Impurity-induced localization of quasiparticles in the presence of a pseudogap in CeNiSn

T. Takabatake, Y. Echizen, T. Yoshino, and K. Kobayashi
Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

G. Nakamoto* and H. Fujii
Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan

M. Sera
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
(Received 23 February 1999)

The effect of doping in CeNiSn has been studied by the measurements of electrical resistivity, Hall coefficient and magnetic susceptibility for single crystals of $CeNi_{1-x}T_xSn$ (T=Co, Cu, and Pt) and $Ce_{1-y}La_yNiSn$ ($x,y=0.01$ and 0.05). All these impurities are found to increase the residual resistivity by several times up to 1 mΩ cm for x or $y=0.01$, while for x or $y=0.05$ the resistivities along the orthorhombic b and c axes saturate to values smaller than those for 0.01. Furthermore, the low-temperature increase in the Hall mobility of CeNiSn was found to be strongly suppressed in a similar way by all the impurities. These results indicate that residual carriers in CeNiSn with an anisotropic gap are immobilized by any impurity substituted either in the $4f$ site or the non-$4f$ site. [S0163-1829(99)04121-1]

A class of strongly correlated $4f$-electron compounds exhibiting a small (pseudo)gap in both the charge and spin excitations is often referred to as Kondo insulator or Kondo semiconductor.[1–3] It is generally accepted that hybridization of the $4f$ states with a conduction band plays the central role in the gap formation. However, there are significant differences in the transport properties between cubic Kondo semiconductors and orthorhombic ones. Cubic ones YbB_{12} and $Ce_3Bi_4Pt_3$ show semiconducting behavior in both the resistivity and Hall coefficient which increase by 2–4 orders of magnitude as temperature is decreased from 300 to 1.5 K.[4–6] For the orthorhombic compound CeNiSn, on the other hand, initial measurements of the resistivity also showed semiconductorlike behavior below 10 K.[7] However, it has been found that the a-axis resistivity of a purified crystal shows metallic behavior with a residual value of 25 $\mu\Omega$ cm,[8] although the absolute value of the Hall coefficient increases by a factor of 25 on cooling from 4 to 0.5 K.[2] Therefore, the semiconductorlike resistivity of early samples was attributed to localization of residual carriers by impurities.[8] To explain this unusual property of CeNiSn, an anisotropic hybridization gap model has been proposed by considering the k dependence of the hybridization matrix element which vanishes along the a axis.[9] This model shows that a finite density of states remains at the Fermi level but the metallic conduction along the a axis is easily lost by impurity scattering.[9] Measurements of complex conductivity indeed revealed that the metallic behavior is realized as the result of strong reduction of quasiparticle scattering rate with the gap formation.[10] Band calculations[11–12] and studies by photoemission[13] and polarized neutron diffraction[14] suggested that the hybridization between Ce $4f$and Ni $3d$ states is fundamental in the formation of the renormalized band at low temperatures.

Substitution studies of CeNiSn have been extensively carried out to understand the anomalous ground state. It was expected that the substitution of Co and Cu for Ni gives rise to doping a hole and an electron, respectively. The NMR and specific-heat measurements of $CeNi_{1-x}T_xSn$ (T=Co,Cu) and $Ce_{1-y}La_yNiSn$ indicated that the density of states at the Fermi level increases in proportion to $\sqrt{x}$ or $\sqrt{y}$, leading to the gap closure around x or $y=0.1$.[15–17] Provided that filling of the pseudogap could be controlled by carrier doping, the system would change into a good metal. On the contrary, our preliminary experiments showed that Co and Cu substitution at 1% leads to very strong increase in the residual resistivity.[18] The rate of increase in resistivity, 1 mΩ cm/1%, is extremely large compared with 3 $\mu\Omega$ cm/1% reported for La substitution in a metallic Kondo system $CeCu_6$.[19] This fact invokes an unconventional scattering mechanism from nonmagnetic impurities in CeNiSn.

Nonmagnetic La impurities without $4f$ electron in the Ce sublattice in Kondo semiconductors are theoretically treated as *Kondo holes* which give rise to a bound state in the gap.[20] This idea of Kondo hole has been proved by the observation of large enhancement of both the resistivity and magnetic susceptibility induced by La substitution in $CePd_3$.[21] For $Ce_{1-y}La_yNiSn$, the $\sqrt{y}$ dependence of the induced density of states is also consistent with this model.[15] On the other hand, substitution of Pt for Ni may not dope carriers because of the isoelectronic nature of these two atoms. It is therefore important to investigate whether La and Pt substitutions in CeNiSn increase the residual resistivity as strongly as Co and Cu substitutions do. In this paper, we report and compare the results of transport and magnetic measurements on single crystalline alloys of $Ce_{1-y}La_yNiSn$ and $CeNi_{1-x}T_xSn$ (T =Co, Cu, and Pt).

Single-crystalline samples with x or $y=0.01$ and 0.05 were prepared by a Czochralski method using a radio frequency induction furnace with a hot tungsten crucible as was described elsewhere.[8] Ce metal was supplied by Ames Laboratory. Electron-probe microanalysis of the crystals with

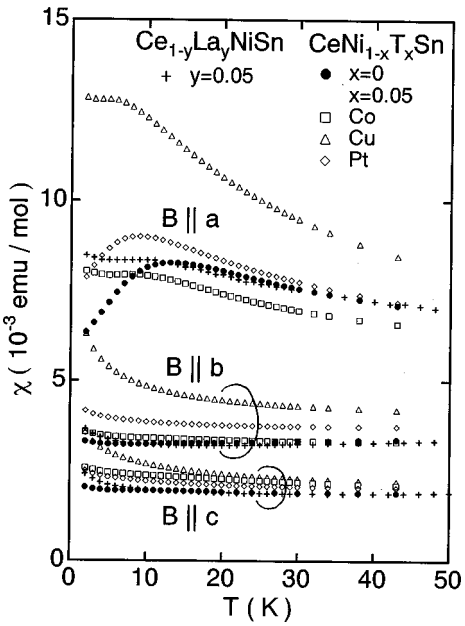

FIG. 1. Temperature dependence of the magnetic susceptibility for single crystals of $Ce_{1-y}La_yNiSn$ and $CeNi_{1-x}T_xSn$ (T=Co, Cu, Pt) for x or $y=0$ and 0.05.

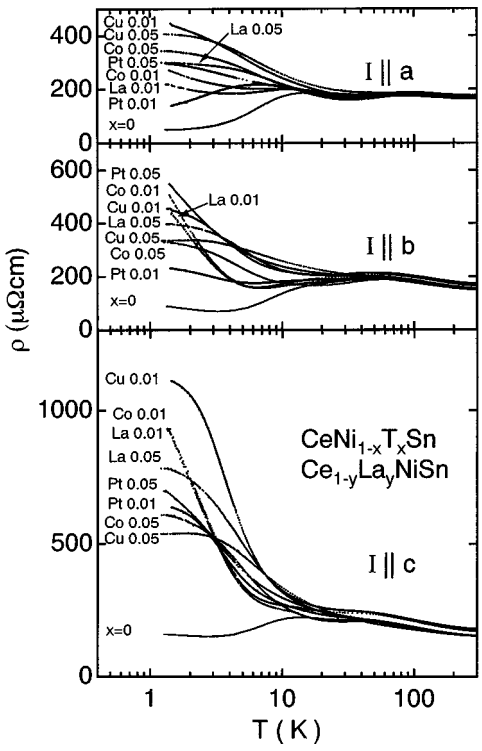

FIG. 2. Temperature dependence of the electrical resistivity for single crystals of $Ce_{1-y}La_yNiSn$ and $CeNi_{1-x}T_xSn$ (T=Co, Cu, Pt) for x or $y=0$, 0.01, and 0.05.

nominally 5 at. % Co, Cu, and La proved the concentration to be homogeneous within 4 and 5 at. % in the whole crystal. However, a significant gradient in Pt concentration was detected, which changes from 4 to 8 at. % on scanning from the tail end to the seed end of the crystal. Therefore, the middle part with 5 at. % was used for the measurements. It was also found that all the as-grown crystals contain an impurity phase of $Ce_2Ni_3Sn_2$ at approximately 0.2%. Nevertheless, we did not remove this impurity phase by using the solid-state electron transport technique[8] because the partially substituted impurities would also be removed.

The electrical resistivity ρ was measured by a standard dc four-probe method in the temperature range 1.4–300 K. The Hall coefficient R_H was measured from 1.6 to 20 K by using a four-wire ac resistance bridge operating at 16 Hz. The magnetic susceptibility $\chi(T)$ was measured in a field of 1 T by using a commercial SQUID magnetometer.

The temperature dependence of χ for samples with x or $y=0.05$ and of a pure CeNiSn sample is compared in Fig. 1. The a-axis susceptibility of CeNiSn decreases below the maximum at 13 K, which is thought to be a result of the gap formation in the density of states at the Fermi level. This maximum is maintained for $x=0.05$ Pt but smeared out by the substitution of Co and La. The large enhancement in $\chi_a(T)$ for $x=0.05$ Cu suggests that the pseudogap is filled up by doping of $3d$ electrons. Indeed, it has been observed that the specific-heat coefficient of this sample rises to 0.8 J/mol K^2 with decreasing temperature down to 0.025 K.[22] At temperatures above 150 K, the effect of all the substitutions at 5 at. % on $\chi(T)$ becomes rather weak. From the Curie-Weiss behavior for $B\|a$, the minimum and maximum values of the effective magnetic moment are estimated to be 2.69 and 2.73 μ_B/f.u., respectively, for 5% Cu and 5% Co. Thus, the valence of Ce ions stays close to three in these alloys.

In Fig. 2, we compare the $\rho(T)$ data for current along the three principal directions. Note that the substitution grately affects $\rho(T)$ only below 30 K but not above. The most dramatic change occurs in $\rho_c(T)$ for $x=0.01$ Cu, which exceeds 1100 $\mu\Omega$ cm at 1.4 K and is still rising. This curve is followed by those with $x=0.01$ Co and $y=0.01$ La, which are most identical. When x or y is further increased to 0.05, the upturn of $\rho_c(T)$ occurs at higher temperatures, but the value of ρ_c saturates to a value smaller than that for x or $y=0.01$. Similar trends are observed for $I\|b$. For $I\|a$, in contrast, the saturated value for x or $y=0.05$ is larger than that for x or $y=0.01$ except for T=Cu. We note the close resemblance in the behavior between La substituted samples and the Co substituted ones. As was observed for $\chi(T)$, the effect of Pt substitution on $\rho(T)$ is most weak among these substitutions, reflecting the isoelectronic nature of Pt with Ni.

To obtain a clue to understand the anomalously strong scattering from impurities for x or $y=0.01$, we have measured the Hall coefficient. A magnetic field of 1 T was applied parallel to the c axis and the current flowed along the b axis. For this configuration, the Hall voltage is linear with field up to 5 T.[23] In Fig. 3, $R_H(T)$ for CeNiSn exhibits a maximum at 8.4 K, changes sign at 5.5 K and dramatically decreases with decreasing temperature as a pseudogap is formed. The carrier density at 1.7 K is estimated to be 1.3×10^{-3} per formula unit, assuming a single type of carrier. For x or $y=0.01$, both the temperatures where $R_H(T)$ has the maximum and where $R_H(T)$ becomes negative shift to lower temperatures. The absolute value of R_H at 1.7 K is reduced most strongly by the substitution of Cu and to a lesser extent for those of La and Co, and least that of Pt, as in the sequence of the effect on $\rho_c(T)$. This reduction is $|R_H|$ indicates a significant decrease in the concentration of electronlike carriers. For x or $y=0.05$, however, $R_H(T)$ gradu-

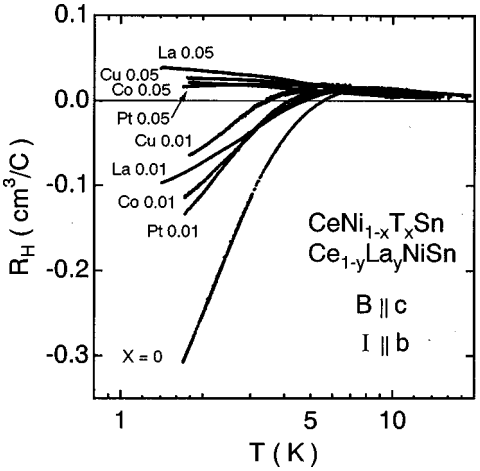

FIG. 3. Temperature dependence of the Hall coefficient for single crystals of $Ce_{1-y}La_yNiSn$ and $CeNi_{1-x}T_xSn$ (T=Co, Cu, Pt) for x or $y=0$, 0.01, and 0.05.

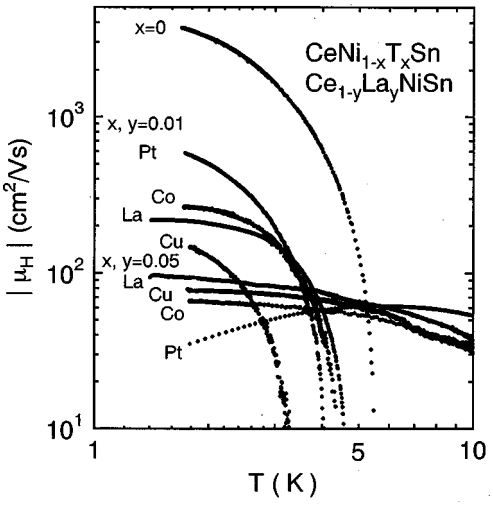

FIG. 4. Temperature dependence of the Hall mobility $\mu_H = R_H/\rho$ for single crystals of $Ce_{1-y}La_yNiSn$ and $CeNi_{1-x}T_xSn$ (T=Co, Cu, Pt) for x or $y=0$, 0.01, and 0.05.

ally increases with decreasing temperature and stays positive as if holelike carriers are predominant.

The most notable in Fig. 3 is that the temperature variation of R_H is controlled systematically by the increase of x or y, but does not largely depend on the sort of substitutes. This fact contradicts the idea of carrier doping into a rigid band with a pseudogap, thereby the Fermi level might shift lower or higher with respect to the center of the gap by electron doping with Cu or hole doping with Co, respectively. Therefore, we need to consider the impurity effect on the carrier lifetime τ. If we assume one type of carrier for simplicity, then the Hall mobility μ_H can be estimated by the relation $\mu_H = R_H/\rho$. The results obtained from the data for $B \| c$ and $I \| b$ are shown in Fig. 4. For CeNiSn, $|\mu_H|$ increases to a large value of 3700 cm^2/V s as temperature is decreased to 1.7 K. Such a strong increase in $|\mu_H|$ due to gap formation in the electronic density of states mimics that reported for the CDW gap opening in a quasi-two-dimensional conductor.[24] The relation $\mu_H = e\tau/m^*$, where m^* is the effective mass of quasiparticles, translates the above result to a significant increase in τ/m^*. This interpretation is consistent with the variation of $\tau(T)$ derived from the complex conductivity measurement.[10] The values of $|\mu_H|$ at 1.7 K for alloys with x or $y=0.01$ are reduced by approximately one order of magnitude. Hence, the drastic change in the resistivity from the metallic behavior for pure CeNiSn to the semiconducting one for x or $y=0.01$ should be caused by the strong decrease in τ.

We have shown, so far, that any substitution either in the Ce sublattice or the Ni sublattice of CeNiSn at a low concentration as small as 1% acts as very strong scatterer for the residual carriers. This result is consistent with the model of anisotropic hybridization gap of heavy fermions.[9] According to this model, the residual carriers can be scattered only in the gapless region along the a axis of CeNiSn, so that the scattering from impurities may reach to the unitarity limit. When the pseudogap is smeared by a larger amount of impurities at 5%, then the doped carriers can be scattered in wider directions and thus the residual resistivity may decrease.

It is noteworthy that the charge number of substitutes controls the strength of impurity effects. In fact, we found that the effect of substitution on $\rho(T)$, $R_H(T)$, and $\chi(T)$ is strongest for Cu, then La and Co, and least for Pt. In particular, substitution of La for Ce and that of Co for Ni give rise to very similar effects. This close resemblance implies that both La and Co introduce a Kondo hole into the renormalized band which is formed by hybridization of Ce $4f$ state with Ni $3d$ state. On the other hand, the increase of $3d$ electron density by Cu substitution weakens the hybridization and thereby enhances both susceptibility and specific heat at low temperatures.

In summary, we have carried out for the first time a systematic study of the effect of doping in CeNiSn by using well characterized single-crystalline samples $CeNi_{1-x}T_xNiSn$ (T=Co, Cu, and Pt) and $Ce_{1-y}La_yNiSn$ (x, $y=0.01$ and 0.05). The combined results of magnetic susceptibility, electrical resistivity and Hall coefficients demonstrate that the residual carriers in the pseudogap state are immobilized by any impurity irrespective of the charge number and of the substitution site in the lattice.

We are thankful to K. Miyake, D. T. Adroja, Y. Isikawa, Y. Kitaoka, and P. Coleman for useful discussions and Y. Shibata for EPMA done at the Instrument Center for Chemical Analysis of Hiroshima University. The Hall effect was measured by using superconducting magnets at the Cryogenic Center of Hiroshima University and the High-Field Laboratory of Institute for Materials Research, Tohoku University. We wish to thank T. Fujita and T. Suzuki for their valuable advice and the generous use of their SQUID susceptometer. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

*Present address: Japan Advanced Institute of Sciences and Technology, 923-12 Ishikawa, Japan.

[1] G. Aeppli and Z. Fisk, Comments Condens. Matter Phys. **16**, 155 (1992).

[2] T. Takabatake F. Iga, T. Yoshino, Y. Echizen, K. Katoh, K. Kobayashi, M. Higa, N. Shimizu, Y. Bando, G. Nakamoto, H. Fujii, K. Izawa, T. Suzuki, T. Fujita, M. Sera, M. Hiroi, K. Maezawa, S. Mock, H. v. Löhneysen, A. Brückl, K. Neumaier, and K. Andres, J. Magn. Magn. Mater. **177-181**, 277 (1998).

[3] H. Tsunetugu, M. Siegrist, and K. Ueda, Rev. Mod. Phys. **69**, 809 (1997).

[4] M. Kasaya, F. Iga, M. Takigawa, and T. Kasuya, J. Magn. Magn. Mater. **47-48**, 429 (1985).

[5] M. F. Hundley. P. C. Canfield, J. D. Thompson, and Z. Fisk, Phys. Rev. B **42**, 6842 (1990).

[6] F. Iga, N. Shimizu, and T. Takabatake, J. Magn. Magn. Mater. **177-181**, 337 (1998).

[7] T. Takabatake, Y. Nakazawa, and M. Ishikawa, Jpn. J. Appl. Phys., Suppl. **26**, 547 (1987).

[8] G. Nakamoto, T. Takabatake, H. Fujii, A. Minami, K. Maezawa, I. Oguro, and A. A. Menovsky, J. Phys. Soc. Jpn. **64**, 4834 (1995).

[9] H. Ikeda and K. Miyake, J. Phys. Soc. Jpn. **65**, 1769 (1996).

[10] T. Shibauchi, N. Katase, T. Tamegai, K. Uchinokura, T. Takabatake, G. Nakamoto, and A. A. Menovsky, Phys. Rev. B **56**, 8277 (1997).

[11] A. Yanase and H. Harima, Prog. Theor. Phys. Suppl. **108**, 19 (1992).

[12] T. J. Hammond, G. A. Gehring, M. B. Suvasini, and W. M. Temmerman, Phys. Rev. B **51**, 2994 (1995).

[13] S. Nohara, H. Namatame, A. Fujimori, and T. Takabatake, Phys. Rev. B **47**, 1754 (1993).

[14] A. Heiss, I. Zobkalo, M. Bonnet, J. Schweizer, E. L. Berbna, F. Tasset, Y. Isikawa, and G. M. Lander, J. Phys.: Condens. Matter **9**, 9321 (1997).

[15] K. Nakamura, Y. Kitaoka, K. Asayama, T. Takabatake, G. Nakamoto, H. Tanaka, and H. Fujii, Phys. Rev. B **53**, 6385 (1996).

[16] S. Nishigori, H. Goshima, T. Suzuki, T. Fujita, G. Nakamoto, H. Tanaka, T. Takabatake, and H. Fujii, J. Phys. Soc. Jpn. **65**, 2614 (1996).

[17] F. G. Aliev, V. V. Moschchalkov, M. K. Zalyalyutdinov, F. I. Pak, R. V. Scolozdra, P. A. Alekseev, V. N. Lazukov, and I. P. Sadikov, Physica B **163**, 358 (1990).

[18] K. Kobayashi, T. Takabatake, G. Nakamoto, M. Higa, T. Yoshino, H. Fujii, and M. Sera, Physica B **230-232**, 676 (1997).

[19] A. Sumiyama, Y. Oda, H. Nagano, Y. Onuki, and T. Komatsubara, J. Phys. Soc. Jpn. **55**, 1294 (1986).

[20] P. Schlottmann, J. Appl. Phys. **75**, 7044 (1994).

[21] L. M. Lawrence, T. Graf, M. F. Hundley, J. D. Thompson, A. Lacerda, M. S. Torikachvili, J. L. Sarrao, and Z. Fisk, Phys. Rev. B **53**, 12 559 (1996).

[22] A. Brückl, K. Neumaier, Ch. Probst, K. Andres, S. J. Flaschin, A. Krazter, B. M. Kalvius, and T. Takabatake, Physica B **240**, 199 (1997).

[23] T. Takabatake, G. Nakamoto, M. Sera, K. Kobahashi, H. Fujii, K. Maezawa, I. Oguro, and Y. Matsuda, J. Phys. Soc. Jpn. Suppl. B **65**, 105 (1996).

[24] M. Sasaki, G. X. Tai, S. Tamura, and M. Inoue, Phys. Rev. B **47**, 6216 (1993).