivortex pairs that exist below $T_c$ unbind at $T_c$, leading to the charge from superconducting to resistive state as the temperature is increased ($21$). Phase fluctuations are also at the core of models involving the Bose-Einstein condensation (BEC) to Bardeen-Cooper-Schrieffer (BCS) crossover ($22$), which were realized in cold atom ensembles. An alternative scenario for the breakdown of superconductivity is a decrease of the order-parameter amplitude, which is caused by enhanced Coulomb repulsion in disordered systems ($23$). Phase-fluctuation models invoke paired electrons above $T_c$, whereas pairing amplitude models do not.

The challenge to experimentally distinguishing phase-incoherent paired electrons from single electrons is twofold: (i) many properties of paired but uncondensed electrons are the same as for single electrons, including the charge transported per electron, and (ii) spectroscopic signatures of paired electrons are often similar to single-electron phenomena such as charge density waves ($10$). Nevertheless, there have been many interesting observations connected to pairing above $T_c$ reported in different families of unusual superconductors. First, kinks in resistivity versus temperature curves and deviations from assumed normal state resistances have been connected to pairing fluctuations in disordered and cuprate high-temperature superconductors ($3$, $5$, $11$). Second, the Nernst effect has shown the existence of a pseudogap onset temperature above $T_c$ in cuprate, heavy fermion, and disordered superconductors, which is compatible with short-lived Cooper pair fluctuations ($12$, $13$, $19$). Third, in underdoped cuprates, enhanced noise signatures have been observed in planar junctions and interpreted as pairing of electrons, both in the superconducting state and above $T_c$ ($14$). Enhanced noise has even been observed at bias voltages greater than the superconducting gap. Fourth, several spectroscopic techniques show (partially filled) gaps in the spectral weight at the Fermi level, frequently called pseudogaps, that persist above $T_{co}$ in disordered, cuprate, interfacial, and heavy fermion superconductors ($1$, $7$, $10$, $16$, $18$). These observations, which differ in many respects from expectations for the conventional metallic state in ordinary metals, have been interpreted as being due to a finite population of paired electrons.

Our study aimed to determine the nature of the charge carriers in this unconventional normal state in disordered superconductors by focusing on the effective charge of the carriers in tunneling experiments as measured by noise spectroscopy. Shot noise spectroscopy in mesoscopic systems has proven to be a powerful tool to determine the effective charge, e.g., in superconductors or in fractional quantum Hall experiments ($24$). In general, tunneling between two leads biased with voltage $V$ is a Poissonian process. The current noise $S = \langle (I - \langle I \rangle)^2 \rangle$ associated with the granularity of charge is proportional to the effective charge $q^*$ of the carrier and the current $I$, i.e., $S \approx 2q^*|I|$. This relation allows the extraction of the effective charge of the carriers, which in metal-insulator-superconductor interfaces (NIS) is equal to one electron charge ($1e$) at biases above the superconducting gap (Fig. 1B) but equal to $2e$ within the gap. The latter is a result of Andreev reflections from paired electrons, which double the effective charge transported ($25$), as illustrated in Fig. 1C. The signature for paired electrons is thus simple and unambiguous: In a tunneling experiment from a normal metal to a system with bound pairs, the normalized noise should change from $S/2I = 1e$ to $S/2I = 2e$ when the bias is reduced to below the gap energy. Experiments involving conventional superconductors have confirmed the doubling, and even further multiplication, of shot noise as a tell-tale signature of paired electrons ($25$–$28$); however, ensuring a clean vacuum barrier has proven to be challenging.

We chose to use the disordered superconductor titanium nitride (TiN) ($29$) for this study because it exhibits robust signatures of unusual physics above $T_c$ without any competing orders such as charge density waves ($10$). Similar to other disordered superconductors, TiN can be tuned toward a superconductor-metal or superconductor-insulator transition ($I$) and exhibits electronic granularity that might be emergent ($30$) or caused by small superconducting islands coupled to each other. Our TiN films developed a zero-resistance state, i.e., became superconducting below $2.95$ K as determined by transport measurements, and exhibited a mean free path of $0.57$ nm, with a coherence length of $\sim 10$ nm, placing them well within the so-called “dirty limit” of superconductivity. We used 45-nm-thick films fabricated by plasma-enhanced atomic layer deposition (ALD) ($29$) and, as control samples, 60-nm-thick films made by sputter deposition on silicon substrates (the data from

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the sputtered sample were qualitatively similar; figs. S4, C and D, S6, and S7). The samples were inserted into an ultrahigh vacuum chamber and then into a cryogenic scanning tunneling microscope (STM). The noise measurements were done with a custom-built, cryogenic MHz amplifier consisting of a superconducting tank circuit and custom-built high electron mobility transistors, as described elsewhere. From the noise spectroscopic measurements, we measured the current fluctuations around a center frequency of 3 MHz to avoid mechanical resonances and unwanted 1/f noise and ensured that the vacuum tunneling barrier was clean by repeatedly measuring topographies with the STM (fig. S1). Spectroscopic imaging STM at 2.3 K revealed a partially filled gap of 1.78 meV with spatial variations of ~36% (fig. S4).

Local tunneling noise spectroscopy is the key technique used in this study. We performed our experiments at fixed junction resistance ($R_J$), so the noise is expected to be proportional to the bias voltage, $S(q^*,V) = 2q^*|V| = 2q^*|V/R_J|$. At finite temperature ($T$) and low junction transmission, the formula is modified to $S(q^*,V) = 2q^*(V/R_J)^2|\coth(q^*V/2k_B T)|$, where $k_B$ is the Boltzmann constant. We extracted the effective charge $q^*$ by numerically solving this formula for the observed shot noise at each bias (33). As expected, the effective charge at a bias higher than $\Delta$ was equal to one electron charge, $q^* = 1e$, as shown in Fig. 2, A and B. However, a clear change in the effective charge from $q^* = 1e$ to $q^* = 2e$ is visible in the data for voltages below gap energy. This is unambiguous evidence that the electrons in TiN films were paired below an energy of $\Delta$ (indicated in Fig. 2 by blue shading). The reason that the noise did not rise immediately at $\Delta$ but at energies just below $\Delta$ is thermal broadening (33). The shape and values of our noise spectra enabled us to directly deduce pairing as the source of the noise, as opposed to fluctuating orders that might be present in the sample.

The noise enhancement to 2e persisted when warming the sample to temperatures above the zero-resistance $T_c$. Figure 3 shows noise spectra acquired at different temperatures ranging from 2.3 to 7.2 K, which correspond to 0.78 and 2.43 $T_c$, respectively. Up to more than twice $T_c$, the noise spectra still show enhanced noise corresponding to 2e; only at $T = 2.43 T_c$ does the noise decrease below 2e. Given that $T_c$ is far below the temperature at which the noise is enhanced, there is another transition temperature, which we denote here by $T_{p}$, associated with pairing. In a fluctuation picture, this would be the temperature at which the gap opens. Figure 4 summarizes the temperature evolution of the noise.

We can compare how $T_{p}$ scales with the unusual transport properties that have been analyzed for a wide range of disordered superconductors. Figure 4C shows a resistance versus temperature curve showing the superconducting transition at $T_c = 2.95 K$. At ~11 K, the resistance curve shows a so-called V-shaped curvature (fig. S3), as is typical for disordered superconductors not too close to the superconductor-insulator transition (3) and for cuprate high-temperature superconductors (34). This local maximum at 11 K is a signature that has been interpreted as the onset of superconducting fluctuations (3, 35). For the ALD sample in Fig. 4C, this is also roughly the temperature at which the gap is expected to close if the ratio 2$\Delta(0)/k_B T_p$ is given by the BCS value of 3.52; for the sputtered sample, we obtained a lower mean-field prediction for $T_p$ (fig. S7).

Our most unexpected experimental observation was the pairing above $T_c$ even in the absence of a spectroscopic (pseudo)gap. As shown in Fig. 4, A and B, the gap in the differential tunneling conductance of TiN filled up at $T_c$ when increasing the temperature instead of closing, i.e., $\Delta(T)$ was constant while the spectral weight inside the gap was filling up. To ensure that the 2e noise was not incidentally measured in coherent superconducting “puddles,” we measured these
spectra at the same locations where we performed the noise measurements (figs. S1 and S4). Although the measured temperature evolution $\Delta(T)$ resembles findings in other disordered superconductors, the gap filled faster in our samples upon increasing temperature such that the gap was fully filled at $T_c$. Partial gap filling has been observed with various probes in other disordered and unconventional superconductors (7, 36–38). The gap filling can be calculated within models involving strong fluctuations of the order parameter (39) or large level spacing in grains (40); alternatively, one can postulate a large fraction of unpaired electrons, or electrons with very small superconducting gaps, to exist in parallel to the superfluid (36, 41). Our data show that the current noise continued to correspond to $\sim 2e$ at elevated temperatures despite the filling of the gap. The state above $T_c$ thus behaves like an ordinary metal from a spectroscopy point of view but with tunneling current fluctuations that indicate pairing. This is only visible in shot noise experiments. Therefore, a putative coexistence of paired and unpaired electrons, as predicted to exist by theories of short-lived Cooper pairs (1, 12, 13), is not present in TiN.

We note that the combined observation of a filled gap and $2e$ noise cannot be described in the same way as the well-known case of subgap current in break junctions of elemental superconductors (25). In break junctions with low transparencies, the conductance inside the gap is much smaller than outside because Andreev reflections happen with a probability proportional to the square of the transparency of the junction ($t^2$), whereas single-electron tunneling outside the gap occurs with probability $t$. By contrast, in TiN, we measured a similar conductance inside

**Fig. 2. Evidence for pairing in TiN from scanning noise spectroscopy.** (A) Noise in the tunneling junction ($R_J = 5 \, M\Omega$) between the STM tip and TiN sample at 2.3 K, with the thermal amplifier noise subtracted, as function of the bias voltage. (B) Spectroscopy of the effective charge $q^*(V)$ at 2.3 K. In both panels, blue points represent experimental data and dashed lines indicate the expected noise for $q^* = 1e$ and $q^* = 2e$. Blue shading indicates the spectral gap observed in the differential conductance (Fig. 4A). The solid blue curves indicate a step from $1e$ to $2e$, broadened by the respective thermal resolution (fig. S8).

**Fig. 3. Enhanced noise above $T_c$.** (A) Noise spectroscopy on a TiN sample for different temperatures from $2.3 \, K = 0.78 \, T_c$ to $7.2 \, K = 2.43 \, T_c$. Blue points indicate the measured excess noise in the junction ($R_J = 5 \, M\Omega$) as function of bias voltage. The different temperature curves are offset for clarity. Dashed lines indicate the expected noise for $q^* = 1e$ and $q^* = 2e$. Solid lines indicate the expected noise when a change from $1e$ to $2e$ occurs at $\Delta$. including the thermal resolution at the given temperature. Blue shading highlights the spectral gap in the differential conductance. (B to E) Effective charge $q^*(V)$ for the four different temperatures. Data for the ALD (sputtered) sample are shown in blue (orange). The solid blue and orange curves indicate a step from $1e$ to $2e$ at $\Delta$, broadened by the respective thermal resolution (fig. S8).
and outside that gap that was independent of the junction resistance, despite the fact that our transparency was $-2.6 \times 10^{-3} \times 1$. The probability for charge transfer in the range of 2e noise is therefore still linear in transparency. Such a situation could, in principle, arise when the bunching of the probability for subsequent electron transfers is modulated because of Andreev processes within the sample or the diffusive character of the charge in disordered metals (25). More likely, a theory involving the spatial heterogeneity and correlations that are typical for disordered superconductors is needed to understand this peculiar state.

In summary, we have used local noise spectroscopy as an unambiguous probe of pairing in a disordered superconductor. We have shown that (i) pairing dominates up to a temperature scale $T_\mu$ much larger than $T_c$, (ii) the energy of pairing is related to the gap energy, and (iii) even though the spectral gap is partly or fully filled, almost all observed electrons are paired, differentiating between proposals for pairing above $T_c$. Therefore, we have observed a state that exhibits 2e noise despite having the characteristics of an ordinary metal in differential conductance, without a spectroscopic (pseudo)gap. Further, our results contradict theories of the breakdown of superconductivity that involve a large fraction of unpaired electrons.

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**SUPPLEMENTARY MATERIALS**

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Materials and Methods
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