Electronic Correlation Effects and the Coulomb Gap at Finite Temperature

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We have investigated the effect of the long-range Coulomb interaction on the one-particle excitation spectrum of n-type germanium, using tunneling spectroscopy on mechanically controllable break junctions. At low temperatures, the tunnel conductance shows a minimum at zero bias voltage due to the Coulomb gap. Above 1 K, the gap is filled by thermal excitations. This behavior is reflected in the variable-range hopping resistivity measured on the same samples: up to a few degrees Kelvin the Efros-Shklovskii $\ln R \propto T^{-1/2}$ law is obeyed, whereas at higher temperatures deviations from this law occur. The type of crossover differs from that considered previously in the literature.

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The electronic density of states (DOS) near the Fermi level is an important physical quantity for understanding electrical transport mechanisms in strongly localized systems [1], such as impurity bands in doped semiconductors. These consist of sites with random positions and random energies [2,3]. At small impurity concentration N_d, the electron wave function is localized with a localization radius a smaller than the average nearest-neighbor distance $N_d^{-1/3}$ between sites. At low temperatures the electrical resistivity of such systems is governed by variable-range hopping (VRH), which means that the activation energy for a hopping process decreases continuously with temperature [2,3]. The role of the intersite Coulomb interaction between electrons in the hopping regime was first addressed by Pollak [4] and by Srinivasan [5]. They showed that in localized systems the Coulomb interaction creates a deep depletion of the one-particle DOS near the Fermi energy E_{F}. Efros and Shklovskii (ES) called this depletion "Coulomb gap" and showed that the DOS near E_{F} varies as $g(E) = g_0|E - E_{\mathrm{F}}|^{D-1}$ for dimensionalities $D = 2$ and $D = 3$, respectively [3,6]. This leads to a VRH hopping resistance $R \propto \exp(T_{\mathrm{ES}}/T)^{1/2}$ [6,7], in contrast to Mott's $R \propto \exp(T_{\mathrm{M}}/T)^{1/4}$ law in $D = 3$ [2] for which a constant DOS $g(E) = g_0$ is assumed.

A crossover between these two temperature laws has been predicted theoretically [3]. Indeed, there is ample experimental evidence for such a crossover [8–10], although the temperature range where the Mott law is visible depends on the material, especially on the dopant concentration [11,12]. According to the traditional interpretation of this crossover the energy range of the phonon-assisted tunneling (hopping) becomes larger than the width of the Coulomb gap Δ_{CG} above the crossover temperature. In this case the Coulomb gap does not affect the hopping resistance, thus resulting in Mott's law. However, another kind of crossover from an ES-type to Mott-type temperature law may occur, namely the filling of the Coulomb gap by thermal excitations. Such a filling of the Coulomb gap with increasing temperature was predicted by Monte Carlo simulations of a classical Coulomb glass [13–15]. More recently, it was observed by tunneling spectroscopy on Si:B samples near the metal-nonmetal transition [16–18]. The temperature dependence of the DOS should, in turn, affect the temperature dependence of the bulk resistivity. Surprisingly, except for Ref. [15], this effect has not yet been taken into account in the literature.

In this Letter we present evidence that in insulating doped Ge the second mechanism is verified for the three-dimensional case. We show by comparing the temperature dependence of the DOS, derived by tunneling spectroscopy, with that of the VRH resistivity that the observed deviations from the ES law above 1 K correspond to the thermal filling of the Coulomb gap and not to the traditional crossover mechanism.

The electronic DOS in solids can be directly probed by tunneling spectroscopy and photoelectron spectroscopy, for example [19]. But the small size of the width of the Coulomb gap Δ_{CG} strongly restricts the useful spectroscopic techniques. At present tunneling spectroscopy has a better energy resolution. Massey and Lee were the first to directly observe the Coulomb gap in a doped uncompensated semiconductor Si:B [16–18] by this technique. They used planar tunnel junctions between boron-doped Si samples and a Pb counterelectrode with an insulating dielectric as barrier. The superconducting quasiparticle DOS of the lead electrode was observed, proving quantum tunneling. Suppressing superconductivity of lead in a magnetic field of $B = 200$ mT allowed them to measure the DOS of the Si:B electrode against the constant DOS of normal lead. However, planar tunnel junctions are difficult to prepare, especially with germanium.

As an alternative method, we have proposed recently that it is possible to realize tunneling across a semiconductor break junction due to the lateral confinement of

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small point contacts [20]. This is a well-established technique to investigate superconductors and metals, both in the regime of direct metallic contact and tunneling across a vacuum barrier [21]. However, problems may arise because the break-junction technique, with the two electrodes consisting of the same material, does not allow a rigorous independent test of the quality of the tunneling barrier, unless the material properties themselves are well known in advance. Therefore, special care must be applied if one wants to attribute the observed spectra to a tunneling process which probes the excitation spectrum of the bulk material. We adjusted our break junctions in such a way that the bulk resistance of the material (taken in series) could be neglected. To ensure a voltage drop confined to the junction itself, the contact resistance was set to a value larger than about 10 kΩ at 1 K. Our junctions had lateral dimensions of less than about 100 nm. The hopping length amounts to about 150 nm at 1 K, further increasing towards lower temperatures. Charge is therefore transported across the junction by a single hopping event at a rather well-defined energy. This justifies our calling the transport tunneling and the interpretation of the voltage drop as an excitation energy. On the other hand, the contact diameter must be large enough to inhibit the formation of a depletion layer. Such a layer adds an additional tunneling barrier [22], and it may also affect the local DOS in the contact region. We estimate ~10 nm as a lower bound for the lateral size of useful junctions.

Our undoped samples were grown by the Czochralski method using highly enriched (up to 93%) ^{74}Ge. Neutron-transmutation doping ensured excellent homogeneity of ^{75}As as shallow donors [12]. The main nuclear reaction of ^{74}Ge with thermal neutrons is $^{74}\mathrm{Ge}(n,\gamma)^{75}\mathrm{Ge} \rightarrow {}^{75}\mathrm{As}$. As by-product, a small fraction of ^{71}Ga acceptors are produced. This gives a compensation of $K = N_{\mathrm{Ga}}/N_{\mathrm{As}} = 12\%$, and fixes the Fermi level inside the impurity band. The donor concentration $N_d = N_{\mathrm{As}}$ was below, but close to, the disorder-driven metal-insulator transition of Ge which occurs at a critical impurity concentration of $N_c = 3.4 \times 10^{17}\ \mathrm{cm}^{-3}$ [23].

For our tunneling experiments the samples were cut into $1 \times 1 \times 10\ \mathrm{mm}^3$ slabs with a 0.5 mm deep groove to define the break position within the (111) cleaving plane of germanium. The samples were glued onto a flexible bending beam, electrically insulated but thermally well coupled to the cold plate. They were broken at low temperatures in the ultrahigh vacuum chamber of a dilution refrigerator. The contact size could be adjusted *in situ* with a micrometer screw and a piezotube. For further details of the setup see Ref. [24]. The dI/dU spectra of junctions with small resistance (less than about 100 kΩ) were obtained by means of the standard four-terminal method with current biasing. The current-voltage characteristics of junctions with high resistance (larger than about 100 kΩ) were recorded using the standard two-terminal method with voltage biasing. In the latter case the bulk samples contributed at most 5% to the total resistance.

All Ge break junctions investigated have rather similar characteristics. Figure 1 shows typical spectra of a sample with $N_d = 1.26 \times 10^{17}\ \mathrm{cm}^{-3}$ as a function of voltage and temperature. The spectra have a pronounced minimum at low temperatures. We believe that this anomaly represents the Coulomb gap. Between 100 mK and 1 K the spectra depend only weakly on temperature. Above about $T = 1$ K the Coulomb gap becomes filled by thermal excitations. It has almost vanished at $T = 6$ K.

In order to investigate how this temperature dependence of the DOS affects the hopping resistivity, we have measured the resistance of the bulk sample using the standard four-terminal technique. Figure 2 shows the resistance as a function of $T^{-1/2}$ and $T^{-1/4}$, respectively. At low temperatures $\ln R \propto T^{-1/2}$, as expected for the ES law. The resistance deviates from this behavior at $T > 1$ K, nearly coinciding with the temperature at which the Coulomb gap is suppressed according to the tunnel data; see Fig. 1. This crossover cannot be due to the traditional mechanism, because the measured width of the Coulomb gap is $\Delta_{\mathrm{CG}} = 2$ meV. Estimating the crossover temperature T^* as $\Delta_{\mathrm{CG}}/2k_B = (T_{\mathrm{ES}}T^*)^{1/2}$ [3] leads to $T^* \approx 340$ K, which is far from the measured crossover range. Regarding the temperature dependence of the resistance above the crossover region there is no clear-cut $\ln R \propto T^{1/4}$ dependence, but one can clearly see that the ES law no longer applies. The temperature dependence of the resistance is nearer to the Mott than to the ES law. Of course, a theoretical calculation of the temperature dependence of the resistivity in the transition regime should take into account the full temperature variation of the DOS as displayed in Fig. 1. Our present aim is to demonstrate that the deviation from the ES law is due to the thermal smearing of the Coulomb gap.

We turn now to a more detailed discussion of the temperature dependence of the DOS. To extract the DOS from the spectra we first removed the energy-dependent

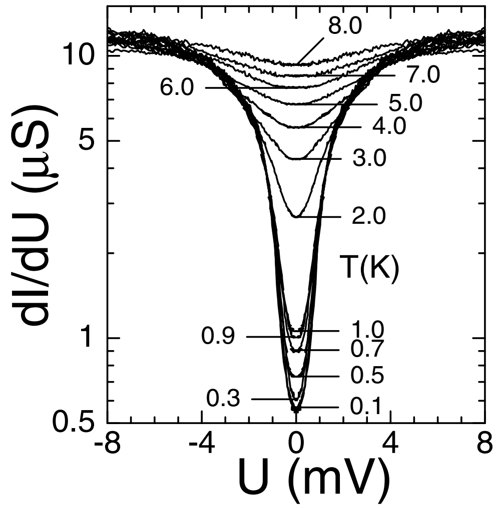

FIG. 1. dI/dU vs U spectra of the Ge sample with $N_d = 1.26 \times 10^{17}\ \mathrm{cm}^{-3}$ at the indicated temperatures.

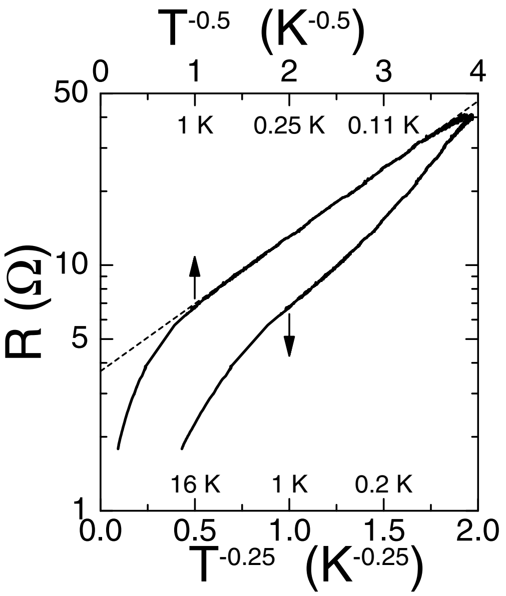

FIG. 2. Electrical resistance of the bulk Ge sample R vs $T^{1/4}$ and $T^{1/2}$, respectively. The dashed line is a fit to the ES law with $T_{\mathrm{ES}} = 0.40$ K. $N_d = 1.26 \times 10^{17}$ cm^{-3}.

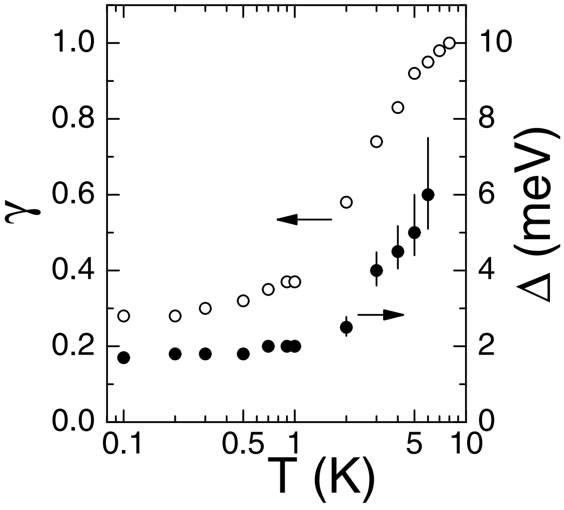

FIG. 3. Coulomb gap Δ_{CG} and residual DOS γ vs temperature T derived from the spectra in Fig. 1.

part at high voltages, $|U| > 4$ mV. Several possibilities were tried, with only slight variation of the final result. According to Ref. [18], this high-energy tail can be roughly described by $g(E) \propto 1 + \sqrt{(E - E_{\mathrm{F}})/\delta}$. In this model, the parameter δ represents a correlation energy, which is almost independent of impurity concentration. From our experiments $\delta \sim 10$ meV is a rather large value when compared to the results for Si:B [18]. Alternatively, a Schottky-type behavior was used with $dI/dU \propto \exp(U/U_{00})$. The parameter U_{00} may then represent the properties of an additional barrier due to the depletion layer. As we do not know which of the two possibilities is correct, we normalize the spectra at low temperatures with respect to that corresponding to the highest temperature. The shape of those normalized spectra is almost flat outside the Coulomb-gap anomaly. All curves are then fitted using

$$g(E,T) \propto \gamma(T) + [1 - \gamma(T)] \times \frac{|E - E_{\mathrm{F}}|^s}{[\Delta_{\mathrm{CG}}(T)/2]^s + |E - E_{\mathrm{F}}|^s}. \quad (1)$$

The parameter γ describes a "residual" DOS at the Fermi level and Δ_{CG} is the width of the Coulomb gap (FWHM). The DOS derived by ES is recovered when $\gamma = 0$ and $s = 2$ [3,6].

The experimental DOS of our samples strongly deviates from the simple square law derived by ES [3,6], and which was also found experimentally for Si:B [16–18]. Taking into account the Fermi distribution and the expression Eq. (1) for the DOS on both sides of the junction, our analysis yields $s = 3$ for the sample with $N_d = 1.26 \times 10^{17}$ cm^{-3}. Figure 3 shows how Δ_{CG} and γ depend on temperature. Both saturate at low temperatures. Analytical as well as numerical simulations for nonmetallic disordered systems have predicted several different relationships: power laws $g(E, T = 0) \propto (E - E_{\mathrm{F}})^{D-1}$ [6,25] and $g(E, T = 0) \propto (E - E_{\mathrm{F}})^{2.7 \pm 0.1}$ [13] as well as an exponential dependence $g(E, T = 0) \propto \exp\{-[\Delta/(E - E_{\mathrm{F}})]^{1/2}\}$ [26]. A power law with $s = 3$ is close to the theoretical value of $s = 2.7$ in Ref. [13].

Our measured temperature dependence of the zero-bias DOS reveals a power law $g(E_{\mathrm{F}}, T) \propto T^x$ with an exponent $x = 0.8$. This differs from $x = 2.7$ derived by [13], but it agrees quite well with $x = 1$ obtained by the simulations of Ref. [14].

Because of the deviation of the experimental DOS from the simple $s = 2$ law the observed ES-type behavior of the bulk resistivity needs an explanation. For a DOS varying as $g(E) \propto (E - E_{\mathrm{F}})^s$ a temperature law $\ln R \propto T^{-\alpha}$ with $\alpha = (s + 1)/(s + D + 1)$ is expected [3,27]. For $s = 3$ and $D = 3$ this yields $\alpha = 0.57$. This can hardly be distinguished from $\alpha = 0.5$, but it can readily be distinguished from $\alpha = 0.25$.

To summarize, the tunnel conductance of small break junctions of our germanium samples shows a minimum of the DOS near the Fermi level. This minimum represents the Coulomb correlation gap. Up to about 1 K, the width of this anomaly depends only weakly on T. This corresponds to the ES regime of the temperature dependence of the variable-range hopping conductivity. Above about 1 K, the anomaly smears out. Consequently, deviations from the ES law occur with a different temperature dependence. According to our interpretation, the observed crossover in the temperature variation of the resistivity is not due to the temperature-broadened range of hopping energies. It rather originates from the suppression of the Coulomb gap by thermal excitations.

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