Suppression of $p$-$f$ mixing and formation of a superzone gap in CeSbNi$_x$

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We report electrical resistivity, Hall coefficient, magnetic susceptibility, magnetization, and magnetoresistance measurements on CeSbNi$_x$ (0$\leq x$$\leq 0.4$), where the Ni atoms are incorporated interstitially into the cubic cell of CeSb. The Ne`el temperature $T_N$ drops from 16 K for $x=0$ to 9 K for $x=0.05$ and then gradually increases to 12.5 K for $x=0.4$. The initial depression of both $T_N$ and saturation moment is ascribed to the collapse of $p$-$f$ mixing by the decrease of the 5$p$-hole concentration in the semimetallic CeSb. The resistivity for $x$$\approx$0.08 shows a sharp rise just below $T_N$, which is quenched by the application of magnetic fields higher than the metamagnetic transition field. This finding indicates that a superzone gap is formed in the 5$d$-electron band of CeSbNi$_x$ for $x$$\approx$0.08 as a result of the type-I antiferromagnetic order.

Cerium monopnicotides CeX ($X=P, As, Sb, Bi$) are antiferromagnets with low-density carriers. They have long been studied experimentally and theoretically,1–3 because of their unusual magnetic properties such as complex magnetic phase diagram,4 large magnetic anisotropy,5 small crystal-field splitting,6 etc., in spite of the simple NaCl-type structure. It has been shown that the magnetic properties of CeSb are very sensitive to any perturbation such as application of pressure7,8 and partial substitution.9,10 For example, the substitution of Te for Sb in CeSb by only 5% results in a large drop of the Ne`el temperature $T_N$ from 16 to 4 K.10,11 This is accompanied by a substantial decrease in the saturation moment from 2.1 to 0.7$\mu_B$/Ce and an increase in the crystal-field splitting $\Delta$ from 37 to 49 K,1,11 where $\Delta$ is the energy splitting from the ground-state doublet $\Gamma_7$ to the excited-state quartet $\Gamma_8$ of Ce$^{3+}$ ion. These observations were explained by taking account of nonlinear $p$-$f$ mixing between the 5$p$-hole valence band of Sb and the 4$f$($\Gamma_8$) state of Ce, as follows.13,14 The Te atoms substituting for Sb have additional 5$p$ electrons which should fill the 5$p$-hole band of semimetallic CeSb. This in turn weakens the $p$-$f$ mixing and causes significant effects on the physical properties mentioned above.

Recently, we have reported that Ni atoms can be incorporated interstitially into CeSb with keeping the cubic structure intact up to the solubility limit of $x=0.4$ in the formula CeSbNi$_x$.15 For a single crystal of $x=0.15$, the magnetic susceptibility reveals an antiferromagnetic (AF) order at $T_N=9.5$ K. The magnetization isotherm at 1.5 K shows a metamagnetic transition at 6.4 T with neither hysteresis nor anisotropy. The disappearance of complex and anisotropic nature in the magnetic properties suggested that the $p$-$f$ mixing in CeSb is strongly reduced by the Ni incorporation. These observations are analogous to those in CeSb$_{1-x}$Te$_x$, mentioned above. The mechanism of the collapse of $p$-$f$ mixing in CeSbNi$_x$ remains to be examined by the careful study of magnetic and transport properties using well characterized samples with different values of $x$. In the present paper, we report such measurements on a single crystal of CeSbNi$_{0.15}$ and polycrystalline samples of CeSbNi$_x$ (0$\leq x$$\leq 0.4$). The effects of Ni incorporation will be discussed by comparing with those of the substitution of Te for Sb.

Polycrystalline samples of CeSbNi$_x$ with $x=0, 0.02, 0.035, 0.05, 0.08, 0.15, 0.25, 0.35$, and 0.40 were synthesized by arc melting. Electron-probe microanalysis indicated that the impurity phases of CeNiSb$_2$, CeNi$_2$Sb$_2$, and CeNi$_3$ were less than a few vol %.15 X-ray powder-diffraction analysis showed that the cubic lattice parameter $a$ increases almost linearly with $x$, at a rate $da/dx=0.085$ Å. The method of the growth of single crystal CeSbNi$_{0.15}$ was described in Ref. 15. The magnetic susceptibility $\chi=M/B$ was measured in a field of 0.5 T in the temperature range 2–300 K. Hall effect was measured by the use of the conventional four-probe dc method in a field of 1 T. Measurements of electrical resistivity $\rho(T)$ were done by a standard four-probe dc technique for 1.3$\leq T$$\leq 300$ K and $B=15$ T. Magnetization curves were recorded up to 15 T by an extraction method.

The temperature dependence of $\chi$ for all the samples of CeSbNi$_x$ (0$\leq x$$\leq 0.4$) was found to obey the Curie-Weiss law at temperatures above 60 K. The effective magnetic moment $\mu_{eff}$ is essentially independent of $x$ and is close to 2.5$\mu_B$/Ce, the value expected for a trivalent Ce ion. However, the paramagnetic Curie temperature $\theta_p$ decreases from 12 K for $x=0$ to 0 K for $x=0.4$. The low-temperature data of $\chi(T)$ are shown in the inset of Fig. 1. For $x=0$, $\chi(T)$ exhibits a sharp peak at $T_N=16$ K followed by a minimum at 10 K, below which an AF phase of the type IA is stabilized.4 For $x<0.05$, $\chi(T)$ is characterized by a broad maximum, of which temperature was taken as $T_N$, because it agrees with an anomaly in $\rho(T)$.

Temperature variations of $\rho(T)/\rho(300$ K) are represented in Fig. 1. Because of the presence of microcracks, the data
are normalized to the room-temperature value. Typical values at 300 K are 150 and 560 $\mu\Omega$cm for $x=0$ and 0.4, respectively. As the temperature is lowered, $\rho(T)$ for $x=0$ passes through a broad maximum at 30 K and drops suddenly at $T_N=16$ K. For $x=0.05$, $\rho(T)$ decreases on cooling, while that for $x>0.08$ increases just below $T_N$. The sharp rise found for $x=0.15$ is tentatively ascribed to an AF superzone gap. If this is the case, the gap should be suppressed when the AF order is destroyed by a sufficiently high magnetic field. To confirm this supposition, we measured the resistivity as the functions of $T$ and $B$ for the single crystal with $x=0.15$.

The inset of the upper panel of Fig. 2 shows the results of $\rho(T)$ for $B//[[100]]$. As expected, the sharp rise in $\rho(T)$ below $T_N$ is suppressed on increasing the applied field, concomitant with the decrease of $T_N$. In fields above 10 T, no anomaly is noticed down to 1.3 K. It is noteworthy that these effects are very similar for two configurations, $B//[[100]]$ and $B \perp [[100]]$ (not shown in Fig. 2). This observation is consistent with the absence of magnetic anisotropy for $x=0.15$. Another interesting observation is the different behavior between the zero-field cooled (ZFC) and field cooled (FC) data. It is assumed that the ZFC state consists of many AF domains, while the FC state may have mono domain with Ce magnetic moments parallel to the direction of applied field if the anisotropy energy is sufficiently low. The different domain structures may cause the observed variations in the zero-field data.

The close relation between the magnetoresistance $\rho(B)$ and the magnetization $M(B)$ for $B//[[100]]$ is demonstrated in Fig. 2. We observed that the virgin curves of $\rho(B)$ for $B//I$ and $B \perp I$ at 1.5 K show a sudden jump and a drop at 1.7 T, respectively. The $M(B)$ curve also exhibits a weak hysteresis at the same field, as is noticed in the inset of the lower panel of Fig. 2. Therefore the anomalies in $\rho(B)$ at 1.7 T is ascribed to the effect of reorientation of domains, as mentioned above. With a further increase of field up to 5 T, both $\rho(B//I)$ and $\rho(B \perp I)$ decrease significantly and $d\rho/dB$ has the maximum at $B=6.5$ T. This field value agrees with the metamagnetic-transition field in $M(B)$. Therefore we may conclude that the superzone gap is eliminated by the metamagnetic transition from the AF state to a field-induced ferromagnetic state.

The dependence of $M(B)$ on $x$ was studied by using polycrystalline samples of CeSbNi$_x$ $(0 \leq x \leq 0.4)$. Figure 3 shows the $M(B)$ curves at 4.2 K up to 15 T. $M(B)$ for $x=0$ exhibits a strong hysteresis with two metamagnetic transitions at 2 and 4 T, as reported previously, and the saturation moment of 1.85$\mu_B$/Ce equals the average value reported for $B//[[100]]$, [110], and [111]. With increasing $x$ up to 0.05, the metamagnetic behavior with hysteresis is weakened but the saturation moment is unchanged. For $x=0.08$, however, both the hysteresis and the metamagnetic transition at 2 T disappear. The saturation is not achieved in the highest field of 15 T, where $M(B)$ reaches a value of about 1.2$\mu_B$/Ce. No significant change in the $M(B)$ curve occurs with further increase of $x$ to 0.4. The measurement of $M(B)$ up to 55 T for $x=0.15$ indicated that $M(B)$ at 4.2 K gradually increases to 2$\mu_B$/Ce.

To examine the change of carrier concentration in CeSbNi$_x$ with $x$, we measured the Hall coefficient $R_H(T)$. In Fig. 4, the data for the single crystal CeSbNi$_{0.15}$ is compared with that reported for CeSb. The absolute value of $R_H(T)$ for CeSbNi$_{0.15}$ is approximately half that for CeSb. This fact suggests that the electron-carrier concentration is increased by the Ni incorporation. The Hall effect in the paramagnetic state is generally analyzed by using the empirical ansatz, $R_H(T)=R_0+4.5\pi \chi(T)R_S$, where $R_0$ and $R_S$ are the normal and anomalous Hall coefficients. However, it
was reported that this equation cannot describe the data for CeSb.\textsuperscript{16} On the other hand, the fit to the data for CeSbNi\textsubscript{0.15} is rather good as is shown by the solid line, which gives the values of \( R_0 = -5.08 \times 10^{-3} \) cm\(^3\)/C and \( R_S = +1.17 \times 10^{-3} \) (cm\(^3\)/C)/(emu/mol). The semimetallic nature does not allow us to estimate the carrier concentration solely from the value of \( R_0 \). In the inset of Fig. 4, the strong increase of \( R_H(T) \) just below \( T_N = 9.5 \) K coincides with the rapid rise in \( \rho(T) \). This fact indicates the sudden loss of the carriers due to the formation of the superzone gap.

The data for CeSbNi\textsubscript{x} (0 \( \leq \) x \( \leq \) 0.4) obtained by the present studies are summarized in Fig. 5; the cubic lattice parameter \( a \), paramagnetic Curie temperature \( \theta_P \), magnetization \( M \) at B = 15 T, and Neél temperature \( T_N \) as a function of x. In the lowest panel, the crystal-field splitting \( \Delta \) obtained by recent studies of inelastic neutron scattering\textsuperscript{18} is shown. Let us now discuss these data by comparing with those reported for CeSb\textsubscript{1-y}Te\textsubscript{y} (0 \( \leq \) y \( \leq \) 0.5).\textsuperscript{7,10} The lattice constant for CeSbNi\textsubscript{x} increases almost linearly with x, while that for CeSb\textsubscript{1-y}Te\textsubscript{y} decreases with y. Nevertheless, the traces of \( \theta_P \), \( M \), \( T_N \), and \( \Delta \) are similar as the functions of x and y, respectively. In fact, both \( T_N \) and \( M \) for CeSbNi\textsubscript{x} and CeSb\textsubscript{1-y}Te\textsubscript{y} strongly decrease in such a small concentration range, x \( \leq \) 0.05 and y \( \leq \) 0.05. The magnetic anisotropy in CeSb disappears for x \( \leq \) 0.05 and y \( \leq \) 0.05, where the type-I ground state is stabilized.\textsuperscript{1,18} The anomalous effects in CeSb\textsubscript{1-y}Te\textsubscript{y} were explained as follows. The substitution of Te for Sb adds the 5\textit{p} electrons which fill the 5\textit{p}-hole band, and thus weakens the \( p-f \) mixing. This collapse of \( p-f \) mixing strongly depresses \( T_N \) and increases \( \Delta \).\textsuperscript{10} In CeSbNi\textsubscript{x}, the 3\textit{d} state of Ni may overlap with the 5\textit{p} band of Sb, and then reduce the 5\textit{p}-hole concentration. This results in similar collapse of \( p-f \) mixing as in CeSb\textsubscript{1-y}Te\textsubscript{y}.

In order to understand the mechanism of the collapse of \( p-f \) mixing, we should recall the unique magnetic structure of CeSb in the ground state. The ferromagnetically coupled double layers are stacked antiferromagnetically along the [001] direction with the sequence \((+++--)\).\textsuperscript{4} The competi-
tation of ferromagnetic and AF couplings between the ferromagnetic layers have recently been explained by considering intraband (ferromagnetic) and interband (AF) exchange interactions between the localized 4f spins and two types of carriers. Following this model, we discuss now why both $T_N$ and $M$ in CeSbNi$_x$ and CeSb$_{1-y}$Te$_y$ strongly decrease for such small amounts of Ni and Te, $x \leq 0.05$ and $y \leq 0.05$. In both systems, the reduction of 5$p$-hole concentration should weaken both the intraband and interband interactions, as described below. The intraband interaction is proportional to the square of the $p-f$ mixing interaction, whereas the interband one is to the product of the $p-f$ mixing and the $d-f$ mixing. As the $p-f$ mixing is reduced with the Ni incorporation, the intraband ferromagnetic interaction is more strongly weakened than the interband AF one. This argument is supported by the steady decrease of $\theta_p$ with $x$, as was shown in Fig. 5(b). When the AF interaction dominates the ferromagnetic one, the double ferromagnetic layers are destabilized and instead the type-I ground state is realized in CeSbNi$_x$ ($x \geq 0.08$) (Ref. 18) and CeSb$_{1-y}$Te$_y$ ($y \geq 0.05$).

Next, we discuss the reason for the opposite change in $\rho(T)$ below $T_N$ for CeSbNi$_x$ and CeSb$_{1-y}$Te$_y$. Below $T_N$, $\rho(T)$ for $x \geq 0.08$ increases abruptly but that for $y \geq 0.05$ decreases, although both undergo the transition into the type-I AF phase. It should be recalled that the Fermi surface of CeSb consists of the Sb 5$p$-hole bands centered at $\Gamma$ point and Ce 5$d$-electron bands centered at $X$ point.

The electron bands are mostly responsible for the electrical conductivity because the mobility of electrons is much higher than that of holes. In CeSbNi$_x$, the effect of addition of Ni 3$d$ electrons is not only the decrease of the 5$p$-hole concentration but also the increase of the 5$d$-electron concentration through the 3$d$-5$d$ mixing. Then, the Fermi level of the electron band may cross the midpoint between $X$ and $\Gamma$ points as a result of the increase of the 5$d$-electron concentration through the hybridization between Ni 3$d$ states and Ce 5$d$ states.

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