

Tunneling Evidence for the Quasiparticle Gap in Kondo Semiconductors CeNiSn and CeRhSb

Toshikazu Ekino,* Toshiro Takabatake, Hiroaki Tanaka, and Hironobu Fujii

Faculty of Integrated Arts and Sciences, Hiroshima University, Highashi-Hiroshima 739, Japan

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The Kondo semiconductors CeNiSn and CeRhSb were investigated by tunneling spectroscopy using a break junction. The differential conductances at 2–4 K show energy gaps of 8–10 and 20–27 meV for CeNiSn and CeRhSb, respectively, which are comparable to the Kondo temperatures. The tunneling spectra give clear evidence for a strong gap anisotropy. With increasing temperature, the zero-bias conductance displays a crossover from a well-developed gap state to a partial-gap state, and to a Kondo-metallic state.

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The semiconducting CeNiSn, CeRhSb, and Ce₃Pt₃Bi exhibit an unprecedented ground state in the Kondo lattice [1,2]. The energy gap opening in these compounds is believed to be due to the hybridization between the strongly correlated 4*f* electrons and a conduction band with the total electron numbers per unit cell tuning to half filling [2]. For these semiconductors, it is predicted that the charge gap is larger than the spin gap in the one-dimensional Kondo-lattice model [3] or that the gap sizes are similar for infinite dimensions [4]. The gap formation in these materials has been indicated by transport, magnetic, specific heat, NMR, and infrared measurements [1,5–7], and thereby an anisotropic gap in CeNiSn and CeRhSb has been suggested. Furthermore, dynamic antiferromagnetic (AF) correlations have been found at a particular direction in **k** space [8,9]. However, there exists no direct observation of the quasiparticle gap to date.

In this Letter, we report tunneling measurements of the Kondo semiconductors CeNiSn and CeRhSb. The tunneling technique provides the most direct probe to investigate the energy gap [10]. Although some mixed-valent compounds have been investigated by this technique [11,12], there is no study on cerium Kondo semiconductors. The present results give the first comprehensive evidence for the quasiparticle energy gap and its strong temperature dependence in the Kondo semiconductors [13]. CeNiSn and CeRhSb crystallize in an orthorhombic ε -TiNiSi type structure [1]. We have used a break-junction technique, where the junction interface is free from any contamination and oxidation of reactive Ce in the materials. In fact, promising results have been obtained using this technique [14]. Prior to the measurements, the sample with its cross section of $0.5 \times 1 \text{ mm}^2$ was mounted on the flexible substrate and cracked in a liquid-helium chamber by applying an adjustable bending force. The tunneling conductances dI/dV were directly obtained by a constant ac-modulation technique with a four-probe method.

Figure 1 shows representative dI/dV data for polycrystalline samples of CeNiSn and CeRhSb at 2.1–4.2 K. We have taken ≈ 80 spectra in total. The junction was very stable for low junction resistance ($R_J < 10 \Omega$ at 50 mV), where the structure was reproducible. Because of the

low sample resistance ($< 1 \text{ m}\Omega$) for this junction size, the voltage drop through it in series with R_J is negligible. Regardless of the low R_J , we believe what we see is the quasiparticle gap due to tunneling rather than the barrierless point-contact spectra, for the following reasons: (i) dI/dV exhibits well-defined symmetric peaks with respect to bias and a sufficient decrease around zero bias as

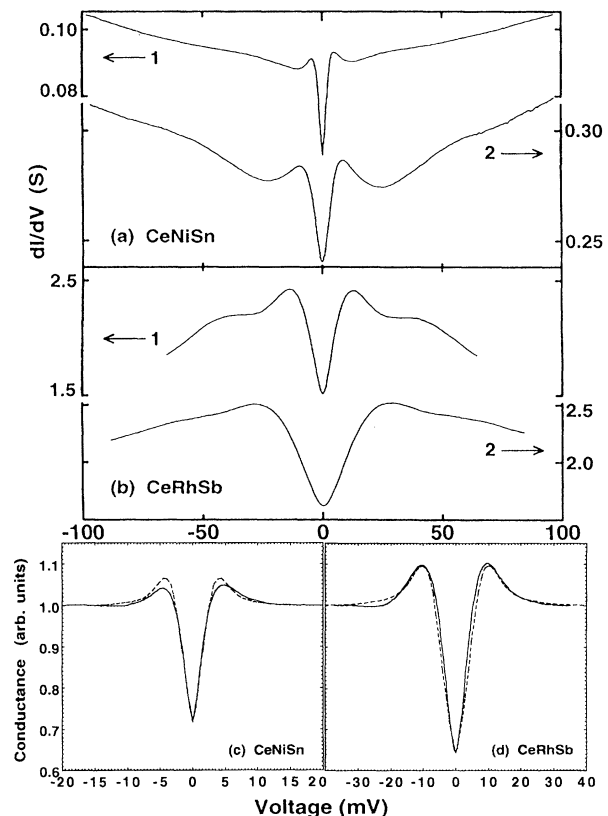


FIG. 1. Tunneling conductance for (a) CeNiSn and (b) CeRhSb polycrystals. $T = 4.2 \text{ K}$ except for curve 1 in (a) (2.1 K). Curves 1 and 2 correspond to the SIN and SIS junctions, respectively. Solid and dashed lines in (c) and (d) represent the experimental data [$T = 2.1 \text{ K}$ (c) and 4.2 K (d)] and the calculated curves, respectively (see text).

in the Giaever tunneling of many-body effects [10], (ii) the above feature is obtained at least up to the high R_J of ≈ 30 k Ω (see Fig. 2), and (iii) the gap area under the normal-state conductance and the area over it have equal weight for many data. When $R_J > 100$ –200 Ω , it was sensitive to adjustment and a V-shaped conductance without the gap feature was often observed. The low R_J is probably due to an effective contact, or it might be due to the tunneling of the renormalized heavy quasiparticles, which would require a thin barrier for the short de Broglie length. From Fig. 1, it is obvious that the lost tunneling spectral weight below the gap energy is recovered just above the gap, in contrast to the optical gap of the Kondo insulator $\text{Ce}_3\text{Pt}_4\text{Bi}_3$ where it is transferred to higher energies far from the gap [7]. In Figs. 1(a) and 1(b) the peak-to-peak (p - p) separation V_{p-p} in dI/dV of curve 2 is twice that of curve 1 for each compound. These double V_{p-p} values can be due to SIS (S = semiconductor, I = insulator) and SIN (N = normal metal) junction formation. The SIS junction is formed by cracking the polycrystal intragrain, and the SIN junction by cracking it at grain boundaries. Within this interpretation, the V_{p-p} of 10 mV [curve 1 in Fig. 1(a)] and 20 mV [curve 2 in Fig. 1(a)] for CeNiSn correspond to $2\Delta_{p-p}/e$ and $4\Delta_{p-p}/e$, respectively, and for CeRhSb those are 26 mV ($2\Delta_{p-p}/e$) [curve 1 in Fig. 1(b)] and 55 mV ($4\Delta_{p-p}/e$) [curve 2 in Fig. 1(b)], where Δ_{p-p}/e is defined by the p - p separation in dI/dV of a SIN junction divided by 2. These differences also might be due to the variations of stoichiometry, but this hardly explains the reproducible double-gap features.

We have often observed the broadened gaps for low R_J . Since the break junction provides a clean interface, these features may not be a surface artifact. Thermal smearing also cannot be the origin of the broadness because eV_{p-p} is much larger than $5.4k_B T$ [10]. Such a broadened gap has been suggested by the T^3 dependence of the nuclear

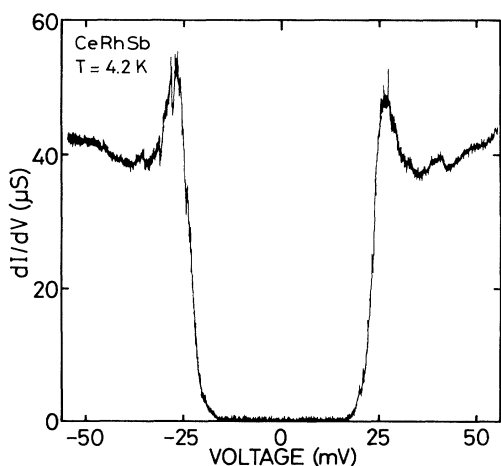


FIG. 2. Tunneling conductance from an SIS junction for a CeRhSb single crystal.

spin-lattice relaxation rate [6]. This feature, as well as the much larger gap value than the transport gap [1,5] could be due to the residual density of states arising from a wide distribution of gaps, as is discussed below. For CeRhSb, the weak and broad structures at $\pm(37$ – $39)$ mV in Fig. 1(b), curve 1 (and Fig. 2), were also reproducible, but the origin is yet to be explored.

We find that the broadened-gap feature can be described by a distribution of the constant gaps. The fitting results are shown in Figs. 1(c) and 1(d) for the SIN tunneling of CeNiSn and CeRhSb, respectively, where we used the gap function $\text{Re}\{|E|/[E^2 - \Delta^2]^{1/2}\}$ and the Gaussian distribution $(2\pi)^{-1/2}\delta^{-1}\exp[-(\Delta_0 - \Delta)^2/2\delta^2]$ [15] with $\Delta_0 = 1.7$ meV and $\delta = 1.7$ meV for Fig. 1(c), and $\Delta_0 = 5$ meV and $\delta = 3.8$ meV for Fig. 1(d). These wide distributions suggest the anisotropic gap or the scattered gaps arising from a sample inhomogeneity. In fact, the wider gap distribution in CeNiSn ($\delta/\Delta_0 = 1$) than in CeRhSb (0.76) is consistent with the larger transport and magnetic anisotropies in CeNiSn than those in CeRhSb at low temperatures [4]. Note that the above agreements of the experimental data with the modified mean-field gap function need not imply broken symmetry.

We have occasionally observed sharp-gap structures in polycrystals. To investigate this issue further, CeRhSb single crystals were measured. Figure 2 shows the dI/dV with no leakage inside the gap voltage. The sample used was cracked perpendicular to the orthorhombic b axis, but the actual tunneling direction is not clear. To obtain this feature, the junction had to be mechanically adjusted several times. Nevertheless, it demonstrates what would be observed for a clean surface. $eV_{p-p} = 54$ meV is in excellent agreement with $4\Delta_{p-p} = 55$ meV of Fig. 1(b), curve 2, in spite of the large difference in R_J [≈ 0.4 Ω and 25 k Ω for Figs. 1(b) and 2, respectively]; thus this is due to the SIS junction. The higher R_J in Fig. 2 indicates a small effective junction size, where the gap at a particular \mathbf{k} direction is detectable when the tunneling probability is proportional to $\exp[-\beta \sin^2 \theta]$ in the Wentzel-Kramers-Brillouin approximation [10]. Here β depends on E_F and the work function of the material, as well as the barrier thickness, and θ is the angle between the tunneling electrons and barrier normal. Since $\beta \approx 20$ – 50 , the tunneling probability rapidly decreases to e^{-1} at $\theta = 13^\circ$ – 8° . By combining the above facts with the saturated behavior of $\rho(T)$ at low T [1,5], we conclude that the absolute gap opens only a part of the Fermi surface. This supports the idea of large gap anisotropy.

Figure 3 shows the temperature (T) variations of dI/dV for (a) CeNiSn [Fig. 1(a), curve 1] and (b) CeRhSb [Fig. 1(b), curve 2]. Since R_J was low, the junction was very stable for heating at 0.3–1 K/h. The variations are thus due to a thermal effect, whereby the features in dI/dV become weakened and eventually disappear with increasing T . This is the first direct observation of the T dependence of the quasiparticle density of states in Kondo semiconductors, where the

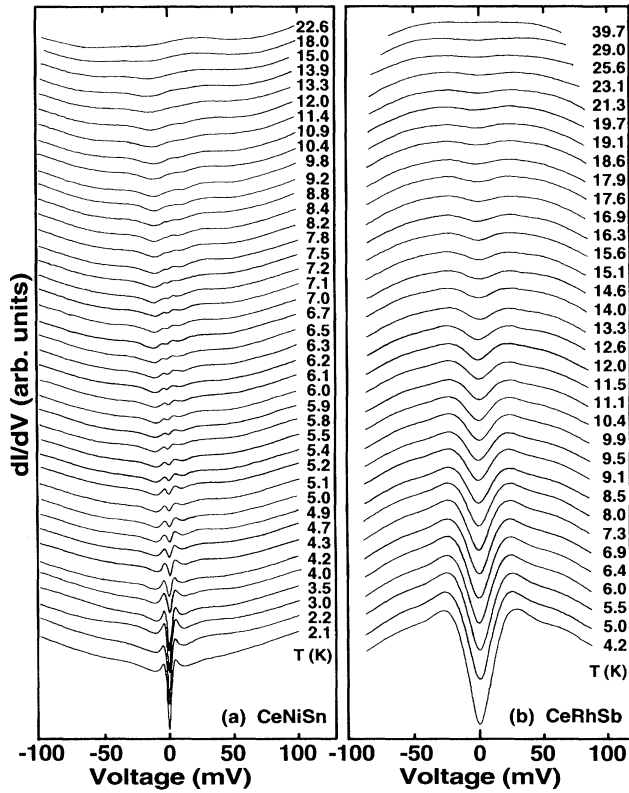


FIG. 3. Temperature variations of the tunneling conductance for (a) CeNiSn [the low- T data are Fig. 1(a), curve 1] and (b) CeRhSb [Fig. 1(b), curve 2].

feature resembles mean-field behavior even though the underlying mechanism is completely different.

Figure 4(a) shows the T dependence of the ratio $dI/dV(0 \text{ mV})/dI/dV(V = 50\text{--}75 \text{ mV}) [= \sigma_0(T)]$ as a measure of the thermally smeared density of states at E_F . For CeRhSb, $\sigma_0(T)$ exhibits a decrease below 23–25 K with decreasing T owing to the partial-gap opening. This structure correlates with a pronounced peak in $\chi(T)$ along the a axis at $T_\chi = 22$ K and a shoulder in $\rho(T)$ below ≈ 25 K [5], suggesting that gap opening is accompanied by a loss of magnetic moment involving strong coupling of $4f$ and conduction electrons. Furthermore, the thermal expansion coefficient $\alpha(T)$ [16] implies the enhancement of c - f hybridization below ≈ 40 K, which is a precursor to the structure at T_χ . However, no anomaly has been observed in C_m/I (where C_m is the magnetic contribution to the specific heat) at T_χ [5] because the specific heat measures a \mathbf{k} -integrated density of states. For CeNiSn, the weak decrease in $\sigma_0(T)$ below 18 K can be connected with the AF correlations that develop below 20 K [9]. Since the kink at ≈ 11 K in $\sigma_0(T)$ for curve 4 corresponds to the peaks in $\rho(T)$ and $\chi(T)$ at $T_\chi \approx 12$ K [1], it is also attributed to the partial-gap opening. The pronounced structure at T_χ in curve 4 is probably due to the SIS tunneling which is much more sensitive to the change in the density of states at E_F . A weak change in the

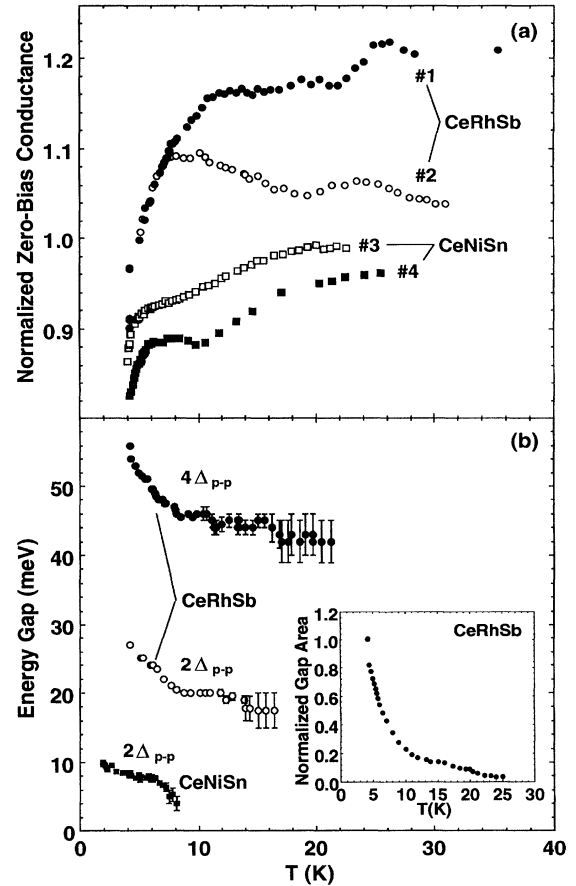


FIG. 4. (a) Temperature dependence of the normalized zero-bias conductance $dI/dV(0 \text{ mV})/dI/dV(V)$ for CeRhSb [curve 1 ($V = 75$ mV) and curve 2 (65 mV)] and CeNiSn [curve 3 (75 mV) and curve 4 (50 mV)]. The low- T data for curves 3 and 4 are shown in Figs. 1(a) 1 and 2, respectively. (b) T dependence of $4\Delta_{p-p}$ [Figs. 3(b)] and $2\Delta_{p-p}$ for CeRhSb and $2\Delta_{p-p}$ [Fig. 3(a)] for CeNiSn. Inset: T dependence of the normalized gap area defined in the text using the junction of Fig. 1(b) 1.

slope of $\sigma_0(T)$ at T_χ is noticed for curve 3. With further decreasing in T , $\sigma_0(T)$ for CeRhSb decreases steeply below $T_{Cp} = 11$ K owing to a rapid gap development, where T_{Cp} is defined by the temperature where C_m/T takes a broad peak [5]. For CeNiSn, the well-defined onset of decrease in $\sigma_0(T)$ at 6 K is in agreement with T_{Cp} [1]. The ratios $2\Delta_{p-p}/k_B T_{Cp}$ are $\approx 17 \pm 2$ and 30 ± 9 for CeNiSn and CeRhSb, respectively, while $2\Delta_{p-p}/k_B T_\chi \approx 9 \pm 1$ (CeNiSn) and 12 ± 2 (CeRhSb). Therefore T_χ is a better parameter to scale $2\Delta_{p-p}$ than T_{Cp} .

In Fig. 4(b), we show the T dependence of $4\Delta_{p-p}$ and $2\Delta_{p-p}$. For CeRhSb, the gap value decreases almost linearly with increasing T up to 8 K and then the decrease is weakened. Above 16 K the $2\Delta_{p-p}$ is smeared out, while the $4\Delta_{p-p}$ of the SIS junction can be defined up to ≈ 21 K. The rapid decrease in the gap on warming up to $T_{Cp} \approx 11$ K and the gap disappearance at 25 K

($\approx T_\chi$) are also clearly visible from the T dependence of the gap area normalized by that at 4.2 K in the inset to Fig. 4(b). The gap area was obtained using the interpolated (normal) background conductance at each temperature. For CeNiSn, the $2\Delta_{p-p}$ decreases and smears out above 8 K, which is higher than $T_{Cp} = 6$ K, and it seems to disappear at 9–10 K. This is in contrast to the neutron data of the T -independent spin-excitation gap of 2 meV below 20 K [8,9], which disappears by a lifetime effect [8]. The two characteristic temperatures T_χ and T_{Cp} distinguish these compounds from the conventional semiconductors, where the gap closes due to a thermal activation of electrons from the rigid band edge.

The size and its T dependence are distinguishing features of the gap. We believe that the well-defined large gap is inherent in the Kondo semiconductors because we do not obtain such a pronounced gap in the isostructural, metallic antiferromagnet CePtSn [17], where only a weak AF gap is observed below $T_N = 7$ K. Furthermore, although the ratio $2\Delta_{p-p}/k_B T_\chi$ is similar to that for the charge density wave compounds, the gap at low T decreases much faster than the mean-field prediction of a phase transition [15,18]. Of course such a description is unsuitable for these compounds because of the lack of long-range ordering. The rapid decrease in the gap magnitude with increasing T indicates the many-body effect as is predicted by considering an indirect hybridization gap with strong correlations [19].

It is interesting to compare Δ_{p-p} to T_K from the viewpoint that Δ_{p-p} is the energy required for decoupling the conduction electrons from the f electron of a local Kondo singlet [3]. The ratios $\Delta_{p-p}/k_B T_K$ are 0.9–1.1 (CeNiSn) and 1.2–1.6 (CeRhSb) with $T_K = 54$ and 96 K, respectively, where the T_K are determined from the specific heat with an $S = \frac{1}{2}$ impurity Kondo model [5]. While the above Δ_{p-p} can be a direct measure of T_K , it strongly depends on T up to $T_{Cp} \approx 0.1T_K$ and disappears at $T_\chi \approx 0.2T_K$ [Fig. 4(b)]. This disagrees with the picture of a T -independent gap ($\Delta_{p-p} \approx T_K$), suggesting that the gap is formed below T_χ by a coherent mechanism involving a strong change in the c - f hybridization.

We now address the relationship among the tunneling data of the mixed-valent compounds. The $2\Delta_{p-p} = 28$ meV in CePd₃ ($T_K \approx 100$ –150 K) [11] and 23 meV in SmB₆ ($T_K \approx 100$ –200 K) [12] are comparable to 20–27 meV of CeRhSb ($T_K = 96$ K). This indicates that they possess the similar energy scale (T_K) that remarkably correlates with Δ_{p-p} in spite of the different ground states. A common mechanism of the gap formation for them can be due to the dynamic scattering of conduction electrons by valence fluctuations of unstable $4f$ electrons.

Finally, the larger quasiparticle gap of $2\Delta_{p-p} = 8$ –10 meV than the spin gap of 2–4 meV [8,9] obtained for CeNiSn should be noted. This fact suggests that in the strong-coupling Kondo-singlet regime [3] extra energy

is needed to scatter an electron charge from one site to another, compared to the singlet-to-triplet excitation of the f -electron spins.

In conclusion, it is found that the quasiparticle energy gaps in the Kondo semiconductors CeNiSn and CeRhSb from the break-junction tunneling measurements are nearly of the same magnitudes as T_K . The low- T tunneling density of states indicates strong gap anisotropy. We have shown *directly* that the gap is well developed at low T , but it is strongly T dependent up to $T_{Cp} \approx 0.1T_K$ and disappears at $T_\chi \approx 0.2T_K$. These two energy scales seem to be indispensable for gap formation in anisotropic Kondo semiconductors.

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*Present address: Faculty of Science, Hiroshima University, Highashi-Hiroshima 739, Japan

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