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Evolution of heavy-fermion behavior from mixed-valence state in the series $Ce(Pt_{1-x}Ni_x)Si$

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We present the room-temperature lattice parameters, the static magnetic susceptibility, and the magnetic resistivity between 2.4 and 300 K for a series of ten polycrystalline $Ce(Pt_{1-x}Ni_x)Si$ samples with $x=0.0$ to 1.0. An abrupt change in the lattice constant as well as in $T_{max}(\chi_m)$ and $T_{max}(\rho_m)$ occurs around $x=0.5$. This is evidence for the transition from heavy-fermion behavior to a mixed-valence state. The magnetic-susceptibility and magnetic-resistivity data support the interpretation of resistivity maximum in terms of a spin-scattering mechanism in the mixed-valence regime, while the Kondo scattering mechanism is expected to be valid at high temperature ($T > T_{SF}$) in the Kondo-lattice regime. From the present study, the heavy-fermion material is believed to be a Kondo-lattice compound with a relatively strong Ruderman-Kittel-Kasuya-Yosida interaction.

Research on heavy-fermion materials has been an active field for the past few years.[1,2] Because relatively few heavy-fermion metals are known, progress in understanding the origin of the behavior of the heavy-fermion state is still developing. Recently CePtSi was found to be a heavy-fermion and coherent Kondo-lattice compound with a large value of the low-temperature magnetic susceptibility $\chi_m(2.4\ \text{K})=24.9\times10^{-3}$ cm^3/mol and an enormous coefficient of the electronic specific heat $\gamma\sim800$ mJ/mol K^2.[3] This heavy-fermion compound shows neither magnetic order nor superconductivity above 70 mK.[3] In this paper we explore the behavior of the heavy-fermion ternary compound CePtSi by studying the variations of the lattice parameters, magnetic susceptibility, and magnetic contribution to the resistivity in the pseudoternary $Ce(Pt_{1-x}Ni_x)Si$ system. Since Ni has a smaller size than Pt, this pseudoternary system provides an excellent opportunity to investigate the effects of alloying as well as pressure on the heavy-fermion behavior of CePtSi.

CePtSi, as well as CeNiSi, crystallizes in the LaPtSi-type tetragonal structure with space group $I4_1md$.[4] Thus an isostructural pseudoternary series $Ce(Pt_{1-x}Ni_x)Si$ ($0\le x\le1$) can be formed. Samples were synthesized from high-purity elements by arc melting together appropriate amounts of the components on a water-cooled Cu hearth in 1 atm of high-purity argon gas in which a Zr button used as an oxygen getter had been previously arc melted. Due to the sufficiently low vapor pressures of these elements at the melting temperature of the pseudoternary compounds, evaporation losses can be neglected. Each sample was wrapped in tantalum (or molybdenum) foil plus zirconium foil, sealed under argon in a quartz tube and annealed for 4 days at 1200 °C (for Pt-rich compounds) or for 7–10 days at 1000 °C (for Ni-rich compounds). This heat treatment was followed by a water quench to room temperature. Powder x-ray diffraction patterns with Cu $K\alpha$ radiation indicated that each sample was single phase, with no impurity reflections. The lattice parameters of the unit cell were determined by the method of least squares[5] using the eight most intense reflections for $2\theta<55°$ and including an internal silicon standard ($a=0.543083$ nm). The lattice parameters a,c

TABLE I. Lattice parameters, $T_{max}(\chi_m)$, and $T_{max}(\rho_m)$ values in the series $Ce(Pt_{1-x}Ni_x)Si$. The number given in the parentheses is the standard deviation in the least significant digit of the reported value.

Composition (x)	a (nm)	c (nm)	V (nm^3)	$T_{max}(\chi_m)$ (K)	$T_{max}(\rho_m)$ (K)
0.0	0.4202(1)	1.4484(4)	0.2558(1)	a	30
0.1	0.4195(1)	1.4450(5)	0.2543(1)	a	28
0.2	0.4184(1)	1.4398(3)	0.2520(1)	a	40
0.3	0.4178(2)	1.4358(8)	0.2506(2)	35	55
0.4	0.4161(1)	1.4304(3)	0.2476(1)	60	67
0.5	0.4153(1)	1.4271(3)	0.2461(1)	70	75
0.6	0.4137(1)	1.4208(4)	0.2432(1)	120	120
0.7	0.4121(1)	1.4163(2)	0.2406(1)	160	160
0.9	0.4088(1)	1.4080(4)	0.2353(1)	265	265
1.0	0.4067(1)	1.4029(1)	0.2321(1)	320	320

[a]No local maximum was observed above 2.4 K.

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and the unit-cell volume are reported in Table I and are plotted in Fig. 1 as a function of the Ni content accompanied by the data for isostructural $La(Pt_{1-x}Ni_x)Si$ compounds. For $x < 0.5$, the variations of the cell parameters of the compounds $Ce(Pt_{1-x}Ni_x)Si$ follow the same linear decrease as observed for the $La(Pt_{1-x}Ni_x)Si$ compounds. For $x > 0.5$, the parameter a as well as the volume for the compounds $Ce(Pt_{1-x}Ni_x)Si$ decreases faster than that of the $La(Pt_{1-x}Ni_x)Si$ compounds. This is an indication of an intermediate-valence state of cerium in these compounds for $x > 0.5$. In fact, the occurrence of the mixed-valence state of Ce in the compound CeNiSi is also evident in a plot of the cube root of the lattice volume of the compounds RNiSi (R=La, Ce, Pr, Nd) as a function of the ionic radii of the trivalent rare-earth elements.[4,6-8] CeNiSi does not obey a linear relationship in this plot. Because the hypothetical tetravalent lattice constant is unknown, it is difficult to make an estimate of the Ce valence in CeNiSi from these data. The effect of this abnormal decrease in lattice parameter a is readily detected in the low-temperature magnetic susceptibility and resistivity measurements.

Figure 2 presents the temperature dependence of the molar magnetic susceptibility χ_m for ten compounds in the series $Ce(Pt_{1-x}Ni_x)Si$ measured in a field of 2.0 kOe between 2.4 and 300 K (Ref. 9) with a commercial superconducting quantum-interference device (SQUID) magnetometer.[10] The salient feature of the magnetic-susceptibility curves is the presence of one broad peak for each sample with $x > 0.2$. These $T_{max}(\chi_m)$ values are listed in Table I. For $x \leq 0.2$ the peak, which we expect will occur at lower temperatures, is obscured by the rather rapid increase of χ_m at low temperatures. This increase may be due to the increasing strength of the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction at low temperatures because of the tendency to form local moments as x decreases; however, the strength of this interaction is still not sufficient to result in magnetic ordering. In fact, the rather rapid increase in χ_m as T approaches 0 K is a general feature of heavy-fermion systems. This property has been discussed by Gschneidner for the spin-fluctuation compound $CeSn_3$.[11]

dc electrical resistivity measurements were made on rectangular samples of uniform thickness (approximate size $6\times1\times1$ mm^3) using a standard four-probe technique between 2.4 and 300 K. Data were taken with the current applied in each direction to eliminate possible thermal effects. Twenty samples of $La(Pt_{1-x}Ni_x)Si$ and

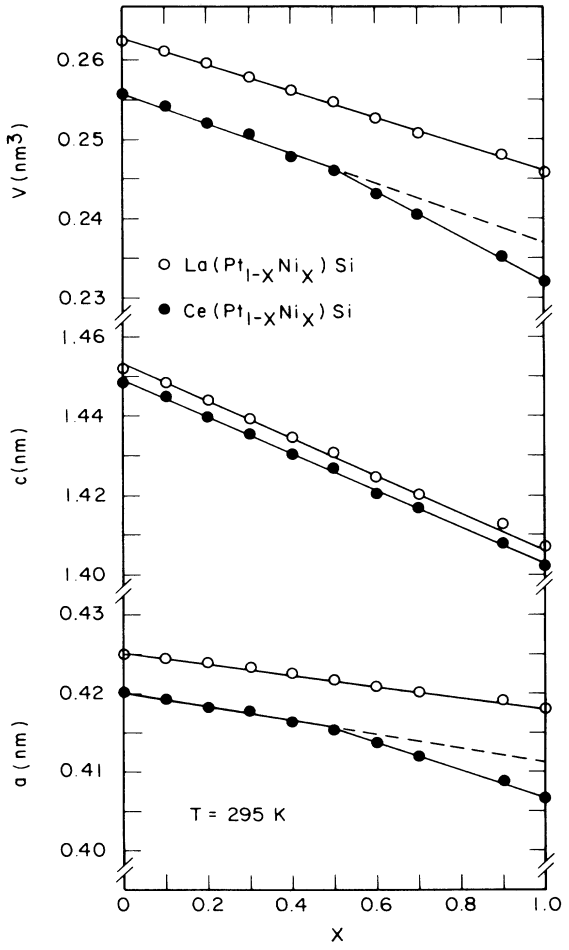

FIG. 1. The room-temperature lattice parameters and unit-cell volume for alloys in the series $Ce(Pt_{1-x}Ni_x)Si$ and $La(Pt_{1-x}Ni_x)Si$.

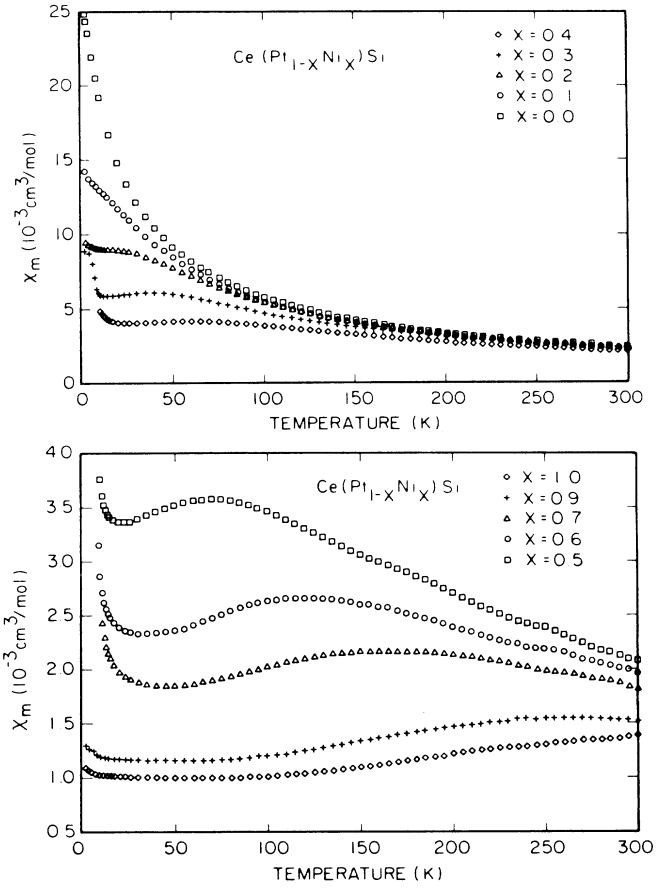

FIG. 2. Molar susceptibility χ_m vs temperature for the ten compounds in the series $Ce(Pt_{1-x}Ni_x)Si$.

$Ce(Pt_{1-x}Ni_x)Si$ have been measured. The La-based compounds were measured in order to estimate the phonon contribution to the resistivities of the Ce-based samples. An interesting phenomenon is that all the La-based compounds in the pseudoternary system are superconducting. Details of these results are in Ref. 12. Since the residual resistivity due to lattice imperfections in the series $Ce(Pt_{1-x}Ni_x)Si$ is very hard to determine because of the existence of Kondo scattering or the disorder in the nonmagnetic sublattice, we assume the residual resistivity is approximately the same in these Ce-based and La-based compounds. The magnetic contribution to the resistivity ρ_m of the $Ce(Pt_{1-x}Ni_x)Si$ compounds was then obtained by subtracting the resistivities of the $La(Pt_{1-x}Ni_x)Si$ compounds. Figure 3 displays the normalized magnetic resistivity versus temperature for the samples $Ce(Pt_{1-x}Ni_x)Si$. The most prominent feature of these magnetic resistivity curves is the presence of a broad peak in each curve. The position of this peak $T_{max}(\rho_m)$ is listed in Table I for each compound.

The characteristic temperatures $T_{max}(\chi_m)$ and $T_{max}(\rho_m)$ represented by the point at which χ_m or ρ_m exhibits a local maximum, are plotted as a function of the lattice parameter a in Fig. 4. As expected from the lattice-parameter data, an obvious kink is observed at the lattice parameter $a=0.4153$ nm (corresponding to $x=0.5$) and $T_{max}=70$ K in Fig. 4. Therefore, we conclude that the system is in a mixed-valence regime when the characteristic temperature $T_{max}(\chi_m)$ or $T_{max}(\rho_m)$ ≥ 70 K or in Kondo-lattice regime when the characteristic temperature is ≤ 70 K. The consistency of this behavior has been pointed out by Brandow.[13] The observed $T_{max}(\chi_m)$ value, which can be treated as a measure of the spin-fluctuation temperature T_{SF} (Refs. 14 and 15), increases as the lattice volume decreases. This is in good agreement with what is generally observed from the relationship between T_{SF} and lattice volume.[16-18] By extrapolation (see Fig. 4) the T_{SF} value of CePtSi can be estimated to be about 6 K. We find this value turns out to be nearly the same as the characteristic temperature found for the nonmagnetic, nonsuperconducting heavy-fermion systems $CeAl_3$, $CeCu_6$, and $CeCu_2Si_2$ by the volume magnetostriction method.[19] Compared to the $T_{max}(\rho_m)$ values obtained from the magnetic-resistivity data, the $T_{max}(\chi_m)$ values obtained from magnetic-susceptibility data are equal to $T_{max}(\rho_m)$ in the mixed-valence regime and are smaller than $T_{max}(\rho_m)$ in the Kondo-lattice regime. This supports the interpretation of the resistivity peak in terms of a spin-scattering mechanism in the mixed-valence regime. In the Kondo-lattice regime, the Kondo scattering mechanism is expected to be valid at high temperature ($T > T_{SF}$). This situation has been observed for $CeAl_3$, another heavy-fermion compound.[14] The low-temperature ρ peak has been assumed to be directly related to the value of the Kondo temperature T_K.[20,21] If this is correct $T_{max}(\chi_m)$ is not a function of T_K alone in the Kondo-lattice regime. It would seem reasonable that in the Kondo-lattice regime both T_K and T_{RKKY} are important in determining the position of $T_{max}(\chi_m)$.

As was previously pointed out,[3] the heat-capacity data of CePtSi could not be fitted to the form $\gamma T+\beta T^3+\delta T^3 \ln T$. The most plausible interpretation would be

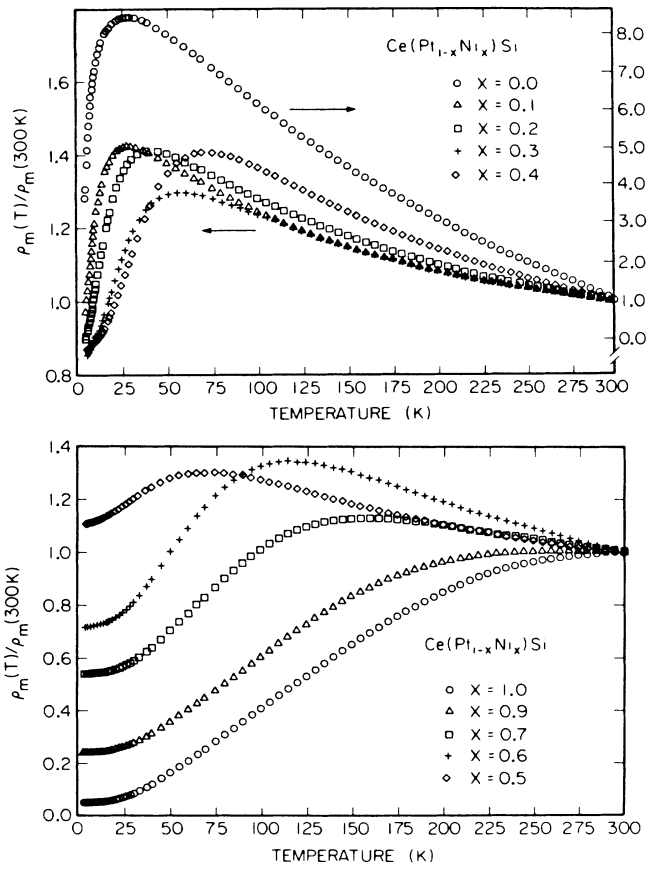

FIG. 3. Magnetic resistivity normalized at 300 K vs temperature for the ten compounds in the series $Ce(Pt_{1-x}Ni_x)Si$.

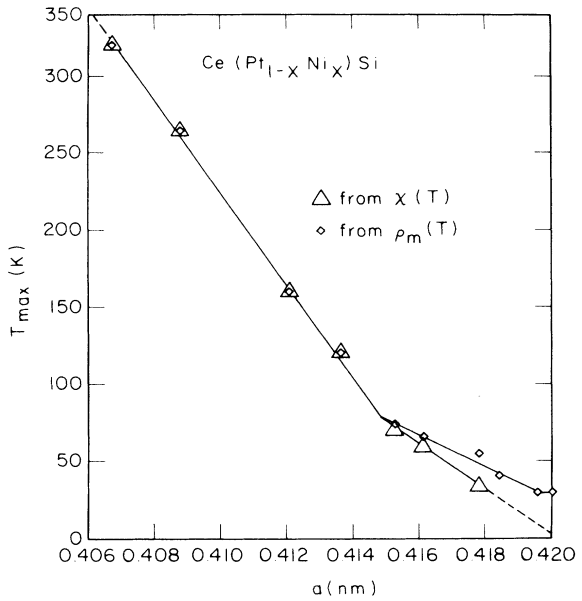

FIG. 4. T_{max} vs lattice parameter a in the series $Ce(Pt_{1-x}Ni_x)Si$.

that since the Ce ions form a periodic array in CePtSi, one must consider the effect of a dense Kondo system in which the spin-fluctuation Kondo effect and RKKY interaction coexist. The importance of this effect is evident in the magnetic-susceptibility data for $x \leq 0.2$ in the series $Ce(Pt_{1-x}Ni_x)Si$ which support the idea that the heavy-fermion CePtSi is a Kondo-lattice system with a relatively strong RKKY interaction. Although not sufficiently strong to result in magnetic ordering, this RKKY interaction can contribute a large amount of heat capacity at low temperatures. For example, in the ferromagnetic dense Kondo compound $CeSi_{1.83}$, the entropy associated with magnetic ordering accounts for only 17% of the total, and the heat-capacity data show a sharp peak.[22] The analysis of the contribution to the heat capacity from the RKKY interaction in the heavy-fermion system CePtSi is in progress.

In conclusion, the evidence for the transition from heavy-fermion behavior to a mixed-valence state has been found consistently in lattice parameters, static magnetic susceptibility, and magnetic resistivity in the series $Ce(Pt_{1-x}Ni_x)Si$. For $x > 0.5$, the compounds are in a mixed-valence regime and the magnetic susceptibility and magnetic resistivity data indicate that spin scattering is the dominant mechanism. For $x < 0.5$, the compounds are in a Kondo-lattice regime with the Kondo scattering mechanism valid at high temperatures ($T > T_{SF}$). Since the spin-fluctuation Kondo effect and RKKY interaction coexist, we do not exclude the possibility that the RKKY interaction can contribute a large amount of heat capacity at low temperatures even though the magnetic moment is unobservably small due to spin fluctuations of the Kondo lattice.

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