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Effect of impurity phases on the anisotropic transport properties of CeNiSn

G. Nakamoto^a, T. Takabatake^{a,*}, Y. Bando^a, H. Fujii^a, K. Izawa^b, T. Suzuki^b,
T. Fujita^b, A. Minami^b, I. Oguro^c, L.T. Tai^d, A.A. Menovsky^d

^aFaculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 724, Japan

^bFaculty of Science, Hiroshima University, Higashi-Hiroshima 724, Japan

^cInstitute for Solid State Physics, University of Tokyo, Tokyo 106, Japan

^dVan der Waals–Zeeman Laboratorium, Universiteit van Amsterdam, The Netherlands

Abstract

We report on the measurements of resistivity, magnetoresistance, thermopower and specific heat on several single crystals of CeNiSn. As impurities of CeNi₂Sn₂ and Ce oxide increase up to about 3%, both the anisotropy and coherence in transport properties are smeared out. The increase in resistivity below 10 K is stronger for less pure crystal, which suggests strong localization of residual carriers in the pseudogap.

CeNiSn is a Kondo-lattice compound with a small energy gap of several degrees Kelvin in the electronic excitation spectrum and thus is called a Kondo semiconductor [1]. Alloying studies of CeNiSn revealed that the gap is closed by any replacement of about 10% either of the Ni sublattice or the Ce sublattice. It was thus inferred that the loss of coherence in the Kondo lattice is very destructive for the gap formation [1]. Low-temperature properties of heavy-fermion systems are in general sensitive to the presence of impurities and lattice imperfections. These facts motivated us to study the effect of impurities involved in single crystalline samples on the anisotropic transport properties of CeNiSn. Here the results of resistivity, magnetoresistance, thermopower and specific heat measurements on several single crystals grown by different methods are reported.

Single crystals of CeNiSn were grown by the following methods: a Czochralski method in a triarc furnace (nos. 1 and 3); a floating-zone melting in an infrared

mirror furnace (no. 2); and the Czochralski method using a hot tungsten crucible in a radio-frequency furnace (no. 4). The crystal 3 was prepared at the University of Amsterdam and the others at Hiroshima University. The characteristics of the crystal growth are listed in Table 1. Metallographic examination and electron-probe microanalysis revealed that impurity phases of CeNi₂Sn₂, Ce oxides and Ce₂Ni₃Sn₂ are distributed over the host phase of CeNiSn. Their typical dimensions in crystal 1 were 5 × 20, 5 × 5 and 2 × 50 μm², respectively. The volume fractions were estimated by microscopic observation and the analysis of specific heat as will be described later.

As shown in Table 1, volume fractions of CeNi₂Sn₂ and Ce oxides decrease on going from crystal 1 to crystal 4. Since Ce metal from Ames Laboratory was used as the starting element, residual oxygen in the Ar atmosphere in the furnace may be responsible for the inclusion of Ce oxides, especially in crystal 1. The Ce₂Ni₃Sn₂ phase of about 0.1% could not be eliminated by starting with off-stoichiometric compositions. For the CeNiSn host phase, no detectable deviation from 1-1-1 stoichiometry larger than 1 at% was ob-

* Corresponding author.

Table 1
Characteristics of the growth and characterization of CeNiSn single crystals

Sample	1	2	3	4
Preparation method	Czochralski	Floating zone	Czochralski	Czochralski
Furnace	Triarc (H) ^a	Infrared	Triarc (A) ^a	Radio frequency
Crucible	Cold Cu	None	Cold Cu	Hot W
Starting composition	1.0:1.0:1.0	1.002:1.0:1.0	1.07:1.0:1.05	1.01:1.0:1.01
Crystalline composition	0.99:1.00:0.99	0.99:1.00:0.99	0.99:1.00:1.00	0.99:1.00:1.00
Impurity (%)				
Ce ₂ O ₃	1.2	0.5	<0.2	<0.2
CeNi ₂ Sn ₂	2.5	0.5	<0.2	<0.2
<i>a</i> (Å)	7.541		7.539	7.540
<i>b</i> (Å)	4.600		4.602	4.602
<i>c</i> (Å)	7.623		7.617	7.614

^aH, Hiroshima and A, Amsterdam.

served. In crystal 4, no contamination from tungsten crucible was detected.

Fig. 1 shows the specific heat in a plot of C/T versus T for single crystals 2 and 4 and a polycrystal. The data of crystal 1 were almost identical to that of the polycrystal. The anomalies at 2 and 6 K were attributed to the magnetic ordering of the impurity phases of CeNi₂Sn₂ [2] and Ce₂O₃ [3], respectively. The entropy associated with the anomalies gave an estimation

Fig. 1. Specific heat divided by temperature C/T versus T for a polycrystal and two single-crystal samples of CeNiSn.

of impurity concentrations as listed in Table 1. When the impurity contribution was subtracted, the overall temperature dependence of C/T above 1.3 K was found to be almost identical for all the crystals. The strong decrease in C/T below 6 K reflects the formation of an energy gap in the quasiparticle band [1]. Therefore, the present results imply a rather weak effect of the impurities on the gap structure.

In contrast to the result of specific heat, the resistivity $\rho(T)$ strongly depends on the sample quality. As shown in Fig. 2, the increase in $\rho(T)$ below 10 K is most remarkable for crystal 1 along all the directions. On going from crystal 1 to 4, the value at 1.4 K decreases by a factor of 13 and 5.3 for ρ_a and ρ_c , respectively. Comparing this result with the impurity concentration listed in Table 1, it was noticed that the purest crystal 4 has the smallest resistivity at low temperatures. Furthermore, the local maximum in $\rho_a(T)$ near 13 K, which was attributed to the development of coherence in the Kondo lattice [1], becomes sharper as the impurity concentration diminishes. For crystal 4 with the least amount of impurities, $\rho_a(T)$ shows metallic behavior down to 1.3 K, and $\rho_c(T)$ also exhibits the coherence peak at 13 K. It should be noted that annealing of crystal 1 at 1000°C for 7 days resulted in a decrease of 10% for both ρ_a and ρ_c , and by 50% for ρ_b .

Measurements of thermopower $S(T)$ were carried out on two selected crystals, 1 and 4, because they exhibit opposite behavior in $\rho(T)$. As shown in Fig. 3, $S(T)$ has a three-peak structure with local maxima at 100, 20 and 3 K, respectively. However, the peaks at

Fig. 2. Temperature variation of resistivity along the three principal axes for four different CeNiSn single crystals.

100 and 20 K and the anisotropy between S_a and S_c are much weaker in crystal 1 than in crystal 4. For crystal 4, the peak at 20 K corresponds to the peak in both ρ_a and ρ_c near 13 K. These peaks can be regarded as the onset of coherence in the Kondo lattice. For crystal 1, the weak maximum near 20 K together with weak anisotropy suggest that the development of coherence is suppressed by the impurity scattering. For both crystals, $S(T)$ strongly increases below 7 K where the pseudogap is formed in the quasiparticle band. After passing through a peak at around 3 K, $S(T)$ seems to tend towards zero at 0 K, being consistent with the recent measurement on crystal 2 down to 0.1 K [4]. The sharp peak for crystal 4 is thought to be an indication of a fine structure in the residual density of states near the Fermi level.

The magnetic field dependence of the normalized magnetoresistance $\Delta\rho(H)/\rho(0)$ at 1.3 K is plotted in Fig. 4. The field was applied parallel to the a -axis, where the strongest effect was observed [5]. Except

Fig. 3. Thermopower versus temperature for CeNiSn single crystals 1 and 4.

for $I \parallel a$ in crystal 4, $\Delta\rho(H)/\rho(0)$ is negative and the absolute value is larger for $I \parallel c$ than for $I \parallel a$, suggesting anisotropic suppression of the energy gap. However, the anisotropy almost vanishes in the least pure crystal 1, as in the cases of $\rho(T)$ and $S(T)$. For

Fig. 4. Magnetoresistance of CeNiSn single crystals at 1.3 K for electrical current along a - and c -axes.

the purest crystal 4, a positive magnetoresistance with a large maximum of 17% is observed for $I||a$. Such a positive magnetoresistance is expected if the center of the pseudogap is located slightly above the Fermi level [6]. In this case, the total conductivity may initially decrease with increasing field until the center of the pseudogap of the up-spin band comes to the Fermi level. This model is consistent with the metallic behavior of $\rho_a(T)$ and the sharp structure of $S(T)$. However, a more realistic model including the effect of spin polarization of the heavy quasiparticle band is required to account for the anisotropy in the magnetoresistance.

Contrary to our expectation, the enhancement of resistivity below 10 K is found to be much stronger in less pure crystal. The anisotropy in $\rho(T)$, $S(T)$ and $\Delta\rho(H)/\rho(0)$ becomes weaker with the increase in the concentration of impurities CeNi_2Sn_2 and Ce_2O_3 . Therefore, it can be assumed that the enhancement of resistivity originates in these impurities which may introduce distortion or strain in the lattice of CeNiSn . On the other hand, the result of specific heat suggests that formation of the pseudogap is not so sensitive to the above impurity phases in comparison to the substituted impurities in the lattice [1]. When the pseudogap is formed below 7 K, the carrier number strongly decreases as was demonstrated by Hall effect measurements [7]. The carriers remaining near the bottom of the pseudogap may be localized in the

presence of impurities, and thus the resistivity is strongly increased. Further studies are required to distinguish the intrinsic properties of the Kondo semiconductor CeNiSn from the impurity effects.

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