Direct Observation of the Coulomb Correlation Gap in a Nonmetallic Semiconductor, Si:B

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(Received 7 June 1995)

Using electron tunneling, we report the first direct spectroscopic measurement of the Coulomb correlation gap in the density of states $N(\varepsilon)$ of a nonmetallic doped semiconductor Si:B. In agreement with analytic models, $N(\varepsilon)$ is found to have a nearly parabolic energy dependence, resulting in a "soft" zero at the Fermi energy, with a gap width $\approx$0.75 meV. Resistivity measurements show that this energy governs the observed crossover temperature between noninteracting and correlated hopping transport.

PACS numbers: 71.30.+h, 73.20.Fz, 73.40.Gk

In barely insulating disordered solids, localized electrons can carry current at nonzero temperature but cannot screen the Coulomb interaction as effectively as in metals. Therefore, such materials provide an excellent forum to study the physics of interacting many-particle systems. Coulomb interactions in a many-electron system always deplete the single-particle density of states $N(\varepsilon)$ near the Fermi energy ε_F, relative to the noninteracting case [1]. Analytic calculations of $N(\varepsilon)$ renormalized by Coulomb correlations exist on both the metallic and insulating sides of a disorder-driven metal-insulator transition (MIT). For the metallic case, Altshuler and Aronov [2] showed that $N(\varepsilon)$ has a cusplike $|\varepsilon - \varepsilon_F|^{1/2}$ dependence near ε_F (in 3D). This has been confirmed on amorphous alloys [3] and granular metals [4] via electron tunneling measurements.

On the barely insulating side, charge transport occurs via inelastic hopping between states localized in both space and energy. Mott showed [5] that at low temperature electrons seek accessible energy states by hopping distances beyond the localization length, leading to variable-range hopping conductivity $\sigma(T) \propto \exp(-T_0/T)^{\nu}$. For noninteracting electrons $\nu = \frac{1}{4}$ in 3D. Efros and Shklovskii (ES) argued [6] that, including Coulomb interactions, the ground state is stable with respect to a one-particle excitation only if $N(\varepsilon)$ has a quadratic dependence on ε near ε_F:

$$N(\varepsilon) = \frac{3}{\pi}\left(\frac{\kappa}{e^2}\right)^3 (\varepsilon - \varepsilon_F)^2, \qquad (1)$$

where κ is the dielectric constant. Because $N(\varepsilon)$ vanishes only at ε_F, this is a "soft" Coulomb correlation gap with a width $\Delta_C = e^3(N_0/\kappa^3)^{1/2}$, where N_0 is the noninteracting density of states. In general, a power law $N(\varepsilon) \propto (\varepsilon - \varepsilon_F)^m$ results in a hopping exponent $\nu = (m + 1)/(m + 4)$ [7] as $T \to 0$, so that (1) gives $\nu = \frac{1}{2}$. When T is high enough for a hopping electron to explore an energy range $k_B[T^3T_0]^{1/4} > \Delta_C$, where $T_0 = 18/k_B\xi^3N_0$ and ξ is the localization length, the influence of the Coulomb gap can be neglected and the $\nu = \frac{1}{4}$ exponent is expected. Below a temperature $T_x = 0.38e^4\xi N_0/k_B\kappa^2$, only states inside the gap are accessible and a crossover to $\nu = \frac{1}{2}$ is predicted.

The ES model considers only one-particle excitations. Pollak and others [8] have argued that interactions among quasiparticles are important and lead to multiparticle excitations that make $N(\varepsilon)$ a stronger function of ε than the quadratic form of the ES model. Numerical simulations [9] have suggested that, accounting for multiparticle effects, the Coulomb gap could have quasiexponential energy dependence. The importance of multiparticle excitations and the energy range over which $N(\varepsilon)$ might be affected by them has yet to be conclusively established.

Despite the long history of work on the Coulomb gap in nonmetallic disordered solids, its existence and form have principally been inferred from activation fits to the conductivity [10], relaxation measurements [11], or other indirect means. Suggestions of a possible ES gap were reported in tunneling data on disordered thin films such as 3D $Au_{1-x}Ge_x$ [3] and quasi-1D granular Al [12]. These experiments focused on the metal side of the metal-insulator transition, however, and could only extrapolate to the insulating side by examining data trends as the samples became less metallic. In the absence of further work, these results alone cannot adequately describe nonmetallic materials. Because of technical problems with tunneling in truly nonmetallic thin films (discussed below), no validation of these suggestions by direct measurement on clearly nonmetallic thin films has been made. With the exception of sodium tungsten bronze [13], a singular case where the gap is large enough to be observed by photoemission, there has until now been no spectroscopic confirmation of the soft Coulomb correlation gap and no firm measurement of the gap shape, width, nor its effect on charge transport in more standard localized insulators.

Using electron tunneling spectroscopy, we have made the first direct observation of the soft Coulomb correlation gap and have measured its quantitative characteristics and its relationship to the conductivity in a localized semiconductor, boron-doped silicon (Si:B). The conductivity of Si:B across its MIT was extensively studied by Sarachik and co-workers [14,15], whose transport measurements show a critical boron density $n_c = 4.0 \times 10^{18}$ cm^{-3}. Electron tunneling in metallic Si:B crystals was reported by Wolf *et al.* [16], using

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Schottky contacts. They observed a conductance cusp similar to that described in Ref. [2].

When a conductor is separated from a conventional metal by a rectangular potential barrier high enough to prevent classical current flow but thin enough to permit quantum tunneling current, the tunneling conductance $G(V) = \partial I/\partial V$ is given by [17]

$$\frac{G(V)}{G_0} = \int_{-0}^{+\infty} \frac{N(\varepsilon)}{N_0}\left[-\frac{\partial f(\varepsilon - eV)}{\partial(eV)}\right] d\varepsilon, \quad (2)$$

where G_0 is the conductance in the noninteracting case, f is the Fermi function, and V is the applied voltage between electrodes. We take $\varepsilon_F = 0$. In many cases, interactions alter $N(\varepsilon)$ within at most a few meV of ε_F, so that G_0 is taken as the conductance at a high enough voltage bias where $I(V)$ is nearly Ohmic. The conductance then gives $N(eV)/N_0$ thermally broadened by $-\partial f/\partial(eV)$. Since a normalized quantity is measured, κ and N_0 cannot be independently obtained. The classic application is in superconductor gap spectroscopy, where $N(\varepsilon)/N_0 = \mathrm{Re}[\varepsilon/(\varepsilon^2 - \Delta^2)^{1/2}]$ has a distinctive shape. When one electrode is a superconductor, observation of this structure definitively establishes that the junction current is due to quantum tunneling.

We fabricated tunnel junctions on ⟨100⟩-oriented single-crystal wafers of Si:B grown by PureSil, Inc. The resistivity ratio $\rho(300\ \mathrm{K})/\rho(4.2\ \mathrm{K})$ gave a boron density $n = 3.4 \times 10^{18}\ \mathrm{cm}^{-3}$, or $n/n_c = 0.85$. Because Schottky contacts always gave unacceptably high resistances (>10 MΩ), we fabricated a more ideal tunnel junction by the following procedure. Both sides of 12 mil thick, 1/4 in. square chips were cleaned [18], and a 150 nm SiO_2 layer was grown. The SiO_2 was stripped off one side (the "back"), and four Al stripes were evaporated onto the Si. Ohmic contacts were formed by briefly annealing the Al stripes at 450 °C in nitrogen. The tunnel junction was made on the "front" by etching a 1 mm wide slot in the SiO_2 down to the Si. A very thin (5 to 8 Å estimated) SiO_2 layer, the tunnel barrier, was then grown using the methods described in Ref. [19]. Barrier thickness was increased to ~20 Å in an O_2 backfilled desiccator. Pb stripes 1 mm wide were evaporated through a mask, crosswise to the patterned slot, to serve as the counterelectrodes.

For tunneling, the chip was immersed in liquid ^{4}He. Temperature was controlled by the He vapor pressure with stability better than 0.5 mK. Tunneling conductance was measured between a Pb stripe and two Al stripes (see Fig. 1 inset) using a four-wire voltage bias. A problem with tunneling measurements in nonmetallic materials is the voltage drop incurred as the current traverses the sample to get to the junction. Particularly in thin films, this "access resistance" can lead to significant extrinsic voltage drops that mask the tunneling density of states. In principle, this difficulty affects our measurements. However, the backside contacts on our single crystals minimize the access resistance by presenting a large cross section and a short path length for current flow to the junction, something not possible with thin-film samples because of the substrate needed. An estimate using the Si:B resistivity at 1.2 K (~1 Ω cm from Fig. 2) and the contact geometry gives an access resistance of about 3 Ω. By measuring two-point resistances across all Al contacts to the Si:B, we determined the access resistance through the Si:B could be no more than 10 Ω at 1.2 K, or <0.1% of the total measured junction resistance of ~15 kΩ. Therefore, the voltage measured is an accurate characterization of the junction.

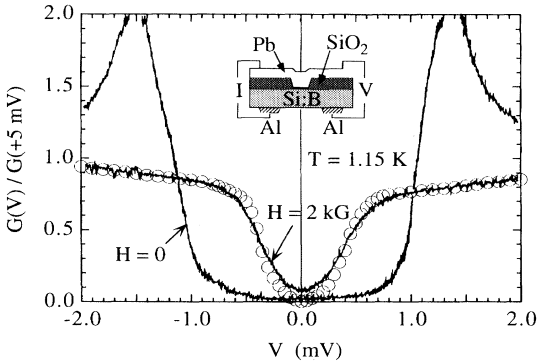

FIG. 1. Normalized conductance vs voltage bias of a Pb-SiO_2-Si:B tunnel junction at 1.15 K. Data are normalized to $G(+5$ mV). The zero magnetic field trace shows the superconducting gap of Pb. The 2 kG field drives the Pb normal. The circles are the 2 kG data with the thermal broadening removed. The dip around $V = 0$ is the Coulomb gap. Inset: Schematic cross section (not to scale) of the junction.

Junction quality was sensitive to the details of the fabrication. The "failure" mode was a junction resistance >10 MΩ. To prove that the conductance was due to quantum tunneling, our criterion for a "good" junction was observation of the superconducting gap of Pb. The Pb could be driven to its normal state by a 2 kG magnetic field, which allowed measurement of the density of states of the Si:B alone. It must be stated that of >30 such junctions made, only four were considered "good" by our criterion. The data described are characteristic of these four junctions.

The Si:B resistivity versus temperature, $\rho(T)$, was also measured using all four of the Al contacts on the back of each chip. Measurement of $\rho(T)$ down to 0.1 K was done by heat sinking the sample to the mixing chamber of a dilution refrigerator. Because both ρ and $d\rho/dT$ of the Si:B became extremely large below 1 K, our dilution refrigerator system did not have adequate temperature stability to allow a reliable recording of the tunneling conductance below 1 K.

Figure 1 shows a normalized tunneling conductance spectrum taken at 1.15 K in both zero field, where the Pb is superconducting, and in 2 kG, where the Pb is normal. The data are normalized to $G(+5\ \mathrm{mV}) = (16.6\ \mathrm{k\Omega})^{-1}$.

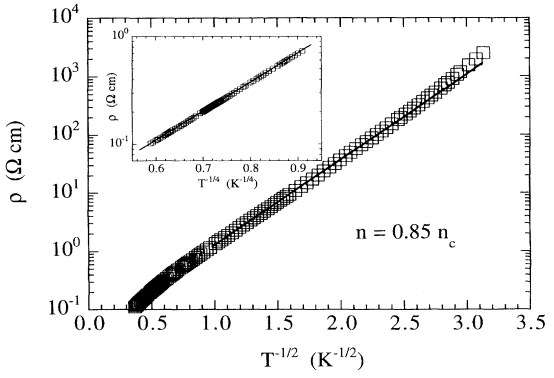

FIG. 2. Resistivity vs temperature of the Si:B itself. The line is the ES hopping form obtained from a fit to the data in the range $0.3 \leq T \leq 0.8$ K. Inset: The higher temperature range $1.5 \leq T < 10$ K plotted logarithmically against $T^{-1/4}$. The line is a fit by the Mott hopping form.

The zero field data clearly show the distinctive superconducting density of states of Pb, *proving* that the junction conductance is due to quantum tunneling. Inside the Pb gap, the conductance at $V = 0$ is zero to within the preamplifier input impedance (10 MΩ), showing that there are negligible nontunneling current paths. The position of the Pb gap peak near ± 1.35 mV is ~ 0.1 mV higher than observed in test Al-oxide-Pb junctions. The peak height is also reduced and width broadened somewhat more than from thermal smearing. These effects are attributable to convolution with a soft depletion in the density of states of the Si:B, which is revealed when a 2 kG field drives the Pb normal. There is a clear dip in $G(V)/G_0$ between ± 0.5 mV, which is the signature of the Coulomb gap. Near $V = 0$, the measured conductance is approximately parabolic but does not quite go to zero.

The Coulomb gap described by (1) is the gap at $T = 0$ K. At 1.15 K the conductance is broadened both by thermal smearing from the Fermi function derivative in (2) and by interactions. For an interacting system, the distribution of occupied states affects the state energies, making $N(\varepsilon)$ itself explicitly temperature dependent. Using the $G(V)/G_0$ data, $N(eV, 1.15\ \mathrm{K})/N_0$ can be separated from ordinary thermal smearing by digitally deconvoluting $-\partial f/\partial(eV)$ from the integral in (2). The result is depicted by the circles in Fig. 1. This gives a functional form $N(eV, 1.15\ \mathrm{K})/N_0 \propto |eV|^{2.2}$ for $|eV| < 0.3$ meV, and a width $\Delta_C \approx 0.75$ meV. Also, most of the small measured conductance at $V = 0$ is removed from $N(eV)$. Numerical simulations [20] indicate that the Coulomb gap has a temperature correction $N(\varepsilon, T) \approx N(\varepsilon, 0)[1 + (k_B T/\Delta_C)^2]$ for ε and $k_B T < \Delta_C$. Because $(k_B T/\Delta_C)^2$ is mall, we take these values to be characteristic of the zero-temperature gap.

Figure 2 shows the resistivity of the Si:B plotted logarithmically against $T^{-1/2}$ and, in the inset, against $T^{-1/4}$ over the higher temperature range. The Si:B obeys a $\nu = \frac{1}{4}$ hopping law from ~ 10 to ~ 1 K, from which we obtain $T_0 = 1500$ K. The hopping exponent ν can be determined without prior assumptions about the hopping form by plotting $\log[\partial \ln(\rho)/\partial \ln(1/T)]$ against $\log(T)$, the linear slope of which gives $-\nu$ [21]. This is shown in Fig. 3. Clearly, a single line does not fit the data over the entire temperature range. A linear fit for $T > 1.3$ K yields a slope of -0.25, indicative of Mott hopping. The behavior below 1 K is more complex. A fit over a limited temperature range ($0.3 \leq T \leq 0.8$ K) yields a slope of -0.5, consistent with ES hopping. However, there is an upward deviation at the lowest temperatures. As discovered by Dai, Zhang, and Sarachik [15], this deviation is due to spin correlations that appear in addition to Coulomb interactions at very low temperature. Because of this, extraction of an ES hopping temperature is field dependent (for $H \geq 1$ T) and has questionable meaning. Nevertheless, because it occurs at a comparatively high temperature, the empirical crossover temperature T_x between noninteracting and Coulomb correlated regimes can be defined where the slope $= -0.5$ and slope $= -0.25$ lines in Fig. 3 intersect. This gives $T_x = 1.4$ K.

The independent measurements of both density-of-state structure and resistivity on the same Si:B sample allow us to definitively establish the influence of the Coulomb gap on charge transport. The measured Coulomb gap functional form $N(\varepsilon) \propto \varepsilon^{2.2}$ predicts a hopping exponent $\nu = 0.52$ near 1 K, which is consistent with the transport data in this temperature range. This demonstrates that the shape of the gap determines the hopping characteristics in the expected manner. Moreover, the size Δ_C of the Coulomb gap, as measured by tunneling, determines the crossover temperature T_x, as measured by the resistivity. This can be shown by noting that, within the ES model, Δ_C, T_x, and T_0 are defined to satisfy the consistency relation $\Delta_C = k_B(T_x^3 T_{0M})^{1/4}$. From the data, using the

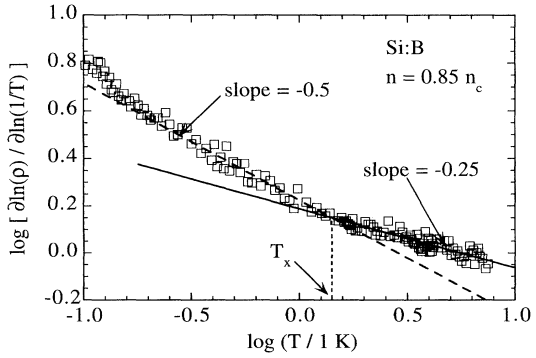

FIG. 3. Plot of $\log[\partial \ln(\rho)/\partial(1/T)]$ vs $\log[T]$. The slope of the data gives the negative of the hopping exponent. The solid line is a linear fit to the range $1.5 < T < 10$ K. The dashed line is a linear fit in the range $0.3 < T < 0.8$ K. These lines intersect at 1.4 K.

independently measured values $\Delta_C = 0.75$ meV, $T_x = 1.4$ K, and $T_{0M} = 1500$ K, we obtain a relation $\Delta_C/k_B = 1.1(T_x^3 T_{0M})^{1/4}$, in reasonable agreement with the model, given our empirical definition of T_x.

No convincing evidence for multiparticle excitation effects was observed over the energy and temperature ranges accessible. While the measured power $m = 2.2$ is 10% larger than the ES prediction, the difference is within the margin of uncertainty. Cuevas *et al.* [22] recently pointed out that in tunneling experiments the presence of a planar metal electrode should enhance the screening of Coulomb interactions directly beneath it. Their computations for a metal in direct contact with a disordered insulator yield a tunneling gap where m is between 1 and 2 in the first few monolayers away from the interface and approaches 2 five or six monolayers deep in the insulator. Thus, in principal we would expect to observe a deviation towards a slightly "softer" gap with $m \leq 2$, which is opposite to what was measured. Screening effects may be less important in our tunnel junctions because the Pb and Si:B are separated by roughly 20–30 Å of SiO_2. Nevertheless, we cannot presently rule out two possibilities. (1) The gap really has m slightly larger than 2.2, but is softened by screening from the Pb electrode. In fact, large array simulations by Möbius, Richter, and Drittler [23] suggest that $m \approx 2.6$. However, we note that nothing measured was suggestive of a quasiexponential gap form. (2) The energy range of importance to multiparticle excitations is $\lesssim 0.1$ meV and therefore unobservable at ~ 1 K.

In summary, we have used electron tunneling to observe and quantitatively characterize the Coulomb correlation gap in the density of states of an interacting localized insulator, Si:B. The gap has the quasiparabolic shape predicted when only one-particle excitations are important. By measuring tunneling conductance and transport resistivity on the same sample, we also showed that the gap structure and width control the form of the hopping conductivity and the crossover from noninteracting to interacting regimes. No evidence for significant multiparticle excitations was observed in the temperature and energy ranges studied.

We thank Steve Jones and David Kellogg for help with the Si processing, and Boris Shklovskii for useful advice. The dilution refrigerator was acquired with the aid of an NSF instrumentation grant. This work was supported in part by NSF Grant No. DMR-9316803.

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