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# Josephson and noise scanning tunneling microscopy on conventional, unconventional and disordered superconductors

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# 6

## Noise above $T_C$ in a disordered superconductor

*The idea that preformed Cooper pairs could exist in a superconductor above its zero-resistance state has been explored for unconventional, interface, and disordered superconductors, yet direct experimental evidence is lacking. In this chapter, we use scanning tunneling noise spectroscopy to unambiguously show that preformed Cooper pairs exist up to temperatures much higher than the zero-resistance critical temperature  $T_C$  in the disordered superconductor titanium nitride, by observing a clear enhancement in the shot noise that is equivalent to a change of the effective charge from 1 to 2 electron charges. We further show that the spectroscopic gap fills up rather than closes when increasing temperature. Our results thus demonstrate the existence of a novel state above  $T_C$  that, much like an ordinary metal, has no (pseudo)gap, but carries charge via paired electrons*

## 6.1. Introduction

Disordered superconductors, like the titanium nitride (TiN) thin films that are the focus of this study, are close to a superconductor-metal or superconductor-insulator transition [1], and often exhibit electronic granularity, either emergent [2] or due to small superconducting islands coupled to each other. Above  $T_C$ , disordered superconductors exhibit unusual normal state properties, often including anomalous resistivity [3–7] and a so-called pseudogap in spectroscopic properties [8]. Similar to the case of high-temperature [9], interface [10, 11], and heavy fermion superconductors [12], these properties have sometimes been interpreted as signatures of short-lived, fluctuating [5, 13], or pre-formed Cooper pairs [1, 14] that do not form a phase-coherent state. Such a situation would be in strong contrast to conventional, elemental superconductors, where pairing and condensation take place concurrently at the critical temperature  $T_C$ .

The concept of pairing without phase coherence (Fig. 6.1a) was introduced even before the famed Bardeen-Cooper-Schrieffer theory explained the microscopic origin of superconductivity [15], and new theoretical models are still being explored. The most well-known models, going back to Fisher [16] and others, postulate a phase-fluctuation driven breakdown of coherence at  $T_C$ . The Berezinskii–Kosterlitz–Thouless formalism brings a particularly intuitive picture of such a transition: fluctuating vortex-antivortex pairs that exist below  $T_C$ , unbind at  $T_C$ , leading to the change from superconducting to resistive state as the temperature is increased [17, 18]. Phase fluctuations are also at the core of models involving the Bose-Einstein condensation to Bardeen-Cooper-Schrieffer (BEC-BCS) crossover [19] which were realized in cold-atom ensembles. An alternative possibility to break down superconductivity is a decrease of the order parameter amplitude, caused by enhanced Coulomb repulsion in disordered systems [20]. The former models invoke paired electrons above  $T_C$ , while the latter does not.

The challenge to experimentally discern phase-incoherently paired electrons from single electrons is twofold. First, many properties of paired but uncondensed electrons are the same as for single electrons, including the charge transported per electron. Second, spectroscopic signatures of paired electrons are often similar to single-electron phenomena like charge density waves [9]. Still, a large number of intriguing observations connected to pairing above  $T_C$  have been reported. Kinks in resistivity versus temperature curves and deviations from assumed normal state resistances have been connected to pairing fluctuations [21]. The Nernst effect has shown unusual signatures in several materials, compatible with short-lived Cooper-pair fluctuations [22, 23]. In underdoped cuprates, enhanced noise signatures have further been reported in planar junctions and interpreted as multiple Andreev reflections enabled by pairing of charge carriers above  $T_C$  [24]. Several spectroscopic techniques show (partially filled) gaps in the spectral weight at the Fermi level, frequently called pseudogaps, that persist above  $T_C$ . Taken together, the observations described here point towards a transition at  $T_C$  from a macroscopic quantum state with zero resistance, towards a state where the resistance becomes finite, but which is in many respects different from the conventional metallic state of ordinary metals.

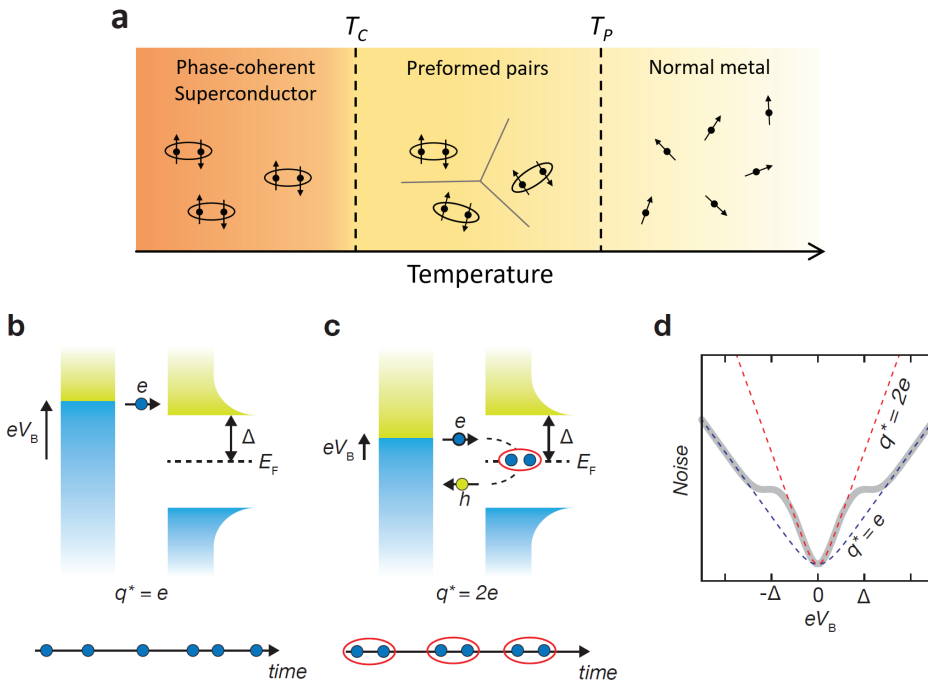


Figure 6.1: **Noise spectroscopy as a direct probe to detect paired electrons.** **a** Illustration of the different electronic states. At high temperature, a conventional metal state consists of single electrons. Below  $T_C$ , these electrons couple to form a phase-coherent state of Cooper pairs. Between these two, an additional state of non-phase-coherent, preformed Cooper pairs is conjectured to exist. **b** 'Normal' NIS transport of single electron charge. The characteristic density of states of the superconducting sample is shown, with filled and empty states denoted by blue and yellow separated by a pair-breaking gap  $\Delta$ . **c** Andreev reflection process in a BCS superconductor. An electron transfers a Cooper pair into the superconductor by reflecting a hole in the opposite direction, effectively transferring  $2e$  charge. **d** Noise as function of bias voltage for  $q^* = 1e$  and  $q^* = 2e$  transport. For a NIS junction the expected noise is indicated by the gray curve.

## 6.2. Charge detection using shot noise

Thus motivated, our study aims 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, measured through 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 [25]. In general, tunneling between two leads biased with voltage  $V$  is a Poissonian process. The current noise  $S$  associated with the granularity of charge is proportional to the effective charge  $q^*$  of the carrier and the current  $I$ , i.e.  $S = 2q^*I$ . This relation allows to extract 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. 6.1b), but

$2e$  within the gap. The latter is a result of Andreev reflections from paired electrons which double the effective charge transported [26] as illustrated in Fig. 6.1c. 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 [26–29], but ensuring a clean vacuum barrier has shown to be challenging.

### 6.3. Experimental methods

We choose to use the disordered superconductor titanium nitride [30] for this study as it exhibits robust signatures of unusual physics above  $T_C$  without any competing orders such as charge density waves [9]. Our TiN films develop a zero-resistance state, i.e. become superconducting below 2.95 K as determined by transport measurements, and exhibit 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 use 45 nm thick films fabricated by plasma-enhanced atomic layer deposition (ALD) [30], and as control samples 60 nm thick films made by sputter deposition on silicon substrates. Data from the sputtered sample are qualitatively similar and shown in Appendix C (see Figs. C.7 and C.8). The samples are first inserted into an ultrahigh vacuum chamber, and subsequently into a cryogenic scanning tunneling microscope (STM). The noise measurements are done with a custom-built, cryogenic MHz amplifier, consisting of a superconducting tank circuit and custom-built high electron mobility transistors (HEMT), as described elsewhere [31]. From the noise spectroscopic measurements, we measure the current fluctuations around a center frequency of 3 MHz to avoid mechanical resonances and unwanted  $1/f$  noise, and we ensure that the vacuum tunneling barrier is clean by repeatedly measuring topographies with the STM [32] (see Appendix C). Spectroscopic imaging STM at 2.3 K reveals a partially filled gap of  $\Delta = 1.78$  meV (with spatial variations of around 36 % (see Fig. C.4).

Local tunneling noise spectroscopy is the key technique used in this study. We perform our experiments at fixed junction resistance ( $R_J$ ), and thus the noise is expected to be proportional not only to the current, but also to the bias voltage,  $S(q^*, V) = 2q^*I = 2q^*V/R_J$ . At finite temperature ( $T$ ) and low junction transmission, the formula is modified to  $S(q^*, V) = 2q^*(V/R_J) \coth(q^*V/2k_B T)$ , where  $k_B$  is the Boltzmann constant. We extract the effective charge  $q^*$  by numerically solving this formula for the observed shot-noise at each bias (see Appendix C for details) [26]. As expected, the effective charge at a bias higher than  $\Delta$  is equal to one electron charge,  $q^* = 1e$ , as shown in Figs. 6.2a and b. However, a clear change in the effective charge from  $q^* = 1e$  to  $q^* = 2e$  is visible in the data for voltages below the gap energy. This is unambiguous evidence that the electrons in TiN films are paired below an energy of roughly  $\sim \Delta$  (indicated in Fig. 6.2 by blue shading). The reason that the noise does not rise immediately at  $\Delta$ , but at energies just below  $\Delta$  is due to thermal broadening as we show in Appendix C. The shape and values of

our noise spectra enable us to directly deduce pairing as the source of the noise, as opposed to fluctuating orders that might be present in the sample.

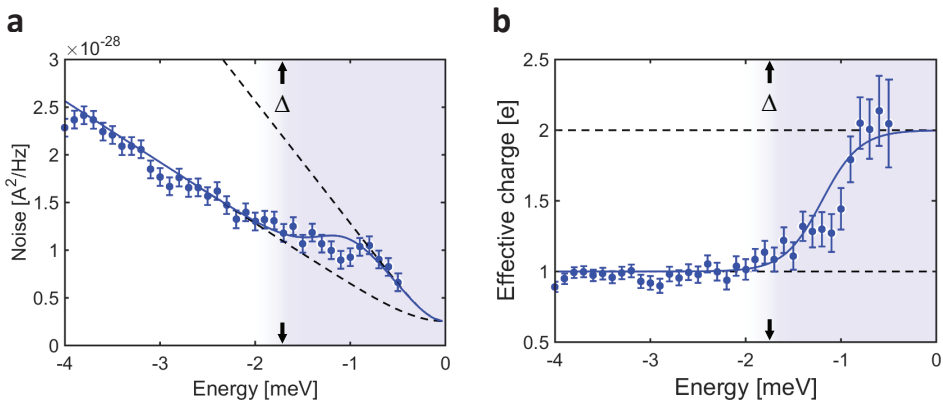


Figure 6.2: **Evidence for pairing in TiN from scanning noise spectroscopy.** **a** The noise (blue dots) in the tunneling junction ( $R_J = 5 \text{ M}\Omega$ ) between the STM tip and TiN sample at 2.3 K with the thermal amplifier noise subtracted, as a function of the bias voltage. Dashed lines indicate the expected noise for  $q^* = 1e$  and  $q^* = 2e$ . Blue shading indicates the spectral gap observed in the differential conductance (Fig. 6.4a). The blue curves represent a guide to the eye to indicate thermal broadening similar to expectations from a random scattering matrix simulation (see Appendix C). **b** Spectroscopy of the effective charge  $q^*(V)$  at 2.3 K.

## 6.4. Shot noise enhancement above $T_C$

Remarkably, the noise enhancement to  $2e$  persists when warming the sample to temperatures above  $T_C$ . Fig. 6.3 shows noise spectra acquired at different temperatures ranging from 2.3 K to 7.2 K, which correspond to  $0.78T_C$  and  $2.43T_C$ . Up to more than twice  $T_C$ , the noise spectra still show enhanced noise corresponding to  $2e$ ; only at  $T = 2.43T_C$  does the noise become less. Given that  $T_C$  is far below the temperature at which the noise is enhanced, there is another transition temperature, we denote it here by  $T_p$ , associated with pairing. In a fluctuation picture, this would be the temperature at which the gap opens. Figure 6.4 summarizes the temperature evolution of the noise.

We can compare how the new temperature scales with the unusual transport properties that have been analysed for a wide range of disordered superconductors. Fig. 6.4c shows a resistance versus temperature curve acquired in the same sample, showing the superconducting transition at  $T_C = 2.95$  K. Above  $T_C$ , the resistance curve shows a so-called N-shaped curvature (see Appendix C) as is typical for disordered superconductors not too close to the superconductor-insulator transition [8], and for cuprate high-temperature superconductors [33]. Around 11 K the resistivity passes a local maximum before it drops to zero below  $T_C$ , a signature that has been interpreted as the onset of superconducting fluctuations [4, 34]. For the ALD sample, this is also roughly the temperature where 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.

Our most surprising experimental observation is that we observe pairing above  $T_C$  even in the absence of a spectroscopic (pseudo)gap. As shown in Figs. 6.4a,b, the gap in the differential conductance of TiN does not close at  $T_C$  when increasing the temperature, but fills up instead, i.e.  $\Delta(T)$  is constant while the spectral weight inside the gap is filling up. While the measured temperature evolution of  $\Delta(T)$  resembles findings in other disordered superconductors, the gap fills faster in our samples upon increasing temperature such that the gap is fully filled at  $T_C$ . Partial gap filling has been observed with various probes in other disordered and unconventional superconductors [8, 35–37]. The phenomena can be calculated within models involving strong fluctuations of the order parameter [38] or significant level spacing in grains [39], alternatively, one can postulate a significant fraction of unpaired electrons, or electrons with very small superconducting gaps, to exist in parallel to the superfluid [35, 40]. Our data clearly show that the current noise continues 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 uniquely 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, 22, 23], is not present in TiN.

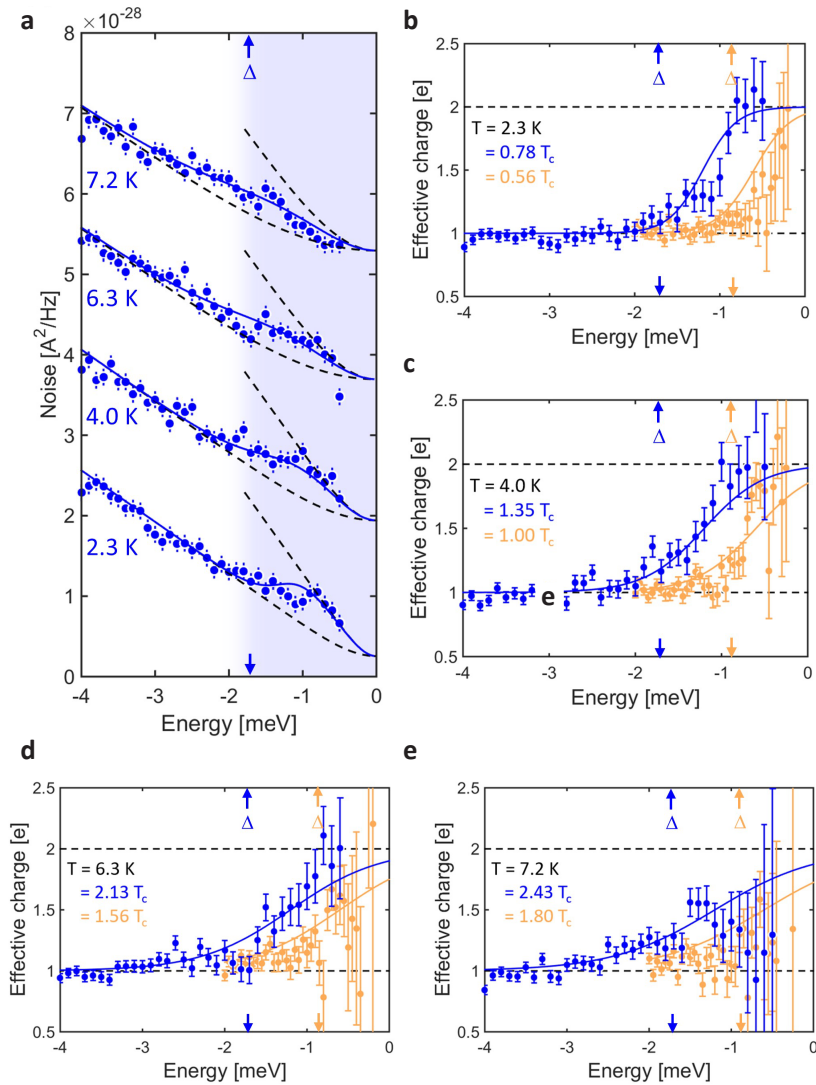


Figure 6.3: **Enhanced noise above  $T_C$ .** **a** Noise spectroscopy on TiN sample for different temperature from 2.3 K =  $0.78T_C$  to 7.2 K =  $2.43T_C$ . Blue dots indicate the measured excess noise in the junction ( $R_J = 5 \text{ M}\Omega$ ) as function of bias voltage. The different temperature curves are offset for clarity. Dashed lines indicate the expected noise for  $q^* = 1e$  and  $q^* = 2e$ . Blue shading highlights the spectral gap in the differential conductance. **b-e** Effective charge  $q^*(V)$  for the four different temperatures. Data for the ALD (sputtered) sample is in blue (orange).



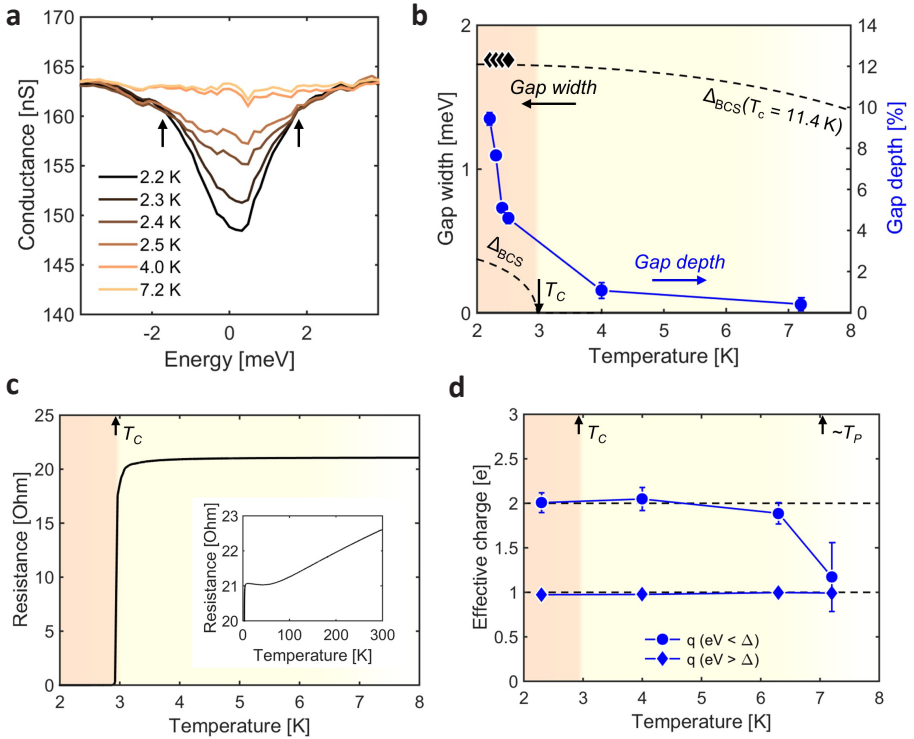


Figure 6.4: **Evidence for a preformed-pair phase above  $T_C$ .** **a** Temperature dependence of the spectral density gap measured by the differential tunneling conductance between 2.2 K ( $0.74T_C$ ) and 7.2 K ( $2.43T_C$ ). Blue arrows indicate the gap width at 2.2 K determined by finding the minimum of second the derivative. Setup conditions:  $V_{\text{bias}} = 5 \text{ mV}$ ,  $I_{\text{set}} = 1 \text{ nA}$ . **b** Gap width (blue diamonds) as a function of temperature for the curves in panel **a**. The dashed curves indicates the mean-field prediction for  $\Delta(T_C = 2.96 \text{ K})$  and  $\Delta(T_C = 11.4 \text{ K})$  from BCS theory. The depth of the gap at zero bias (blue dots) for the curves in panel **a** is shown in percentages with respect to the conductance at energies outside the gap. Conventional Andreev processes or thermal broadening cannot account for the filling observed here (see Appendix C). **c** Resistance versus temperature curve of our ALD TiN sample. The orange shaded region indicates the phase-coherent superconducting phase below the transition temperature. Inset, the resistance-temperature relation up to 300 K. **d** Effective charge outside (diamonds) and inside (circles) the spectral gap as function of temperature. The region consisting of preformed pairs includes temperatures where the gap is fully filled and is indicated by the yellow shading.

We note that the combined observation of both 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 [26]. In break junctions with low transparencies, the conductance inside the gap is much smaller because Andreev reflections happen with a probability proportional to the square of the transparency of the junction,  $t^2$ , while single electron tunneling outside the gap occurs with probability  $t$ . In contrast, in TiN we measure a similar conductance inside and outside that gap, independent of the junction resistance, despite the fact that our transparency is around  $2.6 \times 10^{-3} \ll 1$ . 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 in specific cases involving disordered metals [26]. More likely, a theory involving the spatial heterogeneity and correlations that are typical for disordered superconductors is needed to understand this peculiar state.

## 6.5. Conclusions and outlook

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  $T_p$  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  $T_C$ . Hence, 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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