

## Observation of Bound Quasiparticle States in Thin Au Islands by Scanning Tunneling Microscopy

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Cryogenic scanning tunneling microscopy has been used to measure the structure and the local electronic density of states of thin gold islands in metallic contact with a bulk superconducting NbSe<sub>2</sub> crystal. Peaks are observed in the tunneling conductance below the energy gap corresponding to discrete bound quasiparticle states in the gold. The energies and spatial dependence of the bound states imply that the superconducting pair potential falls off abruptly at the Au-NbSe<sub>2</sub> interface.

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Although the microscopic theory pertaining to spatial variations in superconductivity across normal-metal/superconductor (NS) interfaces has been well developed [1-4], direct electronic measurements on the microscopic scale near such an interface have been beyond the reach of experiment. Recently developed cryogenic scanning tunneling microscopes (STM's) have the spectroscopic capability to resolve the local electronic density of states  $N(E, \mathbf{r})$  by measuring the differential conductance  $dI/dV$  as a function of bias voltage  $V$  and tip position  $\mathbf{r}$ . This allows the possibility of spatially characterizing NS systems with atomic resolution. At present, the only STM experiments dealing with regions of spatially varying superconducting parameters have studied magnetic vortices in the type II superconductor 2H-NbSe<sub>2</sub> [5-7]. It would be advantageous to look instead at artificially prepared NS structures which offer a controlled geometry while decoupling screening currents and magnetic flux from the system.

In this Letter we report spectroscopic STM measurements on a sample consisting of very thin normal-metal islands in good metallic contact with a large superconducting crystal. We find resonances in the tunneling conductance which can be identified as quasiparticle bound states spatially localized in the islands as a result of spatial variations in the superconducting pair potential  $\Delta(\mathbf{r})$ . Bound states have been detected previously in planar thin-film NS structures [8] and have been identified as giving rise to the enhanced conductance observed in the core of magnetic vortices [9-11]. From the energies and spatial variation of the bound states the spatial dependence of  $\Delta(\mathbf{r})$  may be inferred. Our measurements are consistent with a pair potential falling off rapidly within a few angstroms across the NS interface.

The sample consisted of a NbSe<sub>2</sub> crystal (1 mm × 2 mm × 0.3 mm) onto which 7 Å of gold were thermally evaporated as measured by a crystal monitor. Both materials were chosen for their inert surface properties. NbSe<sub>2</sub> is an anisotropic layered superconductor with a transition temperature of 7 K, a bulk superconducting en-

ergy gap  $\Delta_0$  of 1.1 meV, and coherence lengths of 77 and 23 Å parallel and perpendicular to the layers, respectively [12]. Single crystals were grown using an iodine-assisted transport reaction in a gradient furnace [13]. In order to minimize surface contaminants, the evaporation took place in a processing chamber ( $1.4 \times 10^{-7}$  torr) coupled to a helium Dewar. The sample was then transferred onto a variable temperature STM scanning head [14] without breaking vacuum and subsequently immersed in liquid helium. Mechanically ground PtIr and Au tips were used.

Topographic images of the sample, as in Fig. 1, showed thin gold islands on an otherwise clean NbSe<sub>2</sub> surface for which atomic resolution was achieved. Tunneling spectra were obtained by interrupting the scan and holding the tip position fixed for 10 sec while ramping the bias voltage applied to the sample. A small, superimposed sinusoidal voltage of 0.2 mV rms resulted in an ac current proportional to the differential conductance which was detected using a lock-in amplifier. The resulting curves were normalized to the conductance at high bias voltage.

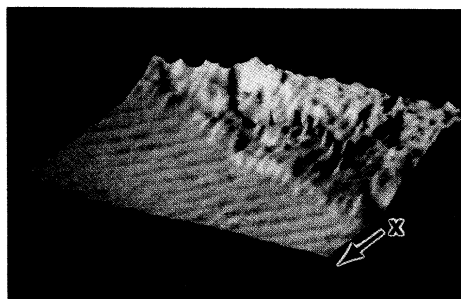


FIG. 1. A 250 Å × 250 Å topographic scan of the sample surface. Atomic resolution images of the flat region on the left are consistent with a clean NbSe<sub>2</sub> surface. The rough plateau on the right rises 6 Å above the plane and appeared only after the gold evaporation. Note that the vertical length scale ( $z$ ) is greatly exaggerated.

Spectra taken on several different gold islands of the Au-NbSe<sub>2</sub> sample are all qualitatively similar. Here we report spectra taken while the tip was positioned at the top and along the edge of the gold island shown in Fig. 1. Figure 2(a) shows a profile of the same gold island and the locations at which the spectra shown in Fig. 2(b) were taken. For comparison, we include a representative spectra obtained on bare NbSe<sub>2</sub>. Although the energy gap of NbSe<sub>2</sub> is clearly seen, the conductance is considerably smeared compared to the BCS tunneling conductance expected at the measurement temperature of 1.6 K. This nonideal behavior has been observed in previous STM experiments [7] and has been attributed to pair breaking due to the high current density near the STM tip. However, we see no significant dependence on tunneling resistance in our experimental range of 10<sup>8</sup>–10<sup>9</sup> Ω. We believe that this deviation from ideal behavior does not affect the conclusions of this experiment.

We see that the overall shape of the spectra taken on the island is similar to that of the bare superconductor. A close comparison to the bare NbSe<sub>2</sub>  $dI/dV$  (solid curves) shows an enhancement in conductance inside the

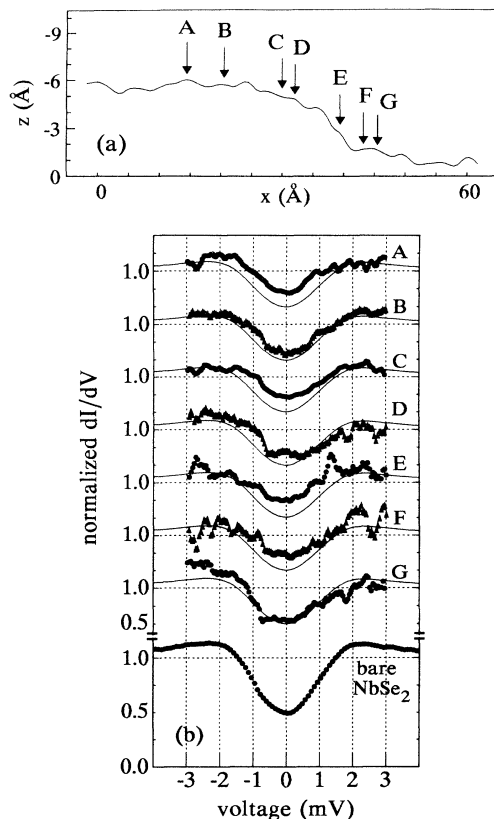


FIG. 2. (a) Topographic profile of the gold island corresponding to the center region of Fig. 1. (b)  $dI/dV$  curves obtained at the positions indicated at  $T=1.6$  K. The relative positions of the curves have been shifted vertically for clarity. The bottom curve and the solid curves are representative of the tunneling conductance we observe on NbSe<sub>2</sub> without gold.

energy gap which is dependent on location. In addition to the enhancement near zero bias, there are distinct conductance peaks occurring at  $\pm 0.8$  mV. The sizes of these peaks are not symmetric with respect to zero bias. There are also periodic structures outside the energy gap with a spacing of roughly 1 meV; these are most evident in curve E. These high-energy peaks are less well characterized since the curves show more noise at high bias, presumably due to a weak voltage dependent tip-sample interaction.

One may be tempted to reason that the gaplike shape of the spectra on the gold is due to a relatively large value of the pair potential induced in the gold island by proximity coupling to the superconducting NbSe<sub>2</sub>. In fact, the observed spectra support quite the opposite conclusion. The problem with this reasoning is the assumption that macroscopic behavior applies to small structures. A region in which the pair potential is reduced will have quasiparticle states below the bulk energy gap as one would expect. But for structures small on the scale of the coherence length, there may be only a few of these states (which are determined by the microscopic Bogoliubov-de Gennes equations) and the overall gaplike appearance of the density of states may persist.

The physics is analogous to the quantum mechanics problem of particles bound in a potential well. The reduction in pair potential  $\Delta(\mathbf{r})$  in the gold island acts like a potential well for quasiparticles, giving rise to bound states with energies below  $\Delta_0$  spatially localized in the well and resonant virtual states with energies above  $\Delta_0$  (also known as Rowell-McMillan oscillations) [8]. A quasiparticle and quasihole of energy  $E_n$  are associated with each bound state contributing to the density of states  $N(E, \mathbf{r})$  at  $\pm E_n$  relative to the Fermi energy  $E_F$ . Hence, the peaks in our observed spectra are consistent with two or more bound states—one of energy near 0.8 meV and one or more at lower energy, giving the enhanced conductance near zero bias.

de Gennes and Saint-James [15,16] have solved the Bogoliubov-de Gennes equations (dG-SJ model) in a geometry consisting of an arbitrarily wide normal-metal layer with constant pair potential  $\Delta_N$  and thickness  $d$ , as shown in Fig. 3. Their analysis leads to the following conclusions: (1) The number of bound states increases with  $d/l$  where  $l$  is a characteristic length given by  $\hbar v_F/\pi\Delta_0$ , where  $v_F$  is the Fermi velocity. (2) Bound states are forbidden below  $\Delta_N$ . That is to say  $\Delta_N < E_n < \Delta_0$ , as one would intuitively expect.

Although the dG-SJ model is a highly idealized model for our system, we expect it to roughly describe the behavior of our bound states. Since the model geometry is one dimensional, the local density of states obtained from it [17] only varies spatially with  $z$ . However, for a three-dimensional island, there may well be an  $x$ - $y$  dependence which is beyond the scope of the model. Figure 4(a) shows a thermally broadened bound state contribution to  $N(E, z)$  as a function of both energy and location calcu-

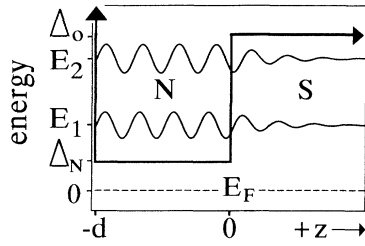


FIG. 3. Schematic representation of bound quasiparticles in the dG-SJ model. The potential well, formed between the rising pair potential in the superconductor and the real potential barrier at the vacuum interface, is assumed to have a rectangular shape.

lated from the model. The surface has four peaks with respect to energy which arise from bound states at 0.3 and 0.8 meV. The modulation in  $z$ , which results from the wave function nature of the bound states, is set approximately by the Fermi wave vector  $k_F$ . The parameters used in the calculation are  $\Delta_0 = 1.1$  meV,  $\Delta_N = 0.0$ ,  $d = 6$  Å,  $l = 0.74$  Å,  $k_F = 4.2$  Å<sup>-1</sup>, and  $T = 1.5$  K.

In order to compare the observed spectra to the theory, we regard curves taken along the edge of the island as sampling the  $z$  dependence of the bound states. We isolate the bound state contributions in the experimental data by subtracting the  $dI/dV$  observed on bare NbSe<sub>2</sub> (which is an approximation for the contribution from scattering states near the gap edge). Figure 4(b) shows the experimental bound state contribution obtained at locations  $B$  and  $E$  (see Fig. 2) compared to the calculated  $N(E, z)$  at  $z = -4.3$  Å and  $z = -2.0$  Å. Good agreement may only be achieved by scaling the calculated amplitude by a factor of 0.25. This attenuation may result from several factors [9–11] including edge effects and high current density effects.

We see from Fig. 4(b) that most of the features in the experimental curves are also present in the calculated curves. The dG-SJ model even predicts the observed asymmetry about zero energy which arises from the differences between quasiparticle and quasihole wave vectors. The asymmetry has not been previously observed as it is a local phenomenon which is destroyed by averaging over  $z$ . The model also predicts that the bound state contributions should extend beyond the interface into the superconductor as an evanescent wave. This is consistent with measurements we have taken near Au islands that show both the atomic structure of NbSe<sub>2</sub> and evidence for bound states.

One of the most striking predictions of the bound state model is the spatial oscillations in the density of states along the  $z$  direction. Because in our configuration  $z$  is varied by sampling along the sloping edge of the Au island, it is difficult to completely map out these oscillations. Further, we expect surface roughness and three-dimensional effects to smear out the sharp features pre-

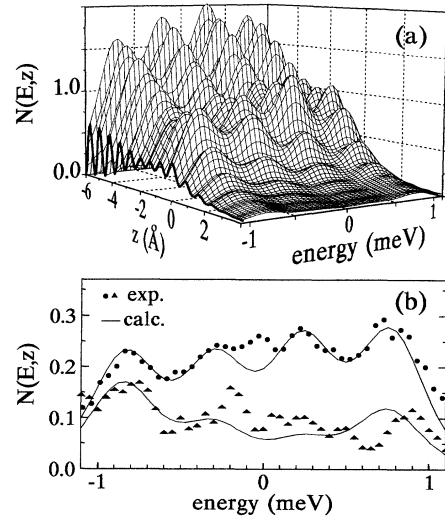


FIG. 4. Thermally broadened bound state contribution to the local density of states. (a)  $N(E, z)$  calculated from the dG-SJ model. (b) The experimental bound state contributions derived from Fig. 2, curves  $B$  (triangles) and  $E$  (dots). The experimental curves are compared to the curves  $z = -4.3$  Å and  $z = -2.0$  Å, respectively, from (a). The amplitude of the calculated curves has been reduced by a scaling factor of 0.25.

dicted by the simple bound state model. Nonetheless, we see evidence for the spatial oscillations in the density of states. In Fig. 5, we plot the measured bound state contribution to the conductance at  $\pm 0.3$  mV for six locations in a region near the top of the island; at these energies the magnitude of  $dI/dV$  is largely determined by a single bound state. The data compare reasonably well to the calculated density of states as a function of  $z$ , averaged over 0.4 Å to simulate the spatial resolution of our STM spectroscopic measurements.

We also find a small zero-bias peak in many of the observed spectra which cannot be generated from the dG-SJ model without sacrificing the good fit at higher energies. This feature may arise from a repulsive electron-electron

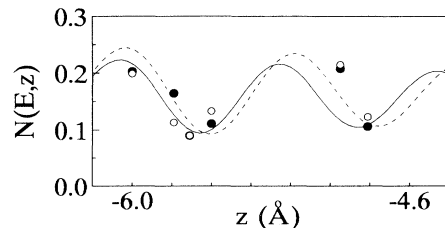


FIG. 5. Experimental bound state contribution to the conductance at  $+0.3$  mV (circles) and  $-0.3$  mV (dots) as a function of  $z$ . The data are compared to the dG-SJ model at  $+0.3$  meV (dashed) and  $-0.3$  meV (solid) using the same parameters as in Fig. 4. The calculated curves have been averaged over 0.4 Å and scaled by 0.17.

interaction in the gold island [3]. In this case the pair potential can become negative and quasiparticle states would be allowed at zero energy. This would also lead to a deeper well which we intuitively expect to hold more bound states for a given  $d$ . This may explain why a characteristic length of only  $0.74 \text{ \AA}$  generates the best fit; this value is substantially smaller than that implied by either  $v_F$  of crystalline gold or the coherence lengths of  $\text{NbSe}_2$ . This characteristic length is, however, consistent with the observed energy spacing of the Rowell-McMillan oscillations in our measurements,  $\Delta E = \hbar v_F / 4d = l\pi\Delta_0/4d$ .

The principle that bound states cannot lie below  $\Delta_N$  leads to the conclusion that the pair potential falls off dramatically inside the gold island. This is contrary to the conventional wisdom which would assume a negligible change in the pair potential for such a thin layer in contact with a bulk superconductor. Since a thin layer should induce a relatively small proximity effect in the  $\text{NbSe}_2$ ,  $\Delta(\mathbf{r})$  must fall off rapidly either within the gold island or at the Au- $\text{NbSe}_2$  interface. It is unlikely that  $\Delta(\mathbf{r})$  decays substantially within the gold island. Moreover an exponential decay would lead to bound states more localized near the top of the island where  $\Delta(\mathbf{r})$  is minimum, whereas we observe strong bound state amplitudes near the bottom of the island. We believe instead that boundary effects dominate the behavior of the pair potential causing an abrupt reduction at the Au- $\text{NbSe}_2$  interface. At sharp NS interfaces  $\Delta(\mathbf{r})$  can be discontinuous on the scale of coherence lengths if the electron-electron interaction constant is reduced or repulsive in the normal layer [2,3]. The discontinuity is enhanced by any finite boundary resistance and is especially pronounced for short coherence length superconductors [4].

In summary, we have performed local spectroscopic measurement near the interface of a gold island of thickness  $6 \text{ \AA}$  in metallic contact with a large superconducting  $\text{NbSe}_2$  crystal. We find conductance peaks in the spectra corresponding to bound quasiparticle states with energies of  $0.8$  and  $0.3 \text{ meV}$  and a zero-bias conductance peak which may arise from an additional bound state near zero energy. Although the largest observed quasiparticle amplitudes occurred near the center of the island, significant amplitudes were also found near the interface. These observations lead to the conclusion that the pair potential falls off abruptly in the gold island. Further work to

study the dependence of the bound states on Au thickness and to better resolve the  $z$  modulation is in progress.

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