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. The tunnel conductance was measured as a function of energy and temperature. At low temperatures, the spectra reveal a minimum at zero bias voltage due to the Coulomb gap. In the temperature range above 1 K the Coulomb gap is filled by thermal excitations. This behavior is reflected in the temperature dependence of 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 are observed, indicating a cross-over to Mott’s \( \ln R \propto T^{-1/4} \) law. The mechanism of this cross-over is different from that considered previously in the literature.

The electronic density of states (DOS) near the Fermi level is an important physical quantity for understanding electrical transport mechanisms in strongly localized systems \[1\], like impurity bands in doped semiconductors. They consist of sites with random positions and random energies \[2\]. The electron wavefunction is localized with a localization radius \( a \) smaller than the average nearest-neighbor distance between sites which is of order \( N^{-1/3} \) (\( N \equiv \text{concentration of impurities} \)). 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 \[2\]. The role of the inter-site 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 \( g(E) = g_0 \left( E - E_F \right)^{D-1} \) for dimensionalities \( D = 2 \) and \( D = 3 \), respectively \[6\]. This leads to a VRH hopping resistance \( R \propto \exp \left( T_{\text{ES}}/T \right)^{1/2} \) \[3\], in contrast to Mott’s \( R \propto \exp \left( T_{\text{M}}/T \right)^{1/4} \) law \[4\] for which a constant DOS \( g(E) = g_0 \) is assumed.

A cross-over between these two temperature laws has been expected theoretically \[3\] and also observed experimentally \[3\]. According to the traditional interpretation of this cross-over the energy range of the phonon-assisted tunneling (hopping) becomes larger than the width of the Coulomb Gap \( \Delta_{\text{CG}} \) above the cross-over 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 \[10\] \[12\]. More recently, it was observed by tunneling spectroscopy on Si:B samples near the metal-nonmetal transition. The temperature dependence of the DOS should, in turn, affect the temperature dependence of the bulk resistivity. Surprisingly, except for Ref. \[12\], 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. 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 cross-over mechanism.

The electronic DOS in solids can be directly probed by tunneling spectroscopy and photoelectron spectroscopy, for example. But the small size of the width of the Coulomb gap \( \Delta_{\text{CG}} \) strongly restricts the useful spectroscopic techniques. At present only the tunneling spectroscopy has the required energy resolution. Massey and Lee were the first to directly observe the Coulomb gap in a doped uncompensated semiconductor Si:B \[13\] \[15\]. They used planar tunnel junctions between boron-doped Si samples and a Pb counter-electrode with an insulating dielectric as barrier. The superconducting quasi-particle DOS of the lead electrode has been observed, proving quantum tunneling. Suppressing superconductivity of lead in a magnetic field of \( B = 200 \text{ mT} \) allowed then 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 alternative method we have proposed recently that it is possible to realize tunneling across a semiconductor break junction due to the lateral confinement of small point contacts [14]. 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 [17]. To ensure a voltage drop confined to the junction itself the contact resistance is set to a value larger than about 10 kΩ at 1 K. Our junctions have lateral dimensions of less than about 100 nm. The hopping length amount to about 150 nm at 1 K increasing towards lower temperatures. Charge is transported across the junction by a single hopping event at a rather well-defined energy. This justifies our calling the transport tunneling and to interpret the voltage drop as an well-defined energy. This justifies our calling the transport tunneling and to interpret the voltage drop as an exciton 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 [13], and it may also vary the local DOS in the contact region. We estimate a ~10 nm lower bound for useful junctions.

Our undoped samples were grown by the Chochralski method using highly enriched (up to 93 % 74 Ge) germanium. Neutron-transmutation doping (NTD) ensured excellent homogeneity of 75As as shallow donors [9]. The main nuclear reaction of Ge with thermal neutrons is 74 Ge(n, γ)75 Ge → 75 As. As by-product, a small fraction of 75Ga is produced as acceptors. This gives a compensation of K = N_{Ga}/N_{As} = 12 %, and sets the Fermi level inside the impurity band. The donor concentration N_d = N_{As} was below, but close to, the disorder-driven metal-insulator transition of Ge at a critical impurity concentration of 3.4 · 10^{17} cm^{-3} [13].

For our tunneling experiments the samples were cut into 1 × 1 × 10 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 isolated but thermally well coupled to the cold plate. They were broken at low temperatures in the ultra-high vacuum chamber of the refrigerator. The contact size could be adjusted in situ with a micrometer screw and a piezo tube. For further details of the setup see Ref. [20]. 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) was 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 investigated Ge break junctions have rather similar characteristics. Fig. [3] shows typical spectra of a sample with N_d = 1.26 × 10^{17} cm^{-3} as 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 resistances of the bulk sample using the standard four-terminal technique. Fig. [2] shows the resistance as function of T^{-1/2} and T^{-1/4}, respectively. At low temperatures ln R ∝ T^{-1/2}, as expected for the ES law. The resistance deviates from this behavior at T^{-1/2} < 0.5 K^{-1/2} or at T > 4 K, nearly coinciding with the temperature at which the Coulomb gap is suppressed according to the tunnel data, see Fig. [2].

We have also considered the traditional scenario of the crossover between the ES and Mott law in which one assumes that the hopping energy range becomes broader than Coulomb gap [21]. From an analysis similar to that of [21] for the traditional cross-over mechanism we obtained a width the Coulomb gap of Δ_{CG} = 0.25 meV which is considerably smaller than the observed Δ_{CG} = 2.5 meV. But the latter value would correspond to a much higher crossover temperature than observed experimentally.

We turn now to a more detailed discussion of the temperature dependence of the DOS. To extract the DOS from the spectra we first tried to remove the energy-dependent part at high voltages. Several possibilities were tried, with only slight variation of the final result. According to Ref. [15], this high-energy tail can be roughly described by g(E) ∝ 1 + (E−E_F)/δ. In this model, the parameter δ represents a correlation energy, which is almost independent of impurity concentration. For our experiments δ ~ 10 meV, a rather large value when compared to the results for Si:B [13]. Alternatively, a Schottky-type behaviour was used with dI/dU ∝ exp(U/U_0). The parameter U_0 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. They are then fitted using

\[ g(E, T) ∝ γ(T) + [1 − γ(T)] \frac{|E − E_F|^s}{(\Delta_{CG}(T)/2)^s + |E − E_F|^s} \]  

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 γ = 0 and s = 2 [3].

The experimental DOS of our samples strongly deviates from the simple square-law derived by ES [3], and which was also found experimentally for Si:B [3, 15]. Taking into account the Fermi distribution and the DOS
Eq. (1) on both sides of the junction, our analysis yields for the sample far from the metal-nonmetal transition $s = 3$. Fig. 3 shows how $\Delta_C$ and $\gamma$ 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 $g(E, T = 0) \propto (E - E_F)^{D - 1}$ [23] and $g(E, T = 0) \propto (E - E_F)^{2.7 \pm 0.1}$ [14] as well as an exponential dependence $g(E, T = 0) \propto \exp[-(\Delta/(E - E_F))^{1/2}]$ [24]. A power law with $s = 3$ is consistent with the results of Ref. [14].

The temperature dependence of the zero-bias DOS also reveals a power law $N(E_F, T) \propto T^x$ with an exponent $x = 0.8$. This differs from $x = 2.7$ derived by [14], but it agrees quite well with $x = 1$ obtained by the simulations of Ref. [1].

Because of the experimental DOS, especially its strong temperature dependence, the observed ES-type behaviour of the bulk resistivity needs an explanation. We propose the following scenario to interpret our results: i) At low temperatures the Coulomb gap is temperature independent. This corresponds to the ES regime of the VRH conductivity; ii) the power law behaviour of the residual DOS $\gamma(T)$ causes the transition from the ES to the Mott law; iii) at high temperature the DOS is constant and one expects a Mott-type VRH conductivity. The mechanism of the transition between ES- and Mott-type behaviour is therefore completely different from that considered in Refs. [22].

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 is the ES-regime. Above about 1 K, the anomaly smears out. Consequentially deviations from the ES law occur. Above about 6 K, the anomaly has vanished, and the DOS becomes constant. The sample is then in the Mott regime. According to our interpretation, the cross-over between ES and Mott law at such low temperatures is not due to the temperature-enhanced range of hopping energies. But it origins from the suppression of the Coulomb gap by thermal excitations. These break-junction tunneling results are consistent with the electrical resistivity of the same samples, which also shows a rather wide temperature range for the transition between ES and Mott variable-range hopping.

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

FIG. 2. Electrical resistance of the bulk Ge sample $R$ vs. $T^{1/4}$ and $T^{1/2}$, respectively. $N_d = 1.26 \cdot 10^{17}$ cm$^{-3}$. 
FIG. 3. Coulomb gap $\Delta_{CG}$ and residual DOS $\gamma$ vs. temperature $T$. $N_d = 1.26 \cdot 10^{17} \text{ cm}^{-3}$. 