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Formation of an anisotropic energy gap in the valence-fluctuating system CeNiSn

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Measurements of susceptibility χ, resistivity ρ, and thermoelectric power S have been performed on single-crystal CeNiSn. Only along the a axis of the orthorhombic structure do $\chi(T)$ and $\rho(T)$ exhibit pronounced peaks at 12 K, whereas no anomaly was found in the specific heat. The gap energies estimated from $\rho(T)$ are 2.4, 5.5, and 5.0 K along the a, b, and c axes, respectively. Near 3 K, $S_a(T)$ and $S_c(T)$ exhibit extremely sharp peaks, which indicate the presence of a density of states within the gap. The magnetic contribution to the specific heat divided by temperature C_m/T versus T reveals a maximum of 0.19 J/K^2mol near 6.7 K. These results suggest that an antiferromagnetic correlation develops near 12 K, which induces the formation of the pseudogap in the narrow band of heavy quasiparticles.

Among valence-fluctuating (VF) systems with unstable $4f$ electrons, only a few compounds, such as SmB_6, gold SmS, TmSe, and YbB_{12}, show semiconductorlike behavior at low temperatures.[1-4] The behavior is thought to originate in the formation of an energy gap of several 10 K near the Fermi level. However, no general understanding of the mechanism of the gap formation has been established yet. Recently, Takabatake, Nakazawa, and Ishikawa[5] have found that CeNiSn is the first example of a VF cerium compound with an energy gap. The resistivity of CeNiSn follows a simple activation law at temperatures below 65 K, from which the gap energy was estimated to be 6 K. Since the gap energy is an order of magnitude smaller than those in the above-mentioned compounds, the gap is easily smeared out by the application of either a magnetic field higher than 200 kOe or pressure higher than 20 kbar.[6,7] The smearing out is also attained by the partial substitution of about 10% of Cu for Ni or La for Ce.[5,8] Furthermore, the substitution of Cu for Ni leads to the development of a heavy-fermion state, which further changes into an antiferromagnetic Kondo state for Cu concentrations higher than 13%.[5] The result suggests that the ground state of CeNiSn with a small energy gap is close to an antiferromagnetic instability.

CeNiSn has the orthorhombic ϵ-TiNiSi-type structure,[9] which distinguishes this system from the above-mentioned compounds, which possess energy gaps and cubic structures. In the structure of CeNiSn, Ce atoms form a two-dimensional network in the b-c plane and the Ce layers are separated by two layers consisting of Ni and Sn atoms. Therefore, we expect this compound to exhibit anisotropic magnetic and transport properties, which usually reflect anisotropic interactions and hybridizations of $4f$ electrons with conduction electrons. In this paper, we present the results of measurements of susceptibility, resistivity, and thermoelectric power on single crystals of CeNiSn. We also present specific-heat measurements of polycrystalline CeNiSn and its isostructural nonmagnetic compound of LaNiSn. Based on the combined results, we will discuss the mechanism of gap formation in this compound.

Polycrystalline samples of CeNiSn were prepared from stoichiometric starting materials by arc melting in a purified argon atmosphere. Single crystals were grown from the ingots by a Czochralski technique in a triarc furnace. We obtained crystals 3 mm in diameter and 10 mm in length, and cut them into specimens along each crystallographic axis for the transport and magnetic measurements. The electrical resistivity was measured by four-probe dc techniques in the temperature range of 1.5–300 K. On the same samples, the thermoelectric power was measured by a differential method. Susceptibility measurements from 2 to 300 K were done by using a Faraday-type Cahn balance and a superconducting quantum interference device magnetometer. The specific-heat measurements were performed by a standard heat-pulse method on the polycrystalline CeNiSn sample annealed for 10 d at 1000 °C just below the decomposition temperature of 1060 °C.

The magnetic susceptibility χ of CeNiSn is shown in Fig. 1 along the three principal axes as a function of temperature. It is noticed that the observed susceptibility has a strong anisotropy and does not follow a Curie-Weiss law. With decreasing temperature, the curves of χ_b and χ_c become less temperature dependent around 150 K. This temperature dependence implies that the system is in an anisotropic VF state at high temperatures, as in CeNiIn.[10] However, $\chi_a(T)$ with the largest values exhibits a remarkable peak at 12 K, whereas the other two show an upturn below 30 K and no peak down to 2 K. We as-

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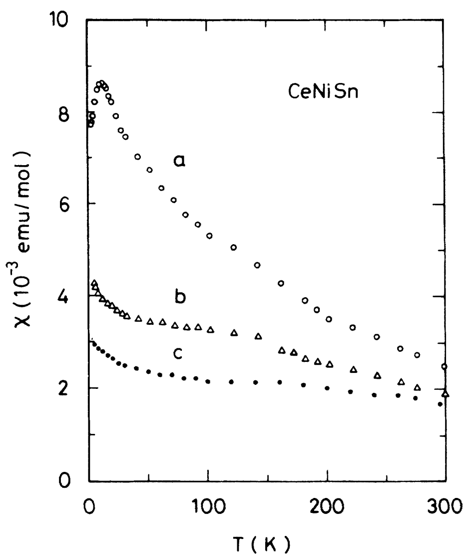

FIG. 1. Magnetic susceptibility vs temperature for CeNiSn along the three principal axes.

cribe the upturn to the effect of some magnetic impurities in view of the absence of such behavior in the Knight shift of ^{119}Sn NMR.[11] From the magnetization measurements at 4.2 K, we found that the magnetic moment per Ce ion along the easy a axis attains only $0.065\mu_B$at 50 kOe.

Figure 2(a) represents the resistivity ρ as a function of temperature. As temperature is decreased, $\rho(T)$ in all directions initially shows a Kondo-like increase. The curve of $\rho_a(T)$ has a hump around 100 K, whereas $\rho_b(T)$ and $\rho_c(T)$ have broad maxima at a lower temperature of about 50 K. Therefore, we believe that anisotropic and incoherent Kondo scattering in the presence of a crystalline field governs the resistivity at high temperatures. Recent experiments of inelastic neutron scattering confirmed the crystalline-field level near 70 K.[12] The most prominent feature in Fig. 2(a) is the occurrence of a peak in $\rho_a(T)$ at 12 K where the susceptibility along the same direction showed the peak in Fig. 1. The low-temperature data are replotted in Fig. 2(b), where we notice that a drastic increase in the resistivity occurs only below about 6 K for all directions. By plotting $\ln\rho$ against $1/T$, we found that a linear relation between $\ln\rho$ and $1/T$ holds in the temperature range between 6 and 2.5 K. Regardless of the small temperature range, we estimated the values of E_g to be 2.4, 5.5, and 5.0 ± 0.3 K for the a, b, and c axes, respectively. We note that E_g is smallest in the direction of the a axis, along which the peak in the susceptibility and resistivity was observed at 12 K.

The thermoelectric power S of CeNiSn also exhibits a strongly anisotropic temperature dependence, as shown in Figs. 3(a) and 3(b). The sign of S for the three directions is positive over the investigated temperature range and the magnitude is rather large, as commonly reported for VF cerium compounds such as $CeSn_3$ and $CePd_3$.[13] For $S_b(T)$, a large maximum manifests itself around 100 K, which is ascribable to the Kondo effect because $\rho_b(T)$ depends on $\ln T$ above 100 K. In Fig. 3(b), the low-temperature data are replotted on an expanded scale. The

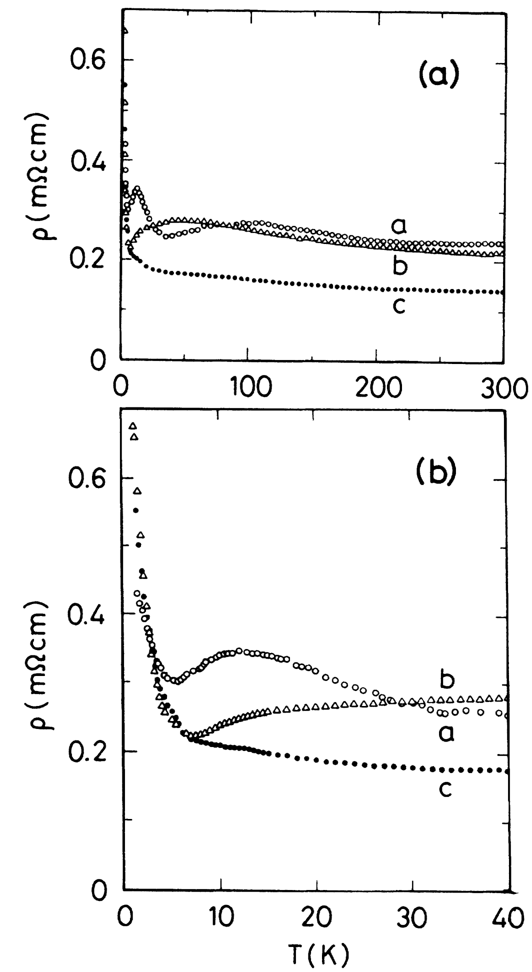

FIG. 2. (a) Electrical resistivity vs temperature for CeNiSn along the three principal axes; (b) the low-temperature part on a larger scale.

curves of $S(T)$ along the three axes commonly start to decrease near 20 K, which may suggest the development of some antiferromagnetic correlation between quasiparticles. With further decreasing temperature, each curve has a minimum of between 5 and 8 K, and then increases drastically. This increase in $S(T)$ is interpreted as a result of the opening of the energy gap in the density of states. In the vicinity of 3 K, an extremely sharp peak of 48 μV/K appears in $S_c(T)$ and a less pronounced one in $S_a(T)$. As for $S_b(T)$, a peak may exist at a lower temperature if it tends to the origin at 0 K. The occurrence of such peaks in $S(T)$ suggests that within the gap there exists a density of states with a temperature-dependent structure. This is also consistent with the facts that the temperature dependence of resistivity deviates from the activation law below 3 K and that the Hall coefficient changes sign from positive to negative near the same temperature on cooling.[14]

For understanding the mechanism of the gap formation in CeNiSn, it is important to check whether the anomaly observed in both $\chi_a(T)$ and $\rho_a(T)$ at 12 K is associated with long-range magnetic ordering. We therefore

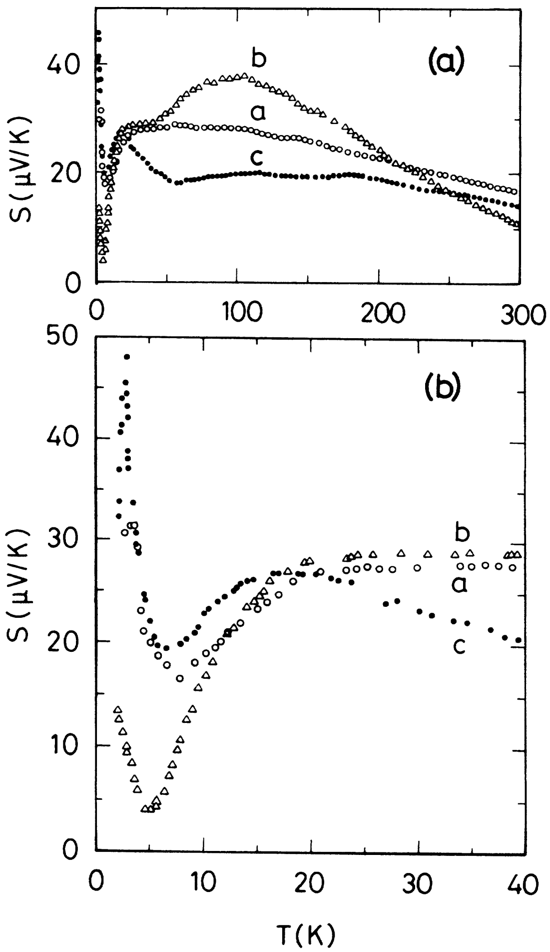

FIG. 3. (a) Thermoelectric power vs temperature for CeNiSn along the three principal axes; (b) the low temperature part on a larger scale.

measured the specific heat of polycrystalline samples of CeNiSn and its isostructural nonmagnetic compound LaNiSn from 1.4 to 80 K. The results are plotted as C/T vs T in Fig. 4. The data of CeNiSn below 6 K is quantitatively similar to that reported for another sample.[6] It is evident that no anomaly exists near 12 K, and hence the anomalies in $\chi_a(T)$ and $\rho_a(T)$ are not likely to originate in long-range magnetic order. In fact, recent NMR measurements performed on the sample used for the specific-heat measurement have confirmed the nonmagnetic nature of CeNiSn down to 0.4 K.[11] Further, we recall that the susceptibility of the nonmagnetic heavy-fermion compound $CeRu_2Si_2$ exhibits a maximum at 10 K only along the easy c axis of the tetragonal structure.[15] The maximum in $\chi_c(T)$ has been attributed to the presence of antiferromagnetic correlations between quasiparticles.[16] We note that for both CeNiSn and $CeRu_2Si_2$, the maximum in $\chi(T)$ occurs only when the magnetic field is applied perpendicular to the layer of Ce atoms. In Fig. 5, C/T of CeNiSn is replotted against T^2. With decreasing temperature, C/T decreases almost linearly down to 0.21 J/K^2mol near 6 K, and then sharply diminishes. The temperature dependence is consistent with the opening of the

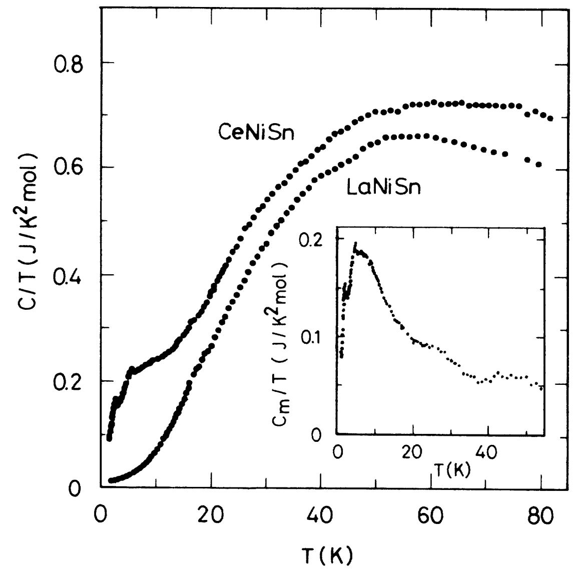

FIG. 4. Specific heat divided by temperature C/T vs T for polycrystalline CeNiSn and LaNiSn. The inset shows the magnetic contribution to the specific heat divided by temperature C_m/T vs T.

gap below 6 K as inferred from the transport properties mentioned previously. Furthermore, the large value of C/T near 6 K indicates the development of a heavy quasiparticle band antecendent to the gap opening. In Fig. 5, we also notice anomalies near 5.4 and 2.6 K, below which C/T appears to drop more rapidly. However, NMR experiments[11] revealed no anomaly in the spin-lattice relaxation rate of ^{119}Sn near these temperatures. Sample dependence of the anomalies in the specific heat must be examined to elucidate whether they are intrinsic or not. The magnetic contribution to the specific heat C_m is estimated by subtracting the data of LaNiSn from that of CeNiSn. As shown in the inset of Fig. 4, C_m/T reveals a pronounced maximum near 6.7 K, but the overall temperature dependence could not be reproduced by assuming

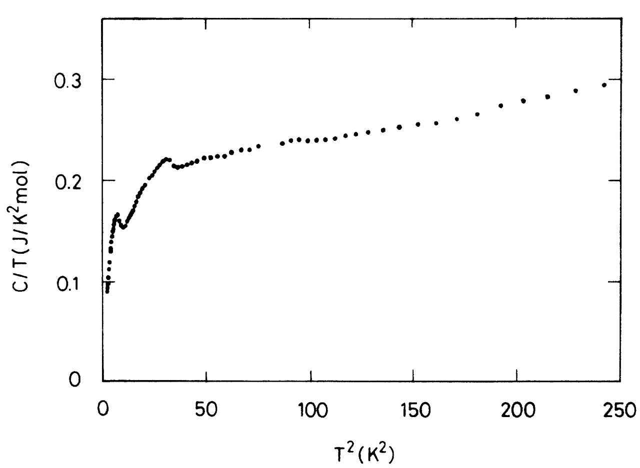

FIG. 5. Specific heat divided by temperature C/T vs T^2 for CeNiSn.

two narrow levels with an appropriate energy splitting. Furthermore, it is noteworthy that the magnetic entropy up to 20 K is only $\frac{1}{2}(R\ln 2)$. These results strongly suggest that the pseudogap gradually opens below about 6 K in the narrow band of heavy quasiparticles.

In summary, the results of this work on single-crystal CeNiSn demonstrate that the magnetic and transport properties are strongly anisotropic as expected from the orthorhombic ϵ-TiNiSi-type structure. At temperatures above 50 K, the transport properties are governed by the interplay between the anisotropic Kondo effect and crystalline field. We found that both $\chi_a(T)$ and $\rho_a(T)$ exhibit pronounced peaks at 12 K. Since no anomaly was observed near the temperature either in the specific heat or the spin-lattice relaxation rate of ^{119}Sn, we ascribed the anomalies to the development of some antiferromagnetic correlations of quasiparticles, in analogy with the case of $CeRu_2Si_2$. The specific-heat measurements revealed that a gap opens in the narrow band of heavy quasiparticles. Here, we would like to mention that the ground state with the pseudogap found in CeNiSn may be a new type of ground state of moderately heavy fermions as predicted for the periodic Kondo-lattice system.[17] The strongly anisotropic behavior in $\rho(T)$ and $S(T)$ at low temperatures indicates that the anisotropic magnetic correlations and hybridizations play important roles in the formation of the pseudogap. The anisotropic hybridization between the $4f$ and conduction electrons in CeNiSn may allow the energy bands near the Fermi level to be very close to the instability for gap formation. At temperatures around 12 K, some antiferromagnetic correlation of heavy quasiparticles develops, which may induce the formation of the pseudogap in the density of states below about 6 K. Inelastic neutron-scattering experiments on single-crystalline samples are attempted to examine what type of antiferromagnetic correlation develops in CeNiSn at low temperatures.

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