High-Temperature Superconductors: Playgrounds for Broken Symmetries

L. H. Greene

Department of Physics, Frederick Seitz Materials Research Laboratory, Center for Nanoscale Science and Technology, University of Illinois at Urbana-Champaign, USA

Abstract. Studies of symmetries and the consequences of breaking them have led to deeper understanding in many areas of science. The high-temperature superconductors, discovered in 1986, motivated an unprecedented worldwide flurry of research, not only because applications are promising, but because they also represent a new state of matter that breaks certain fundamental symmetries. In this narrative for nonspecialists, we provide a general background on broken symmetries and superconductivity. Then we show how planar tunneling spectroscopy can detect the broken symmetries of gauge (superconductivity), reflection (d-wave superconducting order parameter), and time-reversal (ferromagnetism).

Keywords: superconductivity, high-temperature superconductors, unconventional superconductors, ferromagnetism, broken symmetry, tunneling, Andreev reflection

PACS: 74.25.Jb, 74.25.Op,74.45.+c, 74.50.+r, 74.72.-h, 74.72.Bk, 74.78.-w, 74.78.Bz

INTRODUCTION

The history of the universe is studied by cosmologists, high-energy physicists, and nuclear physicists. Conditions existing approximately 10 ms after the Big Bang are described with energy scales of ~170 MeV corresponding to temperatures of $\sim 2\times 10^{12}$ ºK. Condensed-matter physicists who study superconductivity, including superfluidity and Bose-Einstein condensation, use the same physical principles and almost identical terminology, studying the physics of strongly correlated electron systems, particle conversion, and the ramifications of broken symmetries; but at millikelvin temperatures or lower—approximately 10^{16} to 10^{26} times lower in energy.

The discovery of high-temperature superconductors (HTS) sparked a tremendous flurry of worldwide research, first because of their promise of applications and then because it was found that they described new electronic states of matter never before understood. The applications are not stressed in this talk, but they do exist in the marketplace, particularly in cellular telephone systems and the detection of very small magnetic fields, both for research purposes and with great promise for the MRI industry.

To begin with, it must be noted that this proceedings is a narrative for the nonexpert based on the experience and point of view of the author. In lieu of incomplete scholarship and referencing, a short bibliography is provided. The course of the narrative proceeds as follows. First, superconductivity is defined. Then, a general description is given of a symmetric state and a state of broken symmetry, relying on well-known examples to lay the basis for our description of broken gauge, reflection, and time-reversal symmetries. The measurement we use to detect these broken symmetries in superconductors is planar tunneling spectroscopy, which is described. Then a fascinating particle-conversion process, Andreev reflection, is explained. These concepts are applied to the high-temperature superconductors, and it is shown how the emergence of Andreev bound states and the subsequent state of broken time-reversal symmetry are detected in these unconventional superconductors.

A caveat for the metaphors provided in this talk must be given here. Many examples are given to provide some understanding of quantum-mechanical concepts to the nonexpert break down when scrutinized, so must be intrinsically incorrect. The reader is reminded that this is also true of the Bohr model of the atom, which continues to provide an extraordinary foundation for comprehension of the quantum atom.

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DEFINITION OF SUPERCONDUCTIVITY

The modern Webster's dictionary defines superconductivity as "*an electronic state of matter characterized by a) zero resistance, b) perfect diamagnetism, and c) long-range quantum mechanical order,*" the last term being defined as "*phase-coherence or broken-gauge symmetry*." The superconducting state occurs below a critical temperature (T_c) which is typically on the order of a few K for conventional metallic superconductors (9.2K for Nb) and about an order of magnitude higher for HTS (high-T_c) superconductors (90ºK for $YBa_2Cu_3O_7$).

Nearly 100 years ago, H. Kammerlingh-Onnes, working in Leiden, discovered the liquefaction of helium below 4.2ºK. Within 3 years, in 1911, driven by curiosity, he discovered superconductivity in thin wires of mercury. He found the resistance of the metal to decrease with decreasing temperature, as expected, but at just above 4.2 ºK, the resistance dropped abruptly by almost three orders of magnitude, from approximately a mΩ to a resistance below his limit of measurement. Future work showed, indeed, that the resistance below this superconducting critical temperature, T_c, is zero.

The microscopic "BCS" theory of superconductivity was not developed until almost 50 years later by Bardeen, Cooper, and Schreiffer at the University of Illinois at Urbana-Champaign. They showed that the electrons (fermions) in a superconductor can form "Cooper pairs" (boson-like), allowing them to condense into a single quantum state. A simple, normal metal can be well-described by the "free electron theory of metals," in which the positive-ion lattice can be considered as a "bucket" that holds the electrons. Each electron is governed by Fermi statistics, so no two electrons can occupy the same quantum state at the same time. Thus, the electrons exhibit a distribution in energy state occupation called the density of states (DoS). At low temperature, the highest occupied energy level is called the "Fermi level," which is determined by the Pauli exclusion principle and the number of itinerant electrons in the metal. In the superconducting state, Cooper pairs behave much like bosons, and can condense into a single quantum state. The pairing mechanism in conventional superconductors is the electron-lattice or "electron-phonon" interaction. An analogy often given to describe this pairing is the "soft mattress analogy" in which partners in a soft bed roll together, not due to any intrinsic attraction of the partners, but due to the "squishiness" of the mattress. This simple analogy breaks down because of the strong coulombic repulsion. In the approximately 50 years between the discoveries of superconductivity and the development of the BCS theory, the pairing mechanism of the electrons remained the greatest mystery because, as was stated "you cannot repeal Coulomb's law." In fact, BCS determined that the electrons are not paired in real space, but in momentum space, explained as follows. Consider a metal, niobium for example, with a large electron-phonon interaction, allowing the ions to be distorted by a traveling electron. At low enough temperatures, when this interaction becomes greater than the thermal energy (vibrations of the lattice or phonons), the electrons can actually leave a kind of "wake," as shown in Figure 1. We expand the soft mattress analogy by considering the partners repulsed by each other. When one leaves the bed, the other can relax and roll into the depression left by the first. Thus, the attraction of repulsive particles, including the time delay (as determined by how fast the mattress springs back, or the lattice can relax to equilibrium), is demonstrated. In the lattice, the recovery time determines the spatial extent of the electron pairing, known as the coherence length, which can extend hundreds of angstroms or even microns in conventional metallic superconductors and on the order of nanometers in HTS. The "squishiness" of the mattress also determines the strength of the pairing interaction, and in the superconductor, the binding energy of the electrons is the energy gap, Δ, discussed in more detail below.

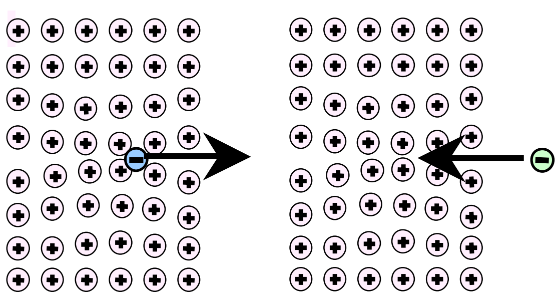

FIGURE 1. Schematic of the electron-phonon momentum-space pairing basis for Cooper pairs. The first electron, traveling to the right, leaves a "positive wake" in the lattice which, with a time delay, attracts the second electron. After Simon and Smith, 1988.

In normal metals where the electrons remain uncorrelated on macroscopic length scales, each electron is described by its own wavefunction, ~ $exp(-ik_x-\omega t+\varphi)$, where φ describes the phase of each separate, uncorrelated electron. In a superconductor, where the charge-carriers are Cooper pairs, the single BCS wave function describes the macroscopic many-body quantum state. In other words, if you know the phase of this macroscopic quantum state in one location of the superconducting material, you can determine the phase anywhere else. This state is one of "long range phase coherence" given in our original definition of superconductivity, which we will define as broken

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“phase” (also called “gauge”) symmetry, discussed below. That this is a macroscopic quantum state helps us understand why superconductors can exhibit zero resistance. Consider an analogy of a bumpy road where the bumps represent impurities or electron scattering centers. A single wheel (single electron) rolling down this road will not get very far, being easily diverted or scattered by the bumps (finite resistance). However, a wide-wheel-base car with independent suspension (superconducting condensate) can navigate this difficult path with smoothness (zero resistance).

Another property that defines a superconductor is perfect diamagnetism. It was discovered in 1933 by Meissner and Ochsenfeld that superconductors can completely expel magnetic fields. When a superconductor is placed in a magnetic field, supercurrents form on its surface which exactly cancel the applied field in the interior of the material (see Figure 2). This is different from Lenz’s Law, in that a field-cooled superconductor expels the magnetic field upon crossing T_c. If T_c marked “perfect conductivity” instead of the macroscopic quantum state “superconductivity,” then according to Maxwell’s equations, the field lines would be fixed within the material when field-cooling below T_c. The observation of this effect was crucial to understanding superconductivity as a quantum phenomenon. This is also the basis for magnetic levitation or “maglev” (see Figure 3). A prototype maglev train in Japan can travel about one kilometer; it is based on conventional superconductors.

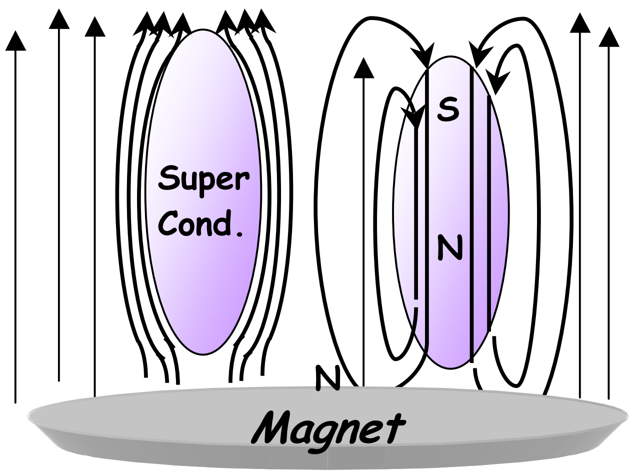

FIGURE 2. Meissner-Ochsenfeld Effect. Magnetic field lines are expelled from the superconductor due to supercurrents forming on its surface. This diamagnetism leads to magnetic levitation.

FIGURE 3. Magnetic levitation by a high-temperature superconductor. From http://research.cm.utexas.edu/jmcdevitt/.

SYMMETRY AND BROKEN SYMMETRY

A symmetric state is one which is homogeneous with respect to the defining coordinate (e.g., distance, angle, phase, or time). The formal definition is that the symmetry of the state is the same as that of the Hamiltonian. Practically, a state is symmetric when changing the defining coordinate does not produce a measurable change in the state. A broken symmetry state is one which is inhomogeneous with respect to the defining coordinate. Formally, the symmetry of the state is lower than that of the Hamiltonian that describes the ground state. Practically, changing the coordinate produces a measurable change. These definitions are clarified with examples below and illustrated in Figure 4.

The simplest example is a state with circular symmetry, as shown in Figure 4. The defining coordinate is angle and if that is changed, i.e., the disk is rotated, there is no measurable effect. If the symmetry is broken with a dot placed near the edge of the disk, rotation becomes obvious. Therefore, it is said that the disk with the dot is a case of broken circular symmetry. Next consider a fluid, perhaps steam. This is a state symmetric to a translational

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coordinate. If a water molecule is moved or if you, as an observer, move between locations, there is no physical evidence. However, if a phase transition occurs to freeze the fluid into ice—a crystalline solid—translational symmetry is lost. That is seen practically by moving a molecule, which will produce a vacancy and an interstitial molecule, so a measurable change has occurred. Freezing a fluid into a solid is a first-order phase transition that spontaneously breaks the translational symmetry. Spontaneous symmetry breakings are also characterized by a "stiffness." It is much more difficult to displace a molecule of ice than of steam or water.

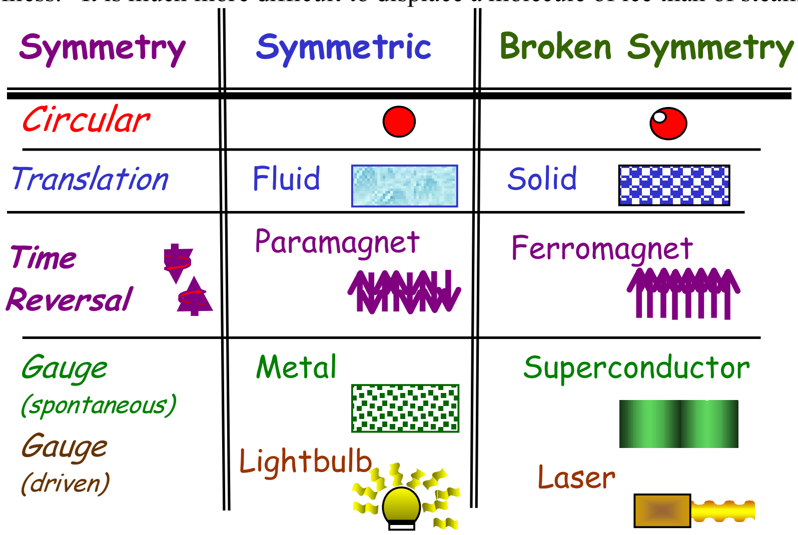

FIGURE 4. Examples of **Symmetric** and **Broken-Symmetry** states. Note that the transition to the broken symmetry state for light is a driven phase transition, so it does not exhibit the "phase stiffness" of the super-conducting state. After Simon and Smith, 1988.

Next, we move to time-reversal symmetry breaking. In a state which is time-reversal symmetric, it is impossible to tell if the time arrow is moving forward or backward. In a broken time-reversal symmetry case, the direction of time is obvious. Consider a game of pool. First the ordered balls are "broken" or scattered by the cue ball, and later the balls move randomly, bouncing around the table surface. Consider a video taken of this process and imagine that this video is observed by running it backward. The backward-run video will first look reasonable when the balls are in random motion, but later (earlier for the forward-time video) during the "collapsing break," the backward-run video looks very silly! Now in our case, broken time-reversal symmetry is simply an expensive way to say ferromagnetism, which is explained here and in Figure 4. In a paramagnetic metal, the magnetic moments of each atom can be driven by the orbital motion of the electrons, which are aligned equally "up" and "down" with no net magnetization. Reversing the direction of the time arrow does not change the state of this system. The direction of each electron orbit reverses, flipping each magnetic moment, and the net magnetization remains zero. In the case of the ferromagnet, however, there is a net magnetization. In Figure 4, it is "up," and reversing the time arrow changes the magnetization to "down." The global magnetization has changed, which is certainly measurable, so time-reversal symmetry is broken. Note that this is also a spontaneous, symmetry-breaking phase transition. A ferromagnetic material above its Curie temperature is paramagnetic. Below this temperature there is a "phase stiffness" in that it is more difficult to flip a single orbital moment than in the paramagnetic case.

Finally, we get to broken gauge symmetry, which could also be called broken phase symmetry. The first example in the fourth row of Figure 4 shows the spontaneous gauge-symmetry-breaking phase transition from a normal metal to a superconductor. As discussed earlier, in the normal state the electrons are uncorrelated over a macroscopic length scale. A single electron can be easily moved or have its phase changed without any measurable ramifications. When the superconducting phase transition is crossed, that is the temperature drops below T_c, the electrons spontaneously condense into a single phase-correlated system. This macroscopic phase coherence is the signature of broken phase, or gauge, symmetry. The phase stiffness in the superconducting state is observed whenever a superconductor is in a magnetic field, even a static one. The field causes a macroscopic surface current to flow, which expels the applied field (Meissner effect) so the phase of the wavefunction is altered. The familiar equation which applies is $i \sim -\delta\varphi$, where $\delta\varphi$ is the change of the phase and i is the current. Practically, we see that a change in phase results in a measurable current, so gauge symmetry is broken. Another case of broken gauge symmetry is when photons are driven to be phase-correlated by a laser. This example is given to compare the familiar broken gauge symmetry of photons with that of electrons, as shown and explained in Figure 5. It must be noted that the electromagnetic field does not intrinsically, spontaneously break gauge symmetry, but this symmetry can be driven to break by a laser. There is no "phase stiffness" in laser light, but the ramifications of broken symmetry are clearly

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observed by long-range diffraction and interference. The Fraunhofer single-slit and Young's double-slit experiments we all did in physics lab map directly onto the DC and RF SQUIDs (superconducting quantum interference devices), respectively, with the detailed comparisons given in Figure 5.

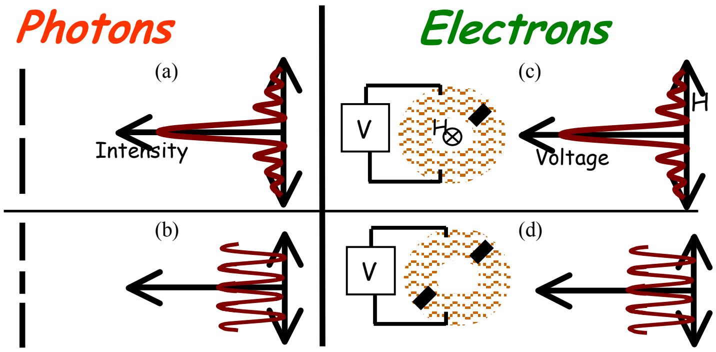

FIGURE 5. Measurable effects of broken gauge symmetry for photons and electrons. In the photon case, we are all familiar with the Fraunhofer pattern produced by a laser beam diffracted through a single slit *(a)* and the Young's double-slit interference pattern *(b)*. These cases are correlated with the DC *(c)* and RF *(d)* SQUIDs which are formed with a superconducting ring having one and two "weak links," respectively. Weak links are formed by a thin insulator or normal metal. The application of a field through the ring causes a current, and the measured voltage drop as a function of applied field is shown. After Greene et al., 2000.

QUASIPARTICLE TUNNELING

Quasiparticle tunneling is a powerful probe of the electronic density of states and it was this measurement that proved the BCS theory of superconductivity. Though apparently a simple measurement, it must be kept in mind that many diagnostics must be performed in order to be certain that the measured results are not arising from a myriad of artifacts. A simple diagram of a junction and the corresponding wavefunctions of the electrons, or quasiparticles, is given in Figure 6. Two free-electron metals are separated by a thin, pinhole-free insulator and the current-voltage measurement is taken across this barrier. Classically, no current can flow, but simply applying the Schrödinger equation and matching the appropriate boundary conditions, for normal metals separated by a narrow strong, potential barrier (e.g., 2-nm-thick Al_2O_3, which has about a 1-volt potential barrier), Ohm's law is easily calculated and can be routinely measured.

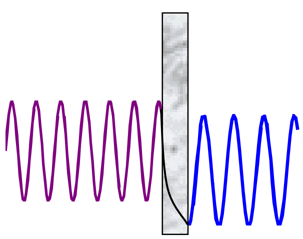

FIGURE 6. Wave-function diagram of NIN tunneling. The wave function of the electrons in the normal metal on the left and right go as $\exp(-ik_l x)$ and $\exp(-ik_r x)$, respectively and in the classically-forbidden region of the potential barrier as $\exp(-\kappa x)$.

When one of the electrodes is superconducting, the picture changes substantially. A schematic of the BCS density of states (DoS) is shown in comparison to a normal metal DoS in Figure 7. Note that a gap appears in the energy spectrum and there is a strong enhancement in the DoS in a narrow region on either side of the gap. This enhancement conserves states. A schematic representing quasiparticle tunneling between a normal metal, N, separated by an insulator, I, from a superconductor, S, is shown in Figure 8. The insulator is thin enough to allow tunneling so the Fermi energies of N and S align at zero bias. The structure of the trilayer and leads for the I-V measurement is shown at the top. The band diagrams are shown for zero and finite bias. At zero bias there is no tunneling because states containing electrons are at the same energy as either full states or where there are no states (within the energy gap). The Pauli Exclusion Principle forbids electrons to tunnel into full states, and the energy gap is like a "no parking zone" for electrons. As a bias is applied, a voltage can be dropped across the insulator and the Fermi energies of the two materials are separated by this bias; an increase in the N bias is shown in Figure 8. (Note that the Fermi energy is normalized to zero because the voltage one measures across a tunnel junction is the difference of the Fermi energies of the two materials as a function of applied voltage.) No current is measured until the energy of the tunneling electron reaches the gap edge, or $V = \Delta/e$. Then, a very large empty density of states is

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available to the electrons at the Fermi energy of N, and, following Fermi's Golden Rule, a very large current may flow. The current-voltage characteristic (I-V) is shown. Note that at higher energies, far away from the gap edge, the band structure regains the N characteristic and at high biases, Ohm's law is regained. A look at the tunneling conductance (G = dI/dV, which should be measured with phase sensitive lock-in techniques and not simply by taking the derivative of the direct-current I-V characteristic) reveals the power of this technique. At low biases, the tunneling conductance gives a direct value of the superconducting gap. The I-V and dI/dV characteristics drawn in Figure 8 are commonly seen in conventional metallic superconductors.

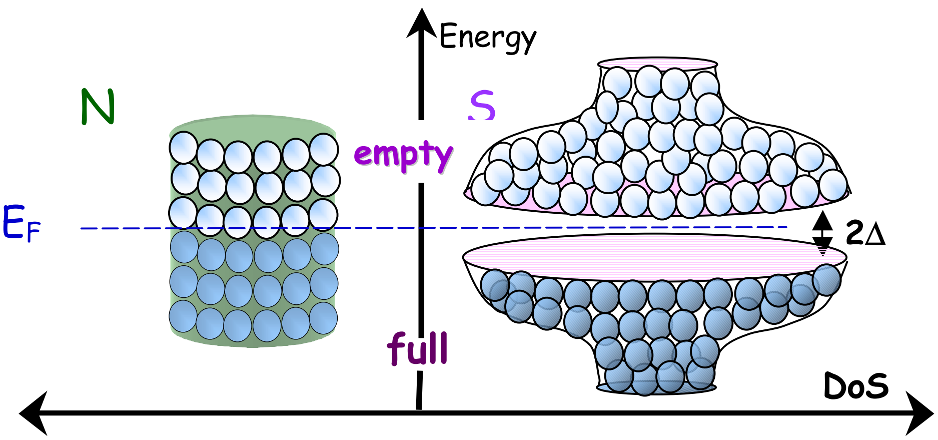

FIGURE 7. Schematic of the density of electronic states for a normal metal (N) and a superconductor (S). At low temperature the electrons fill to the Fermi level, and the energy gap in the superconductor, Δ, is nominally the binding energy of the Cooper pairs. After Simon and Smith, 1988.

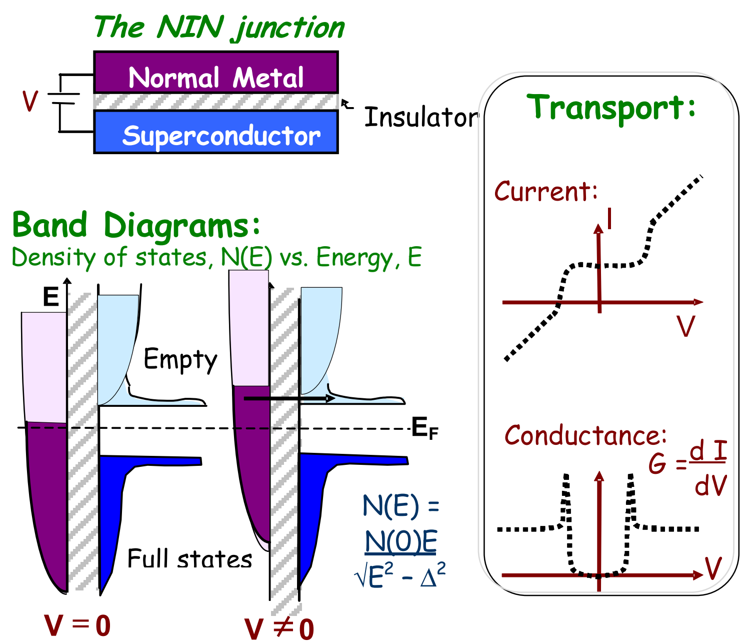

FIGURE 8. Planar quasi-particle tunneling between a normal metal and a super-conductor. The density of states (DoS) of the super-conductor is given by the BCS equation, N(E), as shown. There is no tunneling current at biases below the energy gap, V < Δ/e, and the tunneling conductance can directly give the gap energy. Band diagrams are not to scale.

The conductance of a high-temperature superconductor is shown in Figure 9. Note how different this conductance appears from that shown for conventional superconductors in the previous figure. The central peak or zero-bias conductance peak (ZBCP) arises from Andreev bound states, which are due to the broken reflection symmetry (d-wave) of the superconducting order parameter. In order to understand this phenomenon, we must discuss Andreev reflection and understand what a d-wave superconductor is.

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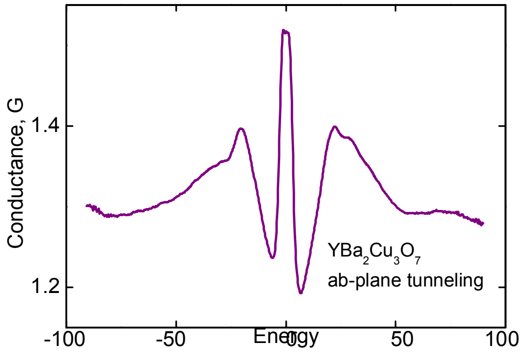

FIGURE 9. Tunneling conductance of a high-T_c superconductor. Note how different this appears from the BCS conductance in the previous figure. The zero-bias conductance peak arises from Andreev bound states, due to the broken reflection symmetry of the superconducting order parameter, as discussed in the text. After Greene et al., 2000.

ANDREEV REFLECTION

Andreev reflection (AR) is a fascinating particle-hole conversion process that occurs at the superconducting interface when an electron is injected below the gap energy. Figure 10 shows a cartoon with a normal metal juxtaposed with a superconductor in good electrical contact. This figure is provided for the sole purpose of explaining the AR process in general. Basically, if an electron is injected from the normal side into the superconductor within the gap energy, as stated before, there are no density of states in the superconductor to receive it. The only process that conserves energy, momentum, and charge is the AR process, in which the electron is retro-reflected as a hole, as also shown in Figure 10. Physicists deal with the idea of particle conversion on a daily basis (e.g., beta decay). We have learned that there is always a finite probability for a conversion, if the conservation laws are obeyed, and this is just another example. We also note from Figure 10, that, very close to the interface—within a distance that is on the length scale of the coherence length in each material—some phase coherence develops in the N side, and there is pair breaking on the S side. We have learned over the past few years that AR provides a microscopic explanation of the superconducting proximity effect.

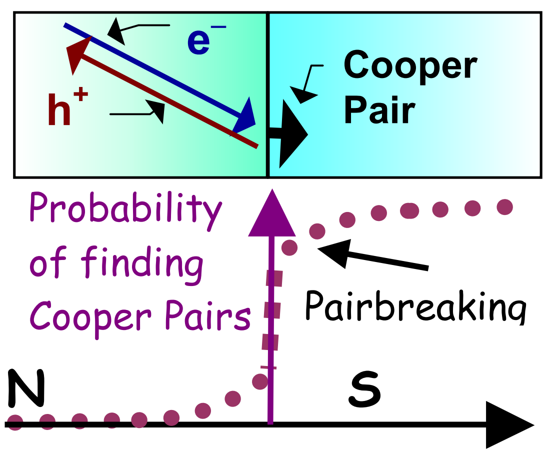

FIGURE 10. Andreev reflection. *Top:* An electron incident on a superconductor is retro-reflected as a hole, as described in the text. *Bottom:* this AR process is the microscopic explanation for the superconducting proximity effect. Some phase coherence is generated on the N side with pair breaking on the S side. The length scales are proportional to the electron coherence length in each material. This is the ONLY example of a clean SN interface in this talk.

The reader may gain some physical insight about Andreev reflection by noting the following. First, the Fermi energy is on the order of several electron volts (eV) for most metals, while the superconducting energy gap is on the order of a few milli-electron volts (meV). Thus, Δ is 3 to 4 orders of magnitude less than E_F (note that the band diagrams in Figure 8 are *grossly* not to scale). An electron impinging from N to S does so at the Fermi energy, and only the potential of the gap is there to stop it. This is like expecting a locomotive to be stopped by a curtain! But entering S is forbidden quantum mechanically (there are no states in the gap), so AR must occur.

ORDER PARAMETER SYMMETRY

The superconducting order parameter (OP) in conventional superconductors is s-wave, meaning that it is homogeneous with respect to direction. It must be stressed that this direction is in momentum space, not real (also

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called x or configurational) space. This means that an electron traveling with its momentum vector pointing any direction, for example either "north" or "southwest," experiences the same value of the OP. An example is shown in Figure 11. Also shown in this figure is extended s-wave symmetry, where there is some structure to the OP in momentum space, and d-wave symmetry, where the OP not only exhibits nodes but also a change in sign around the Fermi surface. Note then that a d-wave symmetry superconductor not only breaks gauge symmetry because it is a superconductor, but the OP also breaks reflection symmetry. It must be stressed that schematics of the OP, not the gap, are being shown in this figure and the OP is basically the wave function that describes the quasiparticle DoS and gap function. We learned in quantum mechanics that one does not directly measure a wave function but measures probability currents and expectation values, which involve the square of the wave function. Similarly, in a superconductor, we do not directly measure the OP, but the gap, which is basically the square of the OP.

The surprise in the past few years was that the sign-change of the OP around the Fermi surface in a d-wave superconductor could be detected by tunneling spectroscopy. It is this sign change, the reflection-symmetry breaking of the OP combined with the gauge-symmetry breaking of the superconducting state, that gives rise to the Andreev bound states seen by the ZBCP in the conductance of a d-wave superconductor.

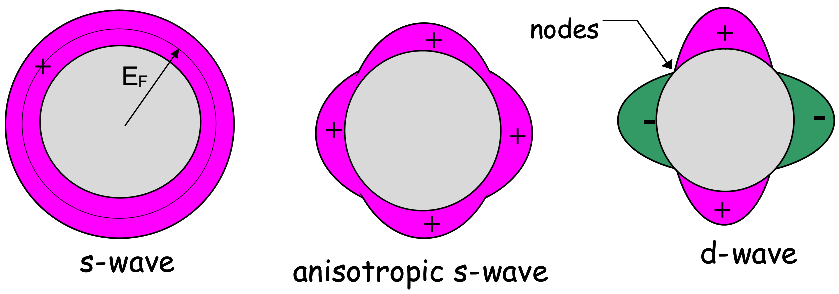

FIGURE 11. Three possible order parameter symmetries: left to right s-wave, extended or aniso-tropic s-wave, and d-wave are shown. The first two are considered "conventional," and most metallic superconductors exhibit s-wave order parameter symmetry. The high-temperature superconductors exhibit d-wave symmetry and are called unconventional because there is a sign change of the OP around the Fermi surface.

ANDREEV BOUND STATES

From now on, we are only considering free superconducting surfaces with no extrinsic normal metal present. Now consider the trajectory of an electron, in both an s-wave and d-wave superconductor, in which there is a reflection from the surface, as shown in Figure 12. For the s-wave case, since the OP is isotropic, the reflection is always normal, not Andreev, so no pairbreaking occurs, consistent with the Anderson theorem (that simple scattering from non-magnetic impurities, in this case the interface, does not break Cooper pairs). In the d-wave case,

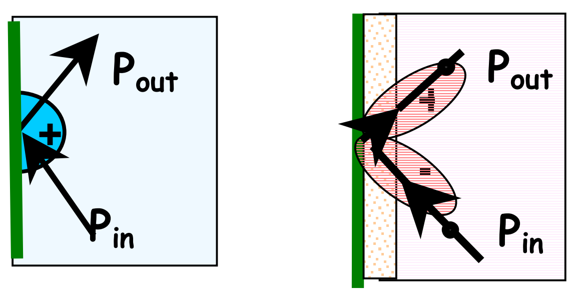

FIGURE 12. Surface reflection within a superconductor. For an s-wave superconductor *(left)*, no change of the OP is seen so no AR occurs. For a d-wave superconductor *(right)* for certain surfaces, the electron experiences a sign change of the OP upon reflection so a dramatic AR occurs resulting in pair breaking near the interface.

however, for certain crystallographic orientations, an electron undergoing a reflection at the surface is scattered into the direction in which the order parameter changes sign. Simply scattering from the surface causes the electron to experience a dramatic change in the OP, so a dramatic AR, which is a quantum mechanical scattering from an OP, occurs. Furthermore, a dramatic AR causes dramatic pair breaking and, therefore, quasiparticles nucleate near the surface of the d-wave superconductor. The broken Cooper pairs, or electrons, form at the Fermi energy and are measured as spectral weight at zero bias in the tunneling conductance. They comprise the Andreev Bound States

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(ABS), so named because they are formed by Andreev reflection and are bound in the near-surface region. It was predicted and found that the ZBCP would split with applied magnetic field. This is called the Doppler Effect because an applied field causes currents to flow on the superconductor surface (Meissner effect) and any quasiparticles near the Fermi surface will be swept along. The extra kinetic energy causes the quasi-electrons and quasi-holes to move from zero bias, and hence a splitting with field is observed. In fact, at low fields (below about 1 Tesla) it was predicted and found that the splitting of the ZBCP was directly proportional to the applied field.

If the splitting of the ZBCP is proportional to field, then a *spontaneous* splitting must indicate the generation of a *spontaneous* magnetic field, or *spontaneous* time-reversal symmetry breaking. As shown in Figure 13, this is exactly what was predicted and what was then measured. The material is the high-temperature superconductor $YBa_2Cu_3O_7$ or YBCO which exhibits a T_c of about 90 ºK. At temperatures approximately 10 times lower than the T_c, the spontaneous splitting is observed. The length scale over which the Andreev bound states are generated, and hence the broken time-reversal symmetry state, is on the order of a few coherence lengths. (The coherence length in this material in this symmetry-breaking direction is about 2 nm.) It is interesting that a superconductor that typically expels magnetic field, at low enough temperatures actually generates a magnetic field. This is due to the combination of symmetry breakings within this unconventional superconductor.

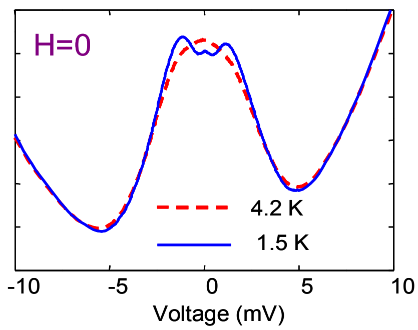

FIGURE 13. Spontaneous splitting of the zero-bias conductance peak observed as a signature of spontaneous time-reversal symmetry breaking in a superconductor. After Greene et al., 2000.

Recall that near the surface of a d-wave superconductor, there are unpaired quasi-electrons and quasi-holes because of the reflection symmetry breaking of the OP, as discussed above. The prediction was that these could condense into another Cooper channel, meaning that the unpaired electrons and holes at the surface would act like most other metals, and at a low enough temperature, superconduct. It has been determined earlier that such a new channel must exhibit a different symmetry than the bulk. We have no idea what this symmetry is, but we hypothesize that it is s-wave. That would cause the surface of the superconductor to be in a “mixed state” of a d-wave (from the bulk) and s-wave (from the near-surface area). It was also determined several years ago that a mixed state would spontaneously break time reversal symmetry. This is because if the free energy of the order parameter at the Fermi energy is minimized, then the state without nodes (d+is) is much preferred, i.e., has lower energy than the d+s state (both states shown in Figure 14).

A schematic of how the OPs might look in this broken symmetry state is shown in Figure 15. The bulk of the superconductor (lower left of diagram) is d-wave. Due to the reflection symmetry breaking of the d-wave OP, pair-breaking occurs and quasi-holes and quasi-electrons are nucleated in the near-surface region. At a low enough

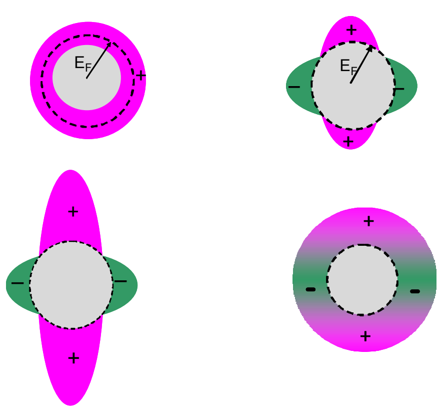

FIGURE 14. Pure *(top)* and mixed *(bottom)* order parameter symmetries. The first mixed state is d+s, which is energetically un-favorable. The second is d+is, which is favored. Note the continuous change of the order parameter on the Fermi surface of the d+is state, which indicates that this state spontaneously breaks time-reversal symmetry. After Greene et al., 2000.

CP795, *Women in Physics: The Second IUPAP International Conference on Women in Physics*, edited by B.K. Hartline and A. Michelman-Ribeiro

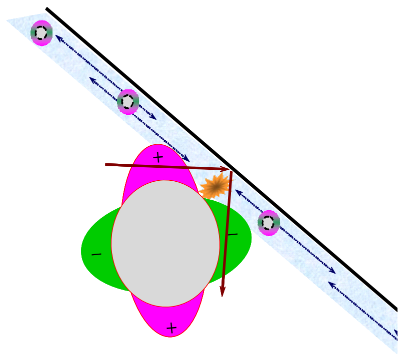

FIGURE 15. Representation of the broken time-reversal symmetry state at the surface of a d-wave superconductor. Note the d+is OP near the surface and the subsequent flow of electrons, represented by vectors along the interface in the near-surface region.

temperature, the electrons and holes in this surface-induced Andreev bound state condense into another superconducting state, say, s-wave, and the d+is mixed state that results at the interface breaks time-reversal symmetry.

SUMMARY AND CONCLUSIONS

It was shown that a superconductor is a quantum state of correlated electron pairs with zero resistance and perfect diamagnetism. Quasiparticle tunneling remains an important measurement in that it reveals several electronic properties of superconductors and symmetry breakings. The high-temperature superconductors break three symmetries: (1) gauge, by virtue of being superconducting; (2) reflection, because of the d-wave OP symmetry; and (3) time reversal, when gauge and reflection symmetries are broken in the presence of a symmetry-breaking surface. The actual mechanism of the Cooper pairing in high-temperature superconductors remains elusive, and searching for this mechanism remains an exciting area of theoretical and experimental research.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge these people who have made major contributions to this work, either in the lab or through fruitful discussions: H. Aubin, M. Aprili, E. Badica, A.V. Balatsky, Yu. S. Barash, M. Covington, W.L. Feldmann, D.G. Hinks, D.M. Ginsberg, P.M. Goldbart, P. Hentges, M. Fogelström, A.J. Leggett, J. Lesueur, T. Löfwander, W.K. Park, M. Randeria, J.M. Rowell, J.A. Sauls, D. Sheehey and N. Trevidi. This work is supported by the U.S. DOE-DMR; DEFG02-ER9645439, through the Frederick Seitz-Materials Research Laboratory.

REFERENCES

Superconductivity, Tunneling and High-Temperature Superconductors (HTS):

1. W.L. McMillan and J. M. Rowell, *Superconductivity*, R.D. Parks, ed., New York: Marshall-Dekkar, 1969, p. 561.
2. J.M. Rowell, in *Tunneling Phenomena in Solids*, E. Burstein, ed., New York: Plenum, 1965.
3. E.L. Wolf, *Principles of Electron Tunneling Spectroscopy,* London: Oxford University Press, 1985.
4. R. Simon and A. Smith, *Superconductors Conquering Technology's New Frontier*, New York: Plenum Press, 1988.
5. *Physical Properties of High-Temperature Superconductors,* Volumes I-V, D. Ginsberg, ed., Singapore: World Scientific, 1989-1996.
6. D.J. Van Harlingen, *Rev. Mod. Phys.* **67**, 515 (1995).

Andreev Reflection:

7. F. Andreev, *Sov. Phys. JETP* **19**, 1228 (1964).
8. G. Deutscher, *Rev. Mod. Phys.* **77**, 109 (2005).

Broken Symmetries:

9. P.W. Anderson, *Basic Notions of Condensed Matter Physics*, Westview Press, USA: Persus Books Group, 1997.
10. I.J.R. Aitchison and A.J.G. Hey, *Gauge Theories in Particle Physics,* 2nd ed., Bristol: Institute of Physics Publishing, 1993.

Reviews on Andreev Bound States and Time-reversal Symmetry Breaking in HTS:

11. L.H. Greene et al., *Physica B* **280**, 159 (2000), and references therein.
12. S. Kashiwaya and Y. Tanaka, *Rep. Prog. Phys.* **63**, 1641 (2000) , and references therein.