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Transition from dense Kondo to the intermediate-valence regime in the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ alloys

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Abstract

Electrical resistivity $\rho(T)$ measurements on polycrystalline samples of the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system exhibit dense Kondo behaviour for alloys with $0 \leq x \leq 0.6$. The temperature at which a maximum appears in $\rho(T)$ shifts from $T_{\text{max}} = 65$ K for $x = 0$ to $T_{\text{max}} = 290$ K for $x = 0.6$ as the system evolves towards the intermediate-valence regime for the CeNi_2Si_2 compound. At low temperatures the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ alloys show a Fermi liquid T^2 contribution to $\rho(T)$ below the coherence temperature T_{coh} . It is observed that $T_{\text{coh}} \approx T_{\text{K}}/(2j+1)$, with a transition that takes place from a dense Kondo regime of $T_{\text{K}} < T_{\text{CF}}$ ($j = \frac{1}{2}$, $E_{\text{R}} \approx E_{\text{F}}$) to a regime of $T_{\text{K}} > T_{\text{CF}}$ ($j = \frac{5}{2}$, $E_{\text{R}} > E_{\text{F}}$). T_{K} ($\propto T_{\text{max}}$) and T_{CF} denote the Kondo and crystalline electric field splitting, E_{F} and E_{R} are the Fermi and the Abrikosov–Suhl resonance energies and j denotes the total angular momentum. An electronic Grüneisen parameter value $\Omega = -\partial(\ln T_{\text{max}})/\partial(\ln V)$ of 19 has been obtained for the alloy system which is in reasonable agreement with $\Omega = 28$ found from pressure studies on CePt_2Si_2 . It is argued that volume effects are mainly responsible for the hybridization in the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system and application of the compressible Kondo lattice model to T_{max} data yields $|JN(E_{\text{F}})| = 0.309 \pm 0.008$, where J is the on-site exchange interaction between conduction electrons and the localized 4f spin and $N(E_{\text{F}})$ is the density of states at E_{F} .

1. Introduction

This study is concerned with electrical transport measurements on the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ alloy system. The low-temperature properties of CePt_2Si_2 have attracted many researchers since it was proclaimed by Gignoux *et al* [1] as a Kondo lattice compound. CePt_2Si_2 crystallizes in a tetragonal structure, but some differences in interpretation exist regarding its appropriate space group, which is indicated to be the $P4/nmm$ CaBe_2Ge_2 type [1–4] or a new CePt_2Si_2 type

structure [5]. The electrical resistivity $\rho(T)$ of polycrystalline CePt_2Si_2 shows a Kondo-like logarithmic increase up to a maximum at $T_{\text{max}} = 76$ K upon cooling and then a steep decrease towards low temperatures [1]. Magnetic susceptibility $\chi(T)$ measurements on polycrystalline CePt_2Si_2 give a normal Curie–Weiss behaviour above 150 K with a large negative paramagnetic Curie temperature ($\theta_p = -86$ K). Upon further cooling a broad maximum in $\chi(T)$ is observed around 60 K and an almost constant value is attained below 20 K [1, 6, 7]. CePt_2Si_2 single crystals exhibit an anisotropy of the magnetization [7] and of $\rho(T)$ [8, 9]. The ratio of specific heat to temperature C/T drops linearly down to 4 K with the electronic specific heat coefficient γ taking a value of 70–86 $\text{mJ K}^{-2} \text{mol}^{-1}$ [1, 6, 10]. Specific heat studies by Ayache *et al* [6] indicate a Kondo temperature $T_K = 70$ K for CePt_2Si_2 , while inelastic neutron scattering measurements indicate $T_K = 170$ K and suggest that CePt_2Si_2 be classified as intermediate between intermediate-valence (IV) and heavy-fermion compounds [11].

The other end compound CeNi_2Si_2 also has a tetragonal structure but of a different type than CePt_2Si_2 , viz it has a ThCr_2Si_2 -type structure [4, 12, 13]. Various studies [14–18] including core-level photoemission spectroscopy [18] and L_{III} absorption spectroscopy measurements [14] indicate that CeNi_2Si_2 is a IV compound. Its valence $v = 3.15$ [14]–3.23 [15] puts it in the class of materials [14] for which local-moment magnetism is absent and for which the presence of both valence states are reflected in its properties. Although the above-mentioned results indicate that CeNi_2Si_2 is a IV compound, resistivity measurements [17, 19] do not show the usual saturation at higher temperatures, which is characteristic for IV compounds. It is noted though that $\rho(T)$ measurements are only reported up to room temperature and hence the expected saturation may occur at higher temperatures.

Previous alloying studies on CePt_2Si_2 comprise a study of $\rho(T)$ of $(\text{Ce}_{1-x}\text{La}_x)\text{Pt}_2\text{Si}_2$ alloys [20] and of $\rho(T)$ and $\chi(T)$ of the $\text{CePt}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ system [21]. In this paper $\rho(T)$ measurements on the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ alloy series ($0 \leq x \leq 1$) are reported. The results show the transition from the dense Kondo-lattice regime to the IV regime.

2. Experimental details

Polycrystalline samples of $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ ($0 \leq x \leq 1$) were prepared by arc-melting stoichiometric amounts of the constituent elements on a water-cooled copper hearth in a high purity argon gas atmosphere. The purities in wt% of the materials used were Ce: 99.98, Pt: 99.97, Ni: 99.99 and Si: 99.999. The ingots were turned over and remelted three times to ensure good homogeneity of the samples. After melting a weight loss of less than 0.5% was observed in all samples.

X-ray powder diffraction measurements on the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ alloys ascertained the phase purity of the samples and the absence of unreacted elements. The lattice parameters a and c of the tetragonal compounds were calculated using standard regression analysis of 22 well-resolved peaks of the powder spectrum of each alloy.

$\rho(T)$ was measured using a standard dc four-probe technique in the temperature range 4.05–300 K on bar-shaped samples cut by spark erosion. Temperatures were measured using a Au–0.07 at.% Fe versus chromel thermocouple with an absolute accuracy of $T \pm 0.5$ K.

3. Results and discussion

3.1. X-ray diffraction analysis

The variation of the tetragonal lattice parameters a and c of the alloy series is shown in figure 1(a). It is observed that the parameter a follows a linear concentration dependence as

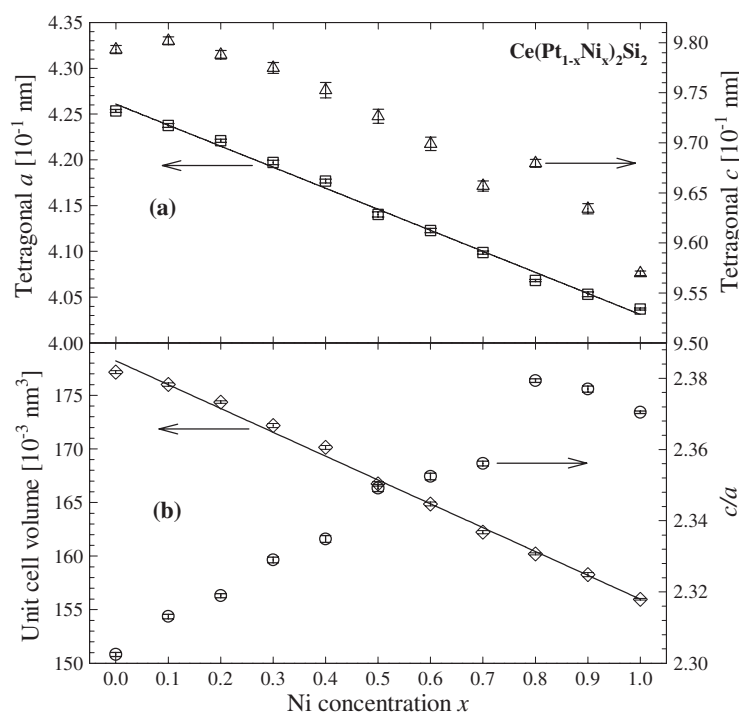


Figure 1. The tetragonal lattice parameters (a) a and c , and (b) the unit cell volume V and the ratio c/a of alloy compositions $0 \leq x \leq 1$ of the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system.

illustrated by the full line, thus following Vegard's rule although the type of tetragonal structure of the two end compounds are different. The effect of the structural differences is more evident on the parameter c and on the ratio c/a which deviates from linearity with x . Substitution of Pt with smaller Ni atoms decreases the parameters a and c , and hence the unit cell volume of the alloy series decreases with the increase in x . The full line in figure 1(b) represents an iterated least-squares fit of the unit cell volume V versus x data and illustrates the validity of Vegard's law for the variation in unit cell volume.

The determined room-temperature tetragonal lattice parameters of CePt_2Si_2 ($a = (4.253 \pm 0.002) \times 10^{-1} \text{ nm}$, $c = (9.793 \pm 0.004) \times 10^{-1} \text{ nm}$) and of CeNi_2Si_2 ($a = (4.037 \pm 0.001) \times 10^{-1} \text{ nm}$, $c = (9.570 \pm 0.002) \times 10^{-1} \text{ nm}$) are in agreement with values from the literature for the CePt_2Si_2 [1–4] and CeNi_2Si_2 [4, 12, 13] compounds.

3.2. Resistivity measurements

The temperature variation of $\rho(T)$ of as-cast samples of the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ alloys is presented in figure 2. Also shown are $\rho(T)$ curves of LaNi_2Si_2 and $\text{La}(\text{Pt}_{0.5}\text{Ni}_{0.5})_2\text{Si}_2$ alloys. The temperature-dependent part of the latter curves represents the approximate phonon contribution for the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ alloy series. In contrast with these two La alloys, $\rho(T)$ of LaPt_2Si_2 exhibits [22] an anomalous bump with a hysteresis at low temperatures and therefore does not constitute an appropriate reference material for the study. The $\rho(T)$ results of the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ alloys show clear evidence of the transition from a dense Kondo to a IV regime. It is observed in figure 2 that the temperature at which a maximum appears in $\rho(T)$, viz T_{max} , shifts to higher temperatures with an increase in x with a value of $T_{\text{max}} = 290 \text{ K}$

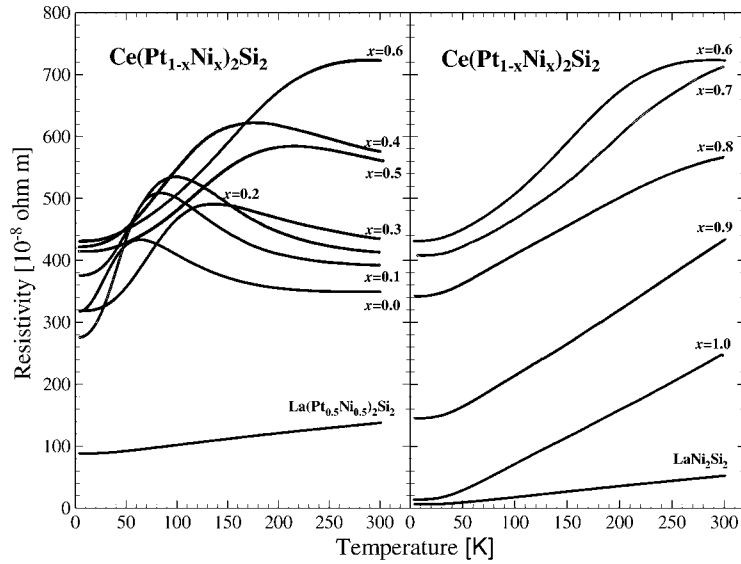


Figure 2. Dependence of the resistivity on temperature for the alloy compositions $0 \leq x \leq 1$ of the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system and for the $\text{La}(\text{Pt}_{0.5}\text{Ni}_{0.5})_2\text{Si}_2$ and LaNi_2Si_2 alloys.

observed for the $x = 0.6$ alloy. The increase of T_{max} with chemical compression of the lattice as x increases is consistent with the compressible Kondo lattice model [23–25], as will be discussed in section 3.2.5.

3.2.1. T^2 contribution to the resistivity. At low temperatures the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ alloys show a T^2 contribution to $\rho(T)$ as shown in figures 3 and 4. This is characteristic of Fermi-liquid behaviour. The temperature from below which a T^2 dependence has been observed for a particular alloy is taken as a measure of the coherence temperature T_{coh} . The Ni concentration dependence of T_{coh} is given in figure 5(a). Iterated least-squares fits to the equation $\rho(T) - \rho_0 = AT^2$ below the temperature T_{coh} give values for A which are depicted in figure 5(b). The full lines in figures 3 and 4 illustrate these fits. It is seen in figure 5(b) that A decreases with the decrease in unit cell volume as x increases, which is consistent with previous observations with hydrostatic pressure on the parent compound CePt_2Si_2 [6]. Values of the residual resistivity $\rho_0(x)$ obtained from the least-squares fits are also plotted in figure 5(b) for alloy compositions $0 \leq x \leq 1$ of the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system. A Nordheim-like contribution to the residual resistivity, $\rho_0 \propto x(x-1)$ [26, 27], is suggested with a maximum around $x = 0.5$. This effect is due to atomic disorder as a result of the presence of two kinds of atoms (Pt and Ni) in the lattice. It is noted that the experimental values of $\rho_0(x)$ in figure 5(b) are not symmetrically disposed around $x = 0.5$ as expected from the Nordheim picture. A possible explanation for this is given in the next section.

It is seen in figures 3 and 4 that $\rho(T)$ deviates noticeably from a T^2 Fermi-liquid behaviour at the lowest temperatures for all $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ alloy compositions. It is found that the power n in the relation $\rho(T) = \rho_0 + AT^n$ for these alloys gradually decreases from 2 and reaches a value of less than 0.5 at 4 K. Such deviations from a Fermi-liquid behaviour have been reported previously for the UCo_2 compound which furthermore shows a shallow minimum, which is believed to be associated with Kondo-like scattering processes [28]. This is attributed to a small concentration of Co atoms on the wrong crystallographic sites, which converts the

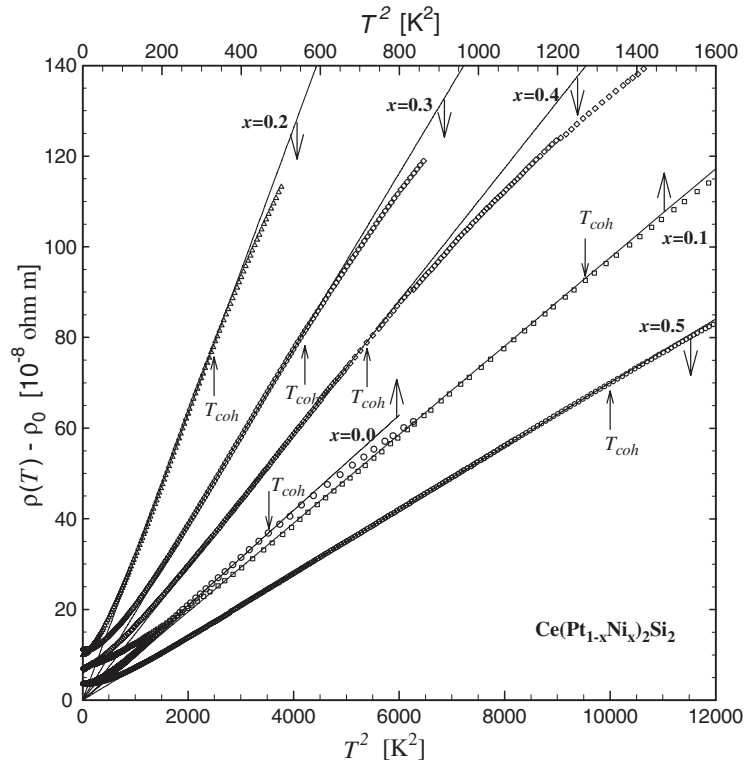


Figure 3. Fermi-liquid behaviour of the resistivity for the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system for Ni concentrations $0 \leq x \leq 0.5$. A deviation from the T^2 dependence is observed at the lowest temperatures.

system to a dilute alloy situation, exhibiting a Kondo-like resistance minimum. It should also be noted that signs of non-Fermi-liquid behaviour have been reported below 4 K on the parent compound CePt_2Si_2 [6, 7, 10].

3.2.2. Influence of crystalline electric fields. Many Kondo properties may be understood as a consequence of the formation of the narrow Abrikosov–Suhl resonance (ASR) [29] in the one-particle density of states near the Fermi level E_F . The position E_R of the ASR relative to the Fermi level E_F depends on the effective total angular momentum j [30]. Based on experimental results of the non-magnetic Kondo lattices CeAl_3 and CeCu_2Si_2 , Brandt and Moshchalkov [29] distinguish two limiting cases $T_K \ll T_{CF}$ and $T_{CF} \ll T_K$ in concentrated Kondo systems (CKS) which would determine the effective j of the 4f shell. T_{CF} indicates the overall crystalline electric field (CEF) splitting of the individual eigenstates j_z ($j_z = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}$ in the case of non-cubic symmetry) in the crystal field environment of a lattice. For CEF splitting $T_{CF} \ll T_K$ the total j contributes to the process of ASR formation, and in Ce-based CKS with $j = \frac{5}{2} > \frac{1}{2}$ one may expect that the ASR will be situated slightly above the Fermi level ($E_R > E_F$). On the other hand, in Ce-based CKS with $T_K \ll T_{CF}$, only the lowest crystal field split states (i.e. $j = \frac{1}{2}$) participate at low temperatures ($T < T_K$) instead of $j(\text{Ce}) = \frac{5}{2}$, and the ASR is formed exactly at Fermi level ($E_R = E_F$) [29]. Chemical pressure studies on $\text{Ce}(\text{Cu}_{1-x}\text{Ni}_x)_2\text{Si}_2$ [16, 31, 32] as well as hydrostatic pressure studies on CeCu_2Si_2 [33] not only support such a claim of $j = \frac{1}{2}$ for CeCu_2Si_2 , but also show evidence of a transition

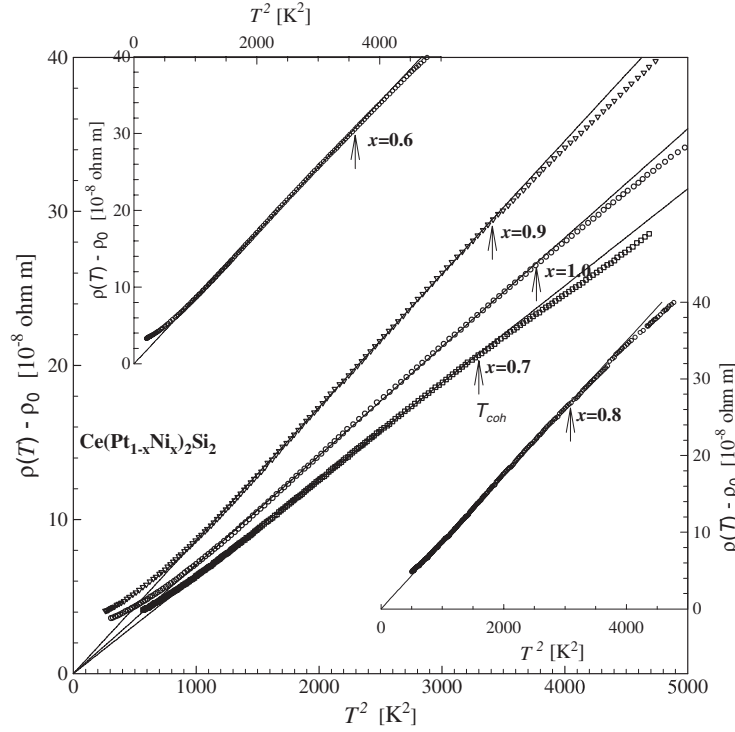


Figure 4. Fermi-liquid behaviour of the resistivity for the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system for Ni concentrations $0.6 \leq x \leq 1$. A deviation from the T^2 dependence is observed at the lowest temperatures.

from a regime of ' $j = \frac{1}{2}$ ' with $T_K < T_{CF}$ (in Cu-rich alloys of $\text{Ce}(\text{Cu}_{1-x}\text{Ni}_x)_2\text{Si}_2$ and at lower pressures in CeCu_2Si_2) to a regime of ' $j = \frac{5}{2}$ ' with $T_K > T_{CF}$ (in Ni-rich alloys of $\text{Ce}(\text{Cu}_{1-x}\text{Ni}_x)_2\text{Si}_2$ and at higher pressure in CeCu_2Si_2).

In the case of the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ alloys in the tetragonal symmetry, the six-fold-degenerate ground multiplet $^2F_{5/2}$ ($j = \frac{5}{2}$) of the Ce^{3+} ions is split into three doublets $\pm\frac{1}{2}$, $\pm\frac{3}{2}$ and $\pm\frac{5}{2}$ by the CEF. The two CEF schemes $\pm\frac{3}{2}$ and $\pm\frac{5}{2}$ of the CePt_2Si_2 compound is approximately at $\Delta_{CF1} = 80$ K and $\Delta_{CF2} = 230$ K from the ground state doublet [6, 7]. The overall crystal field splitting in the CePt_2Si_2 compound is reported to be $T_{CF} \approx 100$ K [34]. Low temperature specific heat and susceptibility measurements suggest that $T_K \approx 42-47$ K [1] for CePt_2Si_2 while specific heat measurements of Ayache *et al* [6] suggest $T_K \approx 70$ K for this compound. Hence for the CePt_2Si_2 compound $T_K < T_{CF}$ and therefore only the lowest doublet may effectively operate ($j = \frac{1}{2}$) at low temperatures ($T < T_K$) for which the ASR is expected to be positioned near the Fermi level ($E_R \approx E_F$).

Theoretical work of Coleman [35] shows that there is a subtlety connected with the Kondo lattice that does not arise for the impurity problem, and it provides a link between the Kondo-lattice and the Anderson-lattice models. He shows that both the coherent and the single-ion states may be described by a single energy scale $T_{coh} \approx T_K/N$, where $N = 2j + 1$ is the ground-state degeneracy. This relation, together with the above discussion, give an insight into the observed variation in T_{coh} against x (i.e. the drop in T_{coh} for $x > 0.5$) as shown in figure 5(a). Figure 6 illustrates the correlation between T_{coh} and T_K/N values for this system. Firstly it is shown for alloy compositions $0 \leq x \leq 0.5$ that, if we assume $T_K \approx T_{max}$ [24]

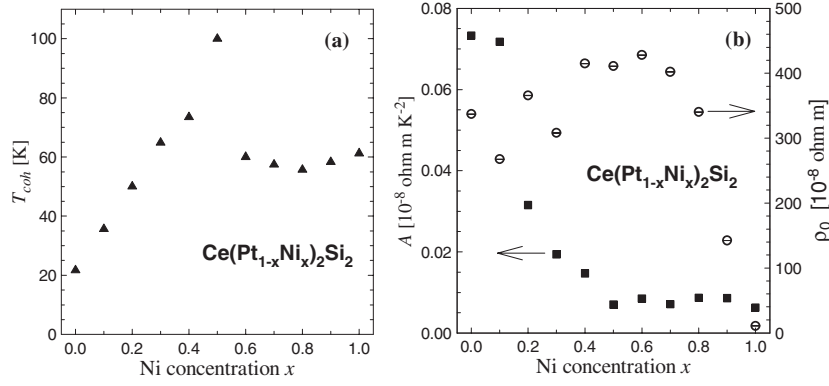


Figure 5. Concentration dependence of (a) the coherence temperature T_{coh} , (b) the T^2 coefficient A and the residual resistivity ρ_0 for the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system with $0 \leq x \leq 1$.

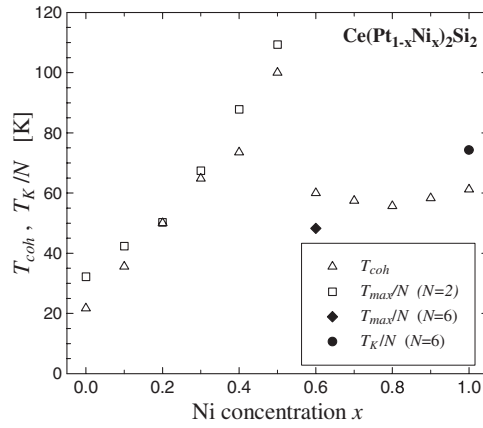


Figure 6. Plot to illustrate the relationship $T_{\text{coh}} \sim T_{\text{K}}/N$ for the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system. T_{max} and T_{coh} are experimentally measured values from figures 2–4, respectively. T_{K} of CeNi_2Si_2 is from [32] and [36].

and $N = 2$ (i.e. $j = \frac{1}{2}$), then an excellent agreement between the observed values of T_{coh} and T_{max}/N is obtained.

The large drop in T_{coh} between $x = 0.5$ and 0.6 is considered to be associated with a transition from a regime with $j = \frac{1}{2}$ ($N = 2$) for $0 \leq x \leq 0.5$ to a regime with $j = \frac{5}{2}$ ($N = 6$) for $0.6 \leq x \leq 1$ in the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system. It is seen in figure 6 that our observed values of T_{max}/N and T_{K}/N using $T_{\text{K}} \approx 440\text{--}450$ K [32, 36] are in reasonable agreement with our observed T_{coh} values for alloy compositions $0.6 \leq x \leq 1$. Hence with the increase in Ni concentration x in the series $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ one could anticipate a shift in the position of the ASR from the Fermi level ($E_{\text{R}} \approx E_{\text{F}}$) to $E_{\text{R}} > E_{\text{F}}$ as the system evolves from $T_{\text{K}} < T_{\text{CF}}$ for $x = 0$ to $T_{\text{K}} > T_{\text{CF}}$ for $x = 1$. The variation of residual resistivity $\rho(0)$ in figure 5(b) may be accounted for by the relation $\rho(0) \propto \sin^2(\pi n_{\text{f}}/(2j+1))$ [37–39]. If only the Nordheim-like contribution $\rho_0 \propto x(x-1)$ [26, 27] is effective, the $\rho_0(x)$ variation should be symmetric around $x \approx 0.5$. The unsymmetrical rapid drop of $\rho(0)$ for $x > 0.6$ may be ascribed to a change in j from $\frac{1}{2}$ to $\frac{5}{2}$, as well as a decrease in f-electron occupation n_{f} which becomes less than unity [18] as the system evolves from a dense Kondo regime with a Ce valence $v \approx 3$ for $x = 0$ [14] to an intermediate valence regime with $v \approx 3.15$ [14]– 3.23 [15] for $x = 1$. Extensive evidence

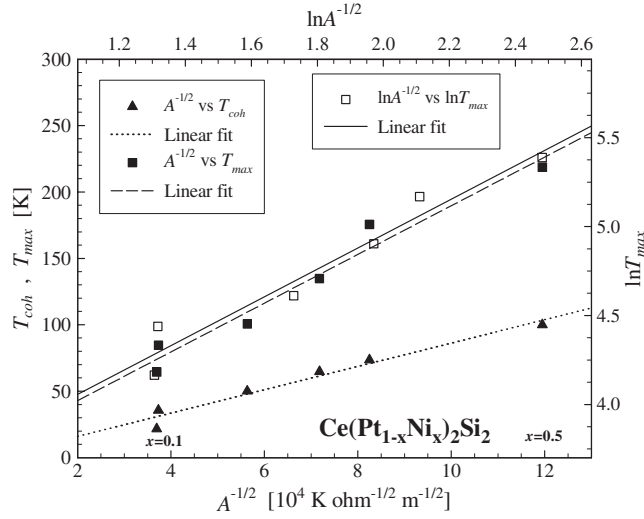


Figure 7. Plot of T_{\max} and T_{coh} against $A^{-\frac{1}{2}}$ for alloy compositions $0 \leq x \leq 0.5$ of the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system. The linear fits shown by dotted and broken lines illustrate the proportionality $A^{-\frac{1}{2}} \propto T_{\text{coh}} \propto T_{\max}$. The full line is a least-squares fit to the plot $\ln T_{\max}$ against $\ln A^{-\frac{1}{2}}$ for these alloys.

of such a transition (i.e. a change in j , v and n_f) from the heavy fermion state to a IV regime has been reported under chemical pressure in the $\text{Ce}(\text{Cu}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system [16, 31, 32] and under hydrostatic pressure for the CeCu_2Si_2 alloy [33].

It follows that increasing the Ni concentration in the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system not only induces a Kondo lattice–IV state transition, but also results in a transition from a low T_K ($< T_{\text{CF}}$), ‘ $j = \frac{1}{2}(E_R \approx E_F)$ ’ regime to a high T_K ($> T_{\text{CF}}$), ‘ $j = \frac{5}{2}(E_R > E_F)$ ’ state.

3.2.3. Scaling between Fermi liquid and Kondo parameters. For alloy compositions $0 \leq x \leq 0.5$ of $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ which are believed to be in the low T_K ($< T_{\text{CF}}$), ‘ $j = \frac{1}{2}(E_R \approx E_F)$ ’ Kondo lattice regime, the proportionality $A^{-\frac{1}{2}} \propto T_{\max} \propto T_{\text{coh}}$ is evident in figure 7. This result is in accordance with the universal scaling relation in heavy-fermion systems obtained from pressure studies in the Fermi-liquid region above the quantum critical point, which implies a simple one-parameter scaling such that $\psi_0^{-1} \propto \gamma^{-1} \propto A^{-\frac{1}{2}} \propto T_{\text{coh}}$, where ψ_0 is the uniform susceptibility and γ characterizes the electronic contribution to the specific heat [40]. The relation $A^{-\frac{1}{2}} \propto T_{\max}$ is observed experimentally in pressure studies both in Ce-based [41–44] and Yb-based [45] compounds. Theoretical studies by Yoshimori and Kasai [46] also show evidence for such a relationship while Cox and Grewe [47] show that $A = 10$ (unitary limit)/ T_K^2 . Figure 7 also depicts the logarithmic derivative $\partial(\ln T_{\max})/\partial(\ln A^{-\frac{1}{2}})$ as 0.97, which is very close to unity. This confirms the relations $\gamma \propto \sqrt{A}$ [48] and $T_K \propto T_{\max}$ [24, 46] because $\gamma_0 = C/T|_{T=0} = 0.68R/T_K$ [49, 50], where C and R are the specific heat and gas constant, respectively.

3.2.4. Grüneisen parameter. In substitution studies of Kondo systems one is generally concerned with the corresponding change in a Kondo parameter like T_K . An often considered cause for a change in T_K in alloy systems is the positive or negative chemical pressure due to the changed inter-atomic spacing due to alloying and this may be described by the compressible Kondo lattice model [23–25]. Experimentally one may consider the variation of

$T_{\max} \approx T_K$ [24] upon substitution. Another cause for change in T_K and other parameters in the case of La substitutions is the Kondo hole (dilution) effect [51–58] whereby the coherence is also destroyed. For La compounds this leads to an additional cause of decreasing T_K with increasing La content over and above the decrease in T_K expected due to negative pressure. It is even possible that ligand substitutions may destroy coherence [59] and furthermore it may influence the hybridization in Kondo systems. However, since the 4f sublattice is not disturbed by Ni substitution and furthermore the energies of the Ni 3d⁸ and Pt 5d⁸ electron bands are far removed from that of the Ce 4f¹ band [60], one could expect that such hybridization effects are of lesser importance. On the other hand, Schilling [61] argues that in heavy-fermion compounds T_K may deviate from the proportionality with T_{\max} when T_K and T_{RKKY} become comparable to each other. Such an argument is based on theoretical work on spin glasses by Larsen [62] who shows the complicated behaviour of T_{\max} quantitatively. From this study the determining factor for the behaviour of T_{\max} in a particular alloy series turns out to be the relative magnitudes of the RKKY and Kondo interactions. In the case of the Ce(Pt_{1-x}Ni_x)₂Si₂ series, it is clear that the alloys evolve towards the IV regime with the increase in x , and hence the increase in T_K . Consequently the system moves further away from the region of influence of the RKKY interaction, and therefore the predicted proportionality $T_K \propto T_{\max}$ [24, 46], which is based on the Kondo effect alone, should be valid. Thus, taking $T_K \propto T_{\max}$ for the Ce(Pt_{1-x}Ni_x)₂Si₂ alloy series the electronic Grüneisen parameter may be written as $\Omega = -\partial(\ln T_{\max})/\partial(\ln V)$ [63, 64]. A plot of $\ln T_{\max}$ and $\ln A^{-\frac{1}{2}}$ against $\ln V$ for alloy compositions $0 \leq x \leq 0.6$ of the Ce(Pt_{1-x}Ni_x)₂Si₂ system is shown in figure 8, where the values of unit cell volume V used are obtained from the iterated least-squares fit in figure 1.

A straight line fits the $\ln T_{\max}$ versus $\ln V$ data well and shows that the gradient $d(\ln T_{\max})/d(\ln V)$ at all points is the same, suggesting that the Grüneisen parameter remains constant through the series for $0 \leq x \leq 0.6$ with the value $\Omega = 18.9 \pm 0.7$. An estimate from the variation of the resistivity T_{\max} under hydrostatic pressure on the CePt₂Si₂ compound gives $\Omega = 28$ [64], which is in reasonable agreement with the value estimated for the system Ce(Pt_{1-x}Ni_x)₂Si₂. For the (Ce_{1-x}La_x)₂Si₂ series on the other hand we found $\Omega = 126$ which we ascribed to the combined effect of volume and Kondo holes [22]. For the Ce(Pt_{1-x}Ni_x)₂Si₂ system it seems that the volume effect dominates.

A similar estimate for Ω can be obtained with the relation $\Omega = -\partial(\ln A^{-\frac{1}{2}})/\partial(\ln V)$ [64] (see also section 3.2.3). The iterated linear fit that is shown by the broken line in figure 8 gives the Grüneisen parameter value $\Omega = 16.8 \pm 0.9$. This is in good agreement with the value determined from T_{\max} . Considering the bulk modulus for CePt₂Si₂ to be 1.0 Mbar [64], we calculate $\partial A^{-\frac{1}{2}}/\partial P \approx 0.13 \times 10^{-4} \text{ K } \Omega^{-\frac{1}{2}} \text{ m}^{-\frac{1}{2}} \text{ kbar}^{-1}$ for $x = 0$ using the volume dependence of compositions $0 \leq x \leq 0.6$. This is in reasonable agreement with the reported value $\partial A^{-\frac{1}{2}}/\partial P = 0.18 \times 10^{-4} \text{ K } \Omega^{-\frac{1}{2}} \text{ m}^{-\frac{1}{2}} \text{ kbar}^{-1}$ found from pressure studies on the CePt₂Si₂ parent compound [64]. This observation also suggests that the volume effect is mainly responsible for the variation of A which is in agreement with what is indicated by the electronic Grüneisen parameters for the Ce(Pt_{1-x}Ni_x)₂Si₂ system.

3.2.5. Compressible Kondo lattice model. The Kondo temperature is exponentially proportional to the on-site exchange interaction J between conduction electrons and the localized 4f spin and the density of states $N(E_F)$ at the Fermi level, $T_K \propto \exp(-1/|JN(E_F)|)$. The volume dependence of $|JN(E_F)|$ is described by the compressible Kondo lattice model [23, 25] as

$$|JN(E_F)| = |JN(E_F)|_0 \exp\left[\frac{-q(V - V_0)}{V_0}\right], \quad (1)$$

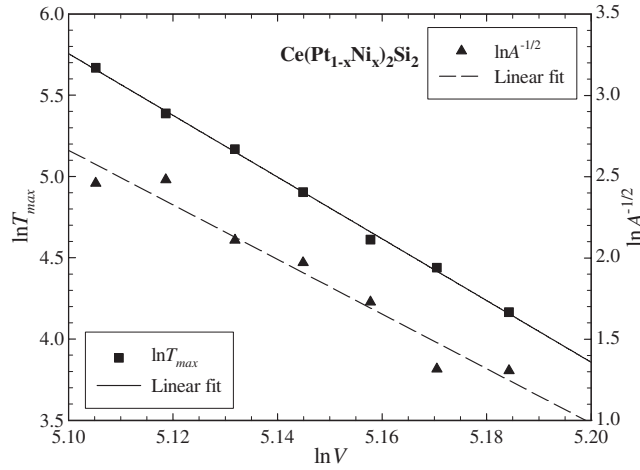


Figure 8. Plot of $\ln T_{\max}$ and $\ln A^{-\frac{1}{2}}$ against $\ln V$ for alloy compositions $0 \leq x \leq 0.6$ of the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system.

where $|JN(E_F)|_0$ indicates the value of the quantity at initial volume V_0 and q refers to the Grüneisen parameter of $|JN(E_F)|$ (i.e. $q = -\partial \ln |JN(E_F)| / \partial \ln V$) [45] and is considered to vary between 6 and 8 [23, 25, 43–45]. Using the relation $T_{\max} \propto T_K \propto \exp(-1/|JN(E_F)|)$, the volume dependence of T_{\max} may be described by

$$T_{\max}(V_x) = T_{\max}(V_{x=0}) \exp\left[\frac{-q(V_x - V_{x=0})}{|JN(E_F)|_{x=0} V_{x=0}}\right] \quad (2)$$

as a function of Ni concentration x as done in many such studies in the literature [21, 43–45]. Moreover, theoretical [40, 46, 47] and experimental [41–44] studies in the literature as well as our results show that $T_K \propto T_{\max} \propto A^{-\frac{1}{2}} \propto T_{\text{coh}}$. Hence equation (2) can be written as [44, 45]

$$-\frac{1}{2} \ln \left[\frac{A(V_x)}{A(V_{x=0})} \right] = \ln \left[\frac{T_{\text{coh}}(V_x)}{T_{\text{coh}}(V_{x=0})} \right] = \frac{-q}{|JN(E_F)|_{x=0}} \frac{(V_x - V_{x=0})}{V_{x=0}}. \quad (3)$$

We apply (2) and (3) to the experimental results of the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system. Since Vegard's rule holds for the variation of volume for this system, the values for volume V obtained by the iterated fit shown in figure 1 have been used in constructing a plot of $\ln[T_{\max}(V_x)/T_{\max}(V_{x=0})]$, $-\frac{1}{2} \ln[A(V_x)/A(V_{x=0})]$ and $\ln[T_{\text{coh}}(V_x)/T_{\text{coh}}(V_{x=0})]$ against $(V_x - V_{x=0})/V_{x=0}$ for the alloy series $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$, as shown in figure 9. The straight lines show the least-squares fits of the data to (2) and (3). As discussed in section 3.2.4, one may anticipate mainly the volume (pressure) effect influencing the hybridization in the $\text{Ce}(\text{Pt}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system and hence, as done in many hydrostatic pressure studies [43–45, 65, 66], a value of 6 is used for q . Hence the full line fit to the $\ln[T_{\max}(V_x)/T_{\max}(V_{x=0})]$ data points in figure 10 gives the value $|JN(E_F)|_{x=0} = 0.309 \pm 0.008$, and the broken and dotted line fits of the data points $-\frac{1}{2} \ln[A(V)/A(V_0)]$ and $\ln[T_{\text{coh}}(V)/T_{\text{coh}}(V_0)]$, respectively, give $|JN(E_F)|_{x=0} = 0.35 \pm 0.02$ and $|JN(E_F)|_{x=0} = 0.23 \pm 0.01$.

It is seen that the $|JN(E_F)|$ values 0.31, 0.35 and 0.23 deduced for the parent compound CePt_2Si_2 from the variation of T_{\max} , $A^{-\frac{1}{2}}$ and T_{coh} , respectively, are of the same order of magnitude. However, the value 0.31 may be regarded as more reliable because the data points of $A^{-\frac{1}{2}}$ and T_{coh} in figure 9 show a significantly larger spread than that of T_{\max} . It is noted that there may be an uncertainty associated with the absolute value of $A^{-\frac{1}{2}}$ because of the possible

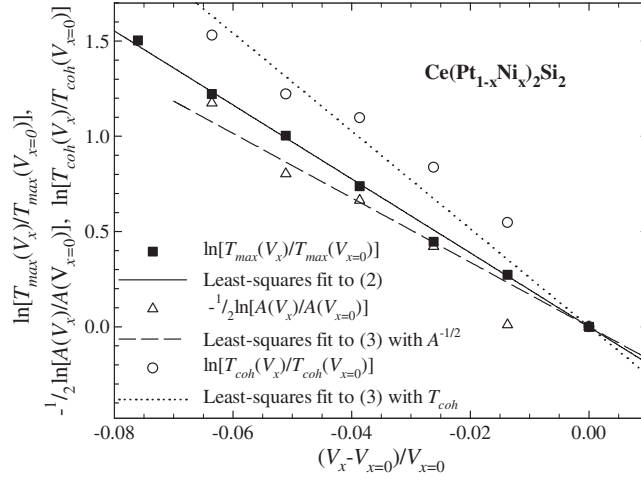


Figure 9. Least-squares fits to the plots of $\ln[T_{\max}(V_x)/T_{\max}(V_{x=0})]$ (for $0 \leq x \leq 0.6$), $-\frac{1}{2} \ln[A(V_x)/A(V_{x=0})]$ (for $0 \leq x \leq 0.5$) and $\ln[T_{\text{coh}}(V_x)/T_{\text{coh}}(V_{x=0})]$ (for $0 \leq x \leq 0.5$) against $(V_x - V_{x=0})/V_{x=0}$ for the Ce(Pt_{1-x}Ni_x)₂Si₂ system.

influence of micro-cracks in the samples and furthermore finding T_{coh} from figures 3 and 4 has a larger error than finding T_{\max} .

Considering the value $|JN(E_F)|_{x=0} = 0.31$ deduced from T_{\max} , $|JN(E_F)|$ values for the complete Ce(Pt_{1-x}Ni_x)₂Si₂ series ($0 \leq x \leq 1$) have been calculated using equation (1) and these values are used to construct the Doniach diagram shown in figure 10. The position of the resistivity peak T_{\max} of alloy compositions $0 \leq x \leq 0.6$ of the Ce(Pt_{1-x}Ni_x)₂Si₂ system have been used as the Kondo energy scale. The Kondo temperature T_K of CeNi₂Si₂ is taken from the literature [32, 36]. The $|JN(E_F)|$ values reported by similar studies in the literature using the variation of T_{\max} under hydrostatic pressure on compounds CeInCu₂ [65], CeCu₆ [66], YbCu₄Ag [45] and Ce₇Ni₃ [44] are also included in figure 10 for comparison. The dotted exponential curve in figure 10 shows the least-squares fit to the relation [67]

$$T_K \propto T_{\max} = D|JN(E_F)|^{1/2} \exp(-1/|JN(E_F)|) \quad (4)$$

for the $|JN(E_F)|$ and T_{\max} values of dense Kondo alloys ($0 \leq x \leq 0.6$) of the Ce(Pt_{1-x}Ni_x)₂Si₂ system (obtained from alloying) and CeInCu₂, CeCu₆, YbCu₄Ag and Ce₇Ni₃ (obtained from hydrostatic pressure). This fit gives the proportionality constant $D = (3.04 \pm 0.09) \times 10^3$ K. It is seen that the order of magnitude of $|JN(E_F)|$ values derived for the Ce(Pt_{1-x}Ni_x)₂Si₂ system show fair agreement with the values obtained independently from previous pressure work on other dense Kondo compounds.

4. Conclusion

Resistivity measurements on the Ce(Pt_{1-x}Ni_x)₂Si₂ system show a transition from dense Kondo behaviour to intermediate valence type behaviour with an increase in Ni concentration x . The unit cell volume decreases with increasing x and hence the hybridization increases, thereby increasing the Kondo energy scale ($\sim T_{\max}$). The validity of the theoretical results connecting the coherent and the single-ion states by a single energy scale $T_{\text{coh}} \approx T_K/(2j+1)$ is evident in the Ce(Pt_{1-x}Ni_x)₂Si₂ system, which suggests a transition from a dense Kondo regime of $T_K < T_{\text{CF}}$ ($j = \frac{1}{2}$, $E_R \approx E_F$) to a regime of $T_K > T_{\text{CF}}$ ($j = \frac{5}{2}$, $E_R > E_F$).

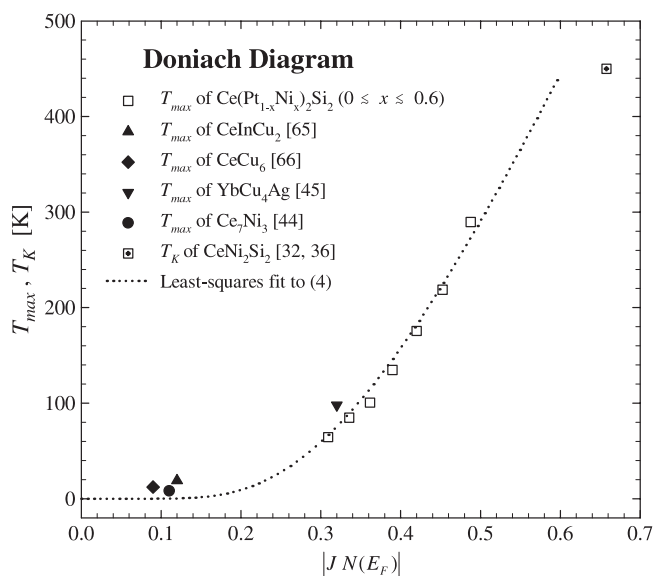


Figure 10. The Doniach diagram constructed for the $Ce(Pt_{1-x}Ni_x)_2Si_2$ system and compared with $|JN(E_F)|$ values of $CeInCu_2$ [65], $CeCu_6$ [66], $YbCu_4Ag$ [45] and Ce_7Ni_3 [44] compounds reported from hydrostatic pressure studies. The dotted curve shows the least-squares fit to (4).

The universal relation $A^{-\frac{1}{2}} \propto T_{max} \propto T_{coh}$ for pressure studies is obeyed in compositions $0 \leq x \leq 0.5$ of the $Ce(Pt_{1-x}Ni_x)_2Si_2$ system, which is presumably in the $j = \frac{1}{2}$ regime. Comparison of the electronic Grüneisen parameter values obtained by atomic substitutions in the $Ce(Pt_{1-x}Ni_x)_2Si_2$ system and pressure studies on the $CePt_2Si_2$ compound suggests that the volume effect is mainly responsible for the hybridization in the $Ce(Pt_{1-x}Ni_x)_2Si_2$ system. Hence, application of the compressible Kondo lattice model for the alloy compositions $0 \leq x \leq 0.6$ of the $Ce(Pt_{1-x}Ni_x)_2Si_2$ system yields $|JN(E_F)|_{x=0} = 0.309 \pm 0.008$. This value is consistent with $|JN(E_F)|$ values obtained in the context of the compressible Kondo lattice model from hydrostatic pressure studies on $CeInCu_2$, $CeCu_6$, $YbCu_4Ag$ and Ce_7Ni_3 .

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