Fizika Nizkikh Temperatur, 2000, v. 26, No 7, p. 687–693

Break-junction experiments on the Kondo semiconductor CeNiSn: tunnelling versus direct conductance

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Received February 28, 2000

We have investigated the rare-earth Kondo semiconductor CeNiSn by point contact and tunneling spectroscopy using mechanically controllable break junctions. $I(V)$ characteristics and their derivatives were recorded for contacts from the metallic to the tunneling regime at temperatures between 0.1–8 K and in magnetic fields up to 8 T. We found that CeNiSn behaves like a compound with typical metallic properties instead of the expected semiconducting behavior. The main spectral feature is a pronounced zero-bias conductance minimum of about 10 meV width, which appears to be of magnetic nature. These break-junction experiments provide no clear-cut evidence for an energy (pseudo)gap of CeNiSn.

PACS: **71.27.+a**, 73.40.Jn, 75.30.Mb

Introduction

Cerium intermetallic compounds show a large variety of extreme properties at low temperatures. The f-electrons of the Ce ions can strongly hybridize with the conduction electrons, resulting in a number of different ground states. The heavy-fermion, the mixed-valent, and the Kondo-lattice state have attracted most of the interest. Among the Ce compounds, CeNiSn is usually classified as a Kondo semiconductor, mainly due to the enhanced electrical resistivity at low temperatures [1].

As soon as high-quality samples became available, the low-temperature resistivity turned out to be metallic, unlike CeNiSn with nonmagnetic impurities [2]. However, an anisotropic gap or V-shaped pseudogap in the electronic density of states is still used today to describe, e.g., specific-heat measurements below 2 K [3]. Another example are the break-junction experiments by Ekino et al. [4]. They observed $dI/dV(V)$ spectra with ~ 10 meV broad zero-bias minima. Assuming the junctions were in the tunneling regime, these anomalies were interpreted as being due to the gap in the electronic density of states. Later, break-junction experiments in high magnetic fields [5] revealed a suppression of the above zero-bias anomaly for fields along the a axis, unlike for fields along the b axis. This field-induced reduction of the gap structure was interpreted as crossover phenomenon from a pseudogap to a metallic heavy-fermion state.

Although the observation of a gap-like conductance minimum of the CeNiSn break junctions is an interesting fact, the tunneling regime in Refs. [4,5] was mainly postulated instead of experimentally verified. It is a severe drawback of the break-junction technique that one can not use a well-known superconductor like lead or aluminum as counter electrode to test the tunneling with a known superconducting quasiparticle density of states. The only way out of this dilemma seems to be to test the tunneling regime via the exponential variation of the contact resistance as the vacuum gap width between the two electrodes is varied or to find a conductance quantization in the metallic regime. Here we report our investigation of mechanically controllable break-junctions of CeNiSn single crystals, both in the true vacuum-tunneling and in the metallic regime.

Spectroscopy on small point contacts

To investigate the interaction between conduction electrons and quasiparticles, point contact spectroscopy uses the nonlinear conductance of metallic point contacts, as reviewed, e.g., in Ref. [6]. Energy-resolved spectroscopy is possible in the ballistic regime, when the electronic inelastic mean free path is much larger than the contact diameter. A voltage V applied to the contact accelerates the electrons to an excess energy eV.

In the opposite limit, when the inelastic mean free path is smaller than the contact diameter, energy is dissipated in the contact region due to relaxation processes. The excess energy is therefore much smaller than eV (see, e.g., the review [7]). Simultaneously, the temperature in the contact region T_{PC} is enhanced with respect to the bath temperature T_{bath} . In this thermal regime

$$T_{PC}^2 = T_{\text{bath}}^2 + \frac{V^2}{4L} \quad (1)$$

with the Lorenz number L. A simple formula

$$R_{PC}(T) \simeq \frac{16\rho l}{3\pi d^2} + \frac{\rho(T)}{d} \quad (2)$$

interpolates the contact resistance from the thermal to the ballistic regime [6]. Here ρ is the electrical resistivity, $\rho l = \hbar k_F / ne^2$, where n is the density of conduction electrons, e is the electron charge, and k_F is the Fermi wave number. The first term of Eq. (2) represents the ballistic resistance, dominating at small contact diameter d. The nonballistic second term depends on scattering processes of the material in the contact region. Therefore, in the thermal regime the nonlinear conductance of the junction is mainly due to the temperature dependence of $\rho(T)$. Since the latter is determined by the electron-quasiparticle interaction and peculiarities of the electronic structure, they can be resolved on point-contact spectra even in the thermal regime as anomalies of the contact conductance. But it is not possible to get more information than from $\rho(T)$ measurements. Additionally, in the thermal regime the energy scale set by eV is not directly related with the spectrum of the quasiparticles or other exitations, in contrast to the ballistic limit.

By reducing the cross-sectional contact area down to an atomic radius a, which corresponds to the Fermi wavelength for metals, on account of the quantum size effect the conductance of a 3D constriction assumes only well-defined values in multiples of $G_0 = 2e^2/h \simeq 77\ \mu\Omega^{-1}$ [8,9]. Hence the maximal resistance* of a contact of atomic dimension is of the order $R_{\max} \simeq G_0^{-1} = 12{,}9\ \text{k}\Omega$.

When the distance between the two electrodes is further increased, the direct metallic contact breaks, a vacuum gap opens, and tunneling across the vacuum barrier starts. It is often believed that the tunneling conductance directly images the density of states (DOS) of the electrodes. Actually, for a classical planar tunnel junction between normal metals the tunnel current depends on the DOS along the transverse direction only. This current, however, is strongly suppressed due to the exponential transmission coefficient of the barrier [10]. The influence of the DOS on the tunnel current can be seen preferentially in special tunneling geometries like a tip-plane setup, or when strong correlation effects break the single-electron representation.

Experiment

We prepared the CeNiSn samples (overall size approximately 1×1×5 mm) by mechanically cutting a 0.5–0.7 mm deep notch to define the break position. The sample is affixed by electrically insulating glue onto a flexible bending beam. Twisted pairs of voltage and current leads were attached with silver epoxy on both sides of sample, which is then mounted onto the mixing chamber inside the vacuum can of the dilution refrigerator. With a micrometer screw the bending beam is bent at low temperatures, thereby breaking the sample at the notch. For further details of the experimental setup see Ref. [11].

The resistance of the break junction or its lateral contact size could be adjusted *in situ* both mechanically with the micrometer screw and with a piezo tube, which allows fine tuning of the contact resistance in the tunneling regime. The current-voltage

* Interestingly, the Sharvin formula for an orifice of atomic radius yields the same value $R_{\text{atom}} = 16\rho l/(3\pi d^2) \simeq 4/(ak_F)^2\, h/(2e^2) = 4/(ak_F)^2\, G_0^{-1}$, where $(ak_F)^2 \simeq 4$ for an ordinary metals [9].

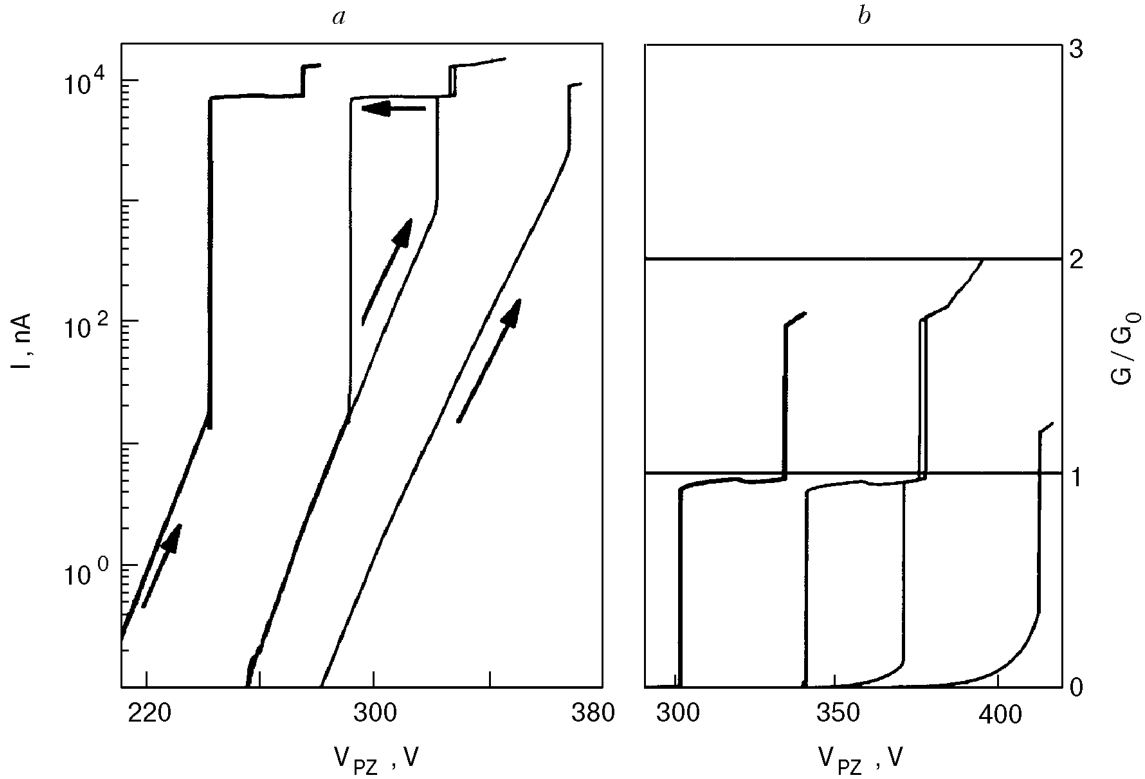

Fig. 1. Current I through a CeNiSn break junction in the c direction versus the piezo voltage V_{PZ} for several successive sweeps of the piezo voltage at $T = 0.1$ K and at a constant bias voltage of 0.1 V (*a*). The data of Fig. 1,*a* are in units of conductance normalized to the quantum conductance $G_0 = 2e^2/h \simeq 77.5$ μS. The curves have been shifted along the V_{PZ} axis to fit into one diagram (*b*).

characteristic and the differential resistance were recorded in the standard four-terminal mode with current biasing at low contact resistances $R \leq 10$ kΩ, while for contacts with $R \geq 100$ kΩ a two-terminal mode was used, and the differential conductance was recorded with voltage biasing.

Three CeNiSn single crystals were investigated. Each had one long side in the a, b, and c directions of the orthorhombic crystal lattice, respectively. At room temperature, the contact resistance of the samples with the notch was between 0.1 and 1 Ω, instead of the expected few mΩ, estimated from the geometrical size. This difference points to microscopic cracks at the constriction. On cooling down, the resistance of some of the contacts further increased by an order of magnitude, probably due to different thermal expansion coefficients of the sample and the bending beam, producing additional cracks.

Note that the notch defines only the macroscopic position of the junction, while the microscopic contact is less well defined. After removing the sample from the refrigerator, the surface of the junction was not mirrorlike or smooth, as expected for a single crystal, and the break was usually tilted with respect to the direction of the notch and thus to the crystal axis. Therefore the current flow through the contact deviates somewhat from the direction defined by the long side of the sample. A magnetic field up to 8 T could be applied perpendicular to the bending beam, i.e., perpendicular to the long side of the sample and to the current flow.

Results

First one has to identify the regime of charge transport through the junctions, because this regime provides the basis for any further interpretation. To solve this problem we measured how the contact resistance depends on the piezo voltage, i.e., on the distance between the two broken pieces of the sample. Figure 1,*a* clearly shows an exponential dependence of the current at constant bias voltage versus piezo voltage for contact resistances above 100 kΩ, as expected for true vacuum tunneling. For resistances below $G_0^{-1} = h/2e^2 \simeq 13$ kΩ, the curves in Fig. 1,*b* reveal a steplike change of conductance, which is characteristic for atomic-size metallic contacts. We therefore conclude that for contacts with resistance above 100 kΩ, the current is due to tunneling, while below 10 kΩ it is due to direct conductance of a metallic constriction. Note, that this interpretation differs from that in Refs. [4,5].

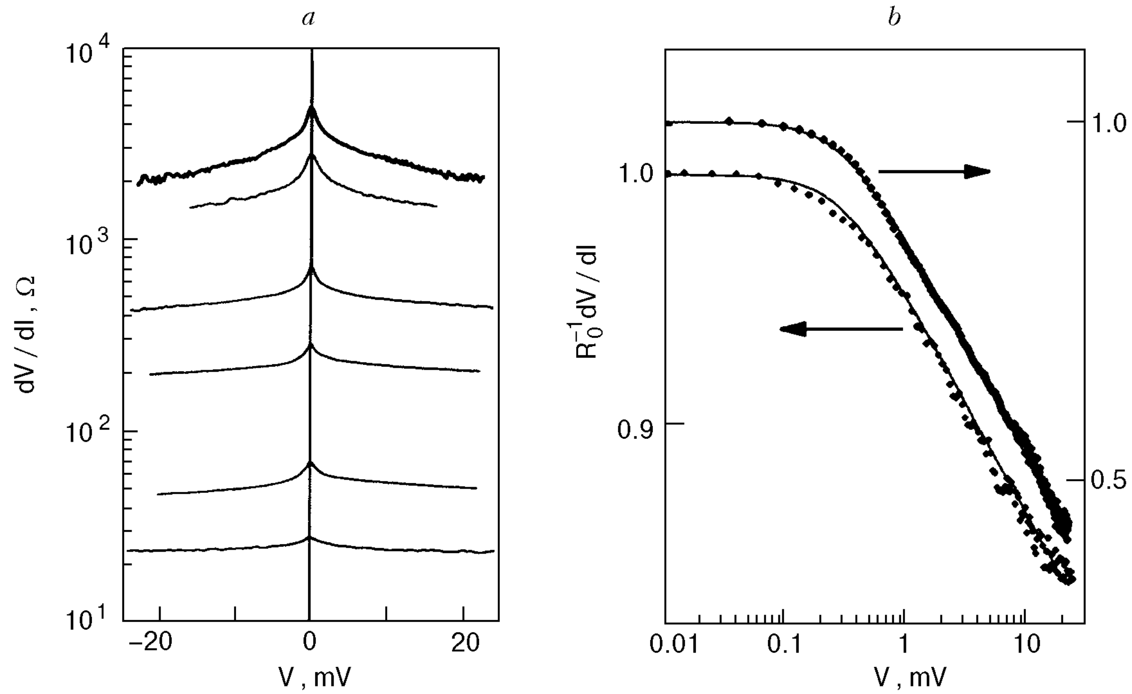

Fig. 2. dV/dI versus V spectra of metallic CeNiSn break junctions in the a direction at $T = 0.1$ K. Note the logarithmic abscissa (a). Normalized dV/dI versus V (symbols) for the two contacts in Fig. 2,a with the lowest and highest resistance. The solid lines are fits to the Daybell formula [12] $R = 1 - A \log(1 + (V/V_0)^2)$ with $A = 0.019(0.066)$, $V_0 = 0.357(0.345)$ mV for the bottom (top) curve, respectively (b).

Figure 2,a shows the dV/dI spectra of several metallic contacts in the 20–5000 Ω range. In general, all the spectra look similar to each other. They have a pronounced peak at zero bias, and the differential resistance decreases logarithmically between 1 and 10 mV. According to Fig. 2,b, the latter dependence can be fitted well by an empirical formula widely used to describe the temperature dependence of Kondo scattering if the temperature is replaced by the applied voltage. This seems to be a reasonable assumption for the thermal regime and follows from Eq. (1).

Figure 3 shows the temperature and field dependence of the dV/dI spectra of the sample in the b direction. In addition to the zero-bias peak, the curves have a background that gradually increases with V, resulting in a double-minimum structure. This kind of anomaly is very similar to that found by Ekino et al. [4] and by Davydov et al. [5] if dV/dI is replaced by dI/dV. Note, however, that the $dV/dI(V)$ dependence looks like the temperature dependence of the zero-bias contact resistance $dV/dI(T, V = 0)$; see the inset of Fig. 3,a. Such behavior characterizes the thermal regime, and not the ballistic one. A detailed discussion of the thermal regime and further literature can be found in Ref. [7]. Since contacts with resistance below about 10 kΩ are not in the tunneling regime, the zero-bias anomalies cannot be attributed directly to the density of states or to the energy gap, as proposed in Refs. [4,5]. A natural explanation for the zero-bias peak in Fig. 3 with its logarithmic dependence could be Kondo scattering. The negative magnetoresistance shown in the inset of Fig. 3,b also favors some magnetic or Kondo type of scattering.

For junctions in the tunneling regime, two cases have to be distinguished: i) Contacts with a large nonlinearity (~ 100%) in the dI/dV spectra also have a sharp zero-bias minimum, similar to the maximum in dV/dI of the metallic contacts (see Fig. 4,a) and dI/dV increases nearly logarithmically in the 0.1–10 mV range. ii) Contacts with small nonlinearity (~ 10%) have a relatively broad zero-bias minimum. They are more asymmetric, and we found them also less reproducible. Applying a magnetic field slightly broadens the zero-bias minimum. Unfortunately, contacts of the first type were unstable when we started applying a magnetic field. We could therefore not check reliably how the field influences the spectra of the first type. The dI/dV spectra with small nonlinearity were measured on a slab prepared in the c direction. As we already mentioned above, the direction of current flow through the microscopic contact can deviate from the expected one along the long side of the slab. For example, according to Fig. 1,a, to increase the

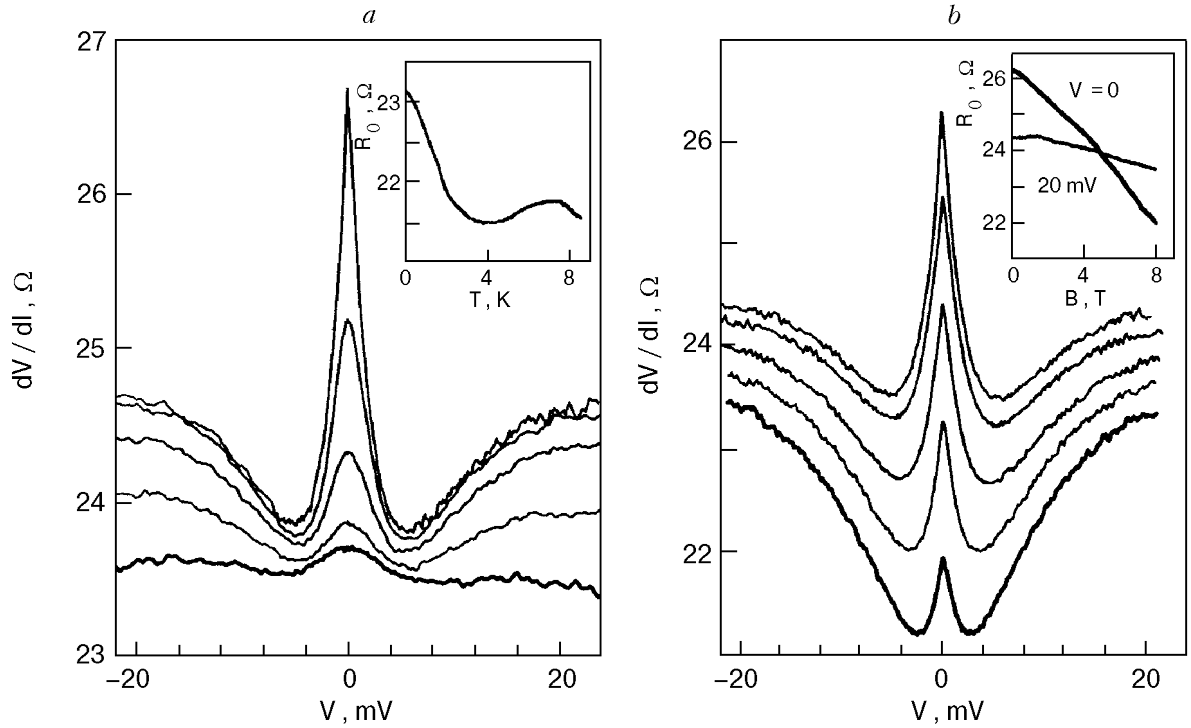

Fig. 3. Temperature dependence of dV/dI versus V for metallic CeNiSn break junctions in the b direction. The temperature is 0.1, 2, 4, 6, and 8 K (from top to bottom). The spectra are slightly offset against each other for clarity. The inset shows the temperature dependence of the contact resistance at zero bias for the same contact. The resistance is slightly lower because the junction changed somewhat after heating to 8 K (*a*). Magnetic field dependence of dV/dI versus V for the contact in Fig. 3,*a* at $T = 0.1$ K. The applied field is 0, 2, 4, 6, and 8 T (from top to bottom). The curves are again slightly offset against each other for clarity. The inset shows the contact magnetoresistance at zero bias and at $V = 20$ mV, respectively (*b*).

tunneling current by one order of magnitude one must increase the piezo voltage by about 15 V, while for the sample along the a direction only about 2 V. This latter value ought to be expected in our setup for a change in the vacuum gap of about 0.1 nm. We conclude that for the sample in the *c* direction the changing vacuum gap between the two electrodes was probably not oriented exactly perpendicular to the *c* axis.

Discussion

For low-ohmic metallic contacts the dV/dI spectra look similar to the temperature dependence of the zero-bias contact resistance (Fig. 3,*a*). Hence they reflect the behavior of the electrical resistivity in the contact region in the thermal limit, when the temperature inside the constriction increases with applied bias voltage according to Eq. (1). The increase of the contact resistance as the temperature is lowed very likely has the same origin as that observed earlier on the less perfect (that is, not very pure) CeNiSn samples [2]. We believe that in our experiments some intrinsic cracks with poor interface quality determine the microscopic properties of the junction. Alternatively, mechanical stress itself could distort the crystal lattice, producing imperfections. We found that the temperature dependence of the contact resistance of very low ohmic CeNiSn contacts of about 70 mΩ for the slab in the *c* direction *before* applying a mechanical force showed a metalliclike decrease of the resistance down to 0.1 K. Hence, after the mechanical break the metal in the contact region may be distorted, or impurities like Ce ions may have been added to the interface, playing the role of scattering centers. The logarithmic Kondo like dependence both for $dV/dI(V)$ and $dV/dI(T, V = 0)$ favors a magnetic kind of scattering mechanism.

In the tunneling regime, the $dI/dV(V)$ spectra with a pronounced sharp minimum and logarithmic increase of conductance in Fig. 4,*a* also look as if they are caused by magnetic scattering. For thin film metal-oxide-metal planar tunnel junctions, evaporating less than one monolayer of magnetic impurities can produce either a maximum or a minimum in the zero-bias conductance [13]. The size of this anomaly is of the order of 10%. And it depends on the sign of the exchange integral between the conduction electron spin and the mag-

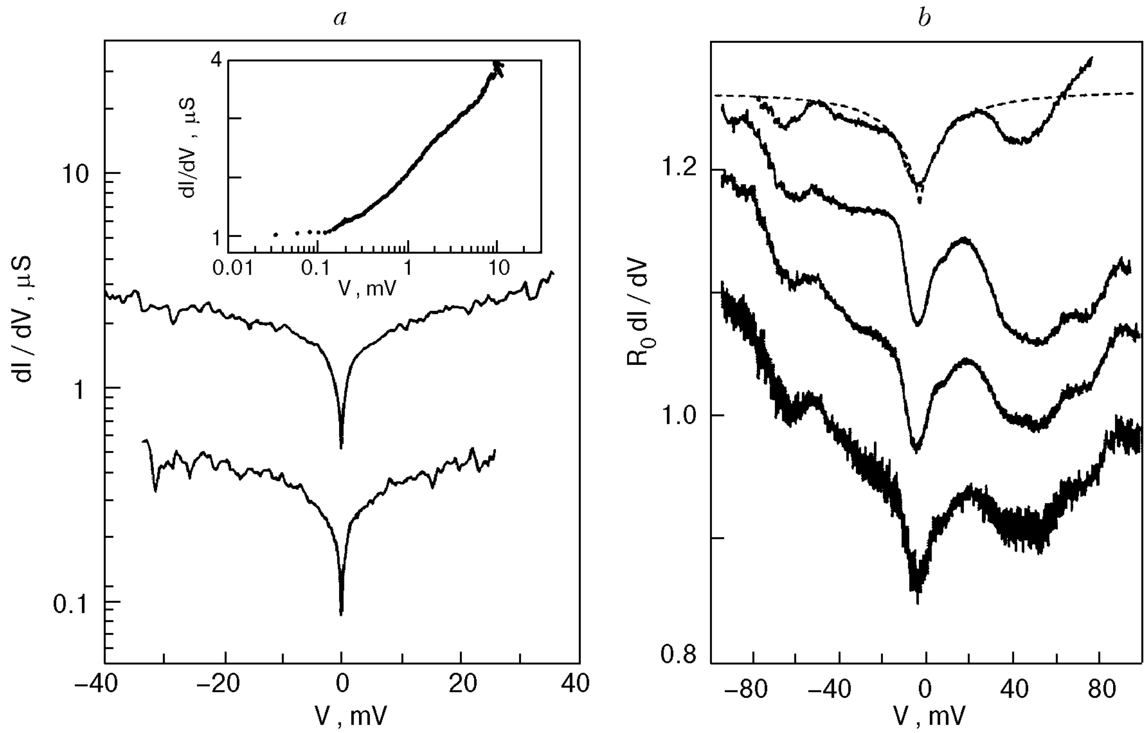

Fig. 4. dI/dV versus V for CeNiSn tunnel junctions in the *a* direction at $T = 0.1$ K. The applied ac voltage was 0.1 mV. The inset shows one curve on a log plot (*a*). dI/dV versus V spectra normalized for zero conductance of CeNiSn tunnel junctions in the *c* direction at $T = 0.1$ K. The zero-bias resistance is 1, 5, and 10 MΩ (from the second curve to the bottom curve). The curves are offset against each other for clarity. The applied ac voltage was 1 mV. The upper curve is a 1 MΩ contact in a magnetic field of 6 T together with a fit (dashed symmetric curve) to Coulomb blockade according to Eq. (3) (*b*).

netic impurity spin. A giant zero-bias resistance maximum similar to the conductance minimum in Fig. 4,*a*, with logarithmic variation between a few mV and 100 mV, was observed in Cr-oxide-Ag tunnel junctions [10]. This anomaly is possibly explained by Kondo scattering as well. However, the change in resistance is too large. Interestingly, a giant resistance peak was observed also for Al-oxide-Al tunnel junctions in which nonmagnetic Ni or Sn was evaporated onto the upper Al film [14]. This observation casts some doubt on the purely magnetic origin of the zero-bias anomalies, and so the nature of the giant zero-bias conductance minimum is still an open to discussion question.

Another explanation for a zero-bias conductance minimum of small point contacts could be Coulomb blockade. When the junction has a capacitance C, the tunneling electrons have to overcome the electrostatic charging energy $E_C = e^2/2C$. At large voltages, C equals the intrinsic capacitance C_0 of the junction [11]. But at small voltages, C is enhanced due to the lead capacitance $Kc\hbar/e|V|$. Here K is the capacitance per length of the setup and c is the speed of light. Consequently, the conductance of an otherwise ohmic junction shows a more or less pronounced zero-bias dip like [11]

$$R\,\frac{dI}{dV} = 1 - \frac{e^2 Kc\hbar}{2(e\,|V|C_0 + Kc\hbar)^2} \qquad (3)$$

due to Coulomb blockade. In our setup the relative size of such a Coulomb anomaly is about 5% [11]. Its width depends on the intrinsic static capacitance of the specific junction. Coulomb blockade could explain at least part of the zero-bias minima of the $dI/dV(V)$ spectra in Fig. 4,*b*, while curves in Fig. 4,*a* have a several times larger anomaly of the conductance, which cannot be explained only by Coulomb blockade.

One could also suppose that in the latter case some free isolated metallic (magnetic) clusters are formed accidentally during the breaking of the junction. These clusters could have rather small capacitances, increasing the effect of Coulomb blockade, while simultaneously depending on the magnetic field.

Let us come back to the $dI/dV(V)$ spectra in Fig. 4,*b*, with small nonlinearities and broad zero-bias maxima. If we assume that this structure reflects the gap in the electronic density of states, then the width of the gap is determined by the position of maximum, corresponding to $2\Delta \simeq$

$\simeq 20$ mV. This is two times larger than that found in Ref. [4], where the value of the gap is also too large when compared to the characteristic temperature of about 10 K.

Conclusion

We have studied CeNiSn using mechanically controllable break junctions from the metallic to the vacuum tunneling regime. We observed quantization of the conductance with a value near the conductance quantum G_0 at the transition from metallic contact to vacuum tunneling. This observation characterizes CeNiSn as a good metal even for temperatures well below 1 K. The pronounced zero-bias anomalies observed both in the metallic and in the vacuum-tunneling regime seem to be mainly due to scattering of electrons on the disordered magnetic Ce ions or other imperfections at the interface between the electrodes, which could also be produced by mechanical stress. This hinders the use of break junction tunneling experiments for unequivocally identifying the proposed energy (pseudo)gap in the electronic density of states of CeNiSn.

This work was supported by the SFB 252 Darmstadt(Frankfurt)Mainz. Y. N. thanks the SFB 252 for financial support during his stay in Darmstadt and is grateful to Prof. I. K. Yanson and Yu. A. Kolesnichenko for valuable remarks.

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