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Effects of La dilution on the $CeNiAl_4$ Kondo lattice

A. Kowalczyk, M. Falkowski*, T. Toliński

Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179 Poznań, Poland

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ABSTRACT

We carried out the magnetic, electrical resistivity and heat capacity measurements for the $Ce_{1-x}La_xNiAl_4$ compounds. The values of the effective paramagnetic moment μ_{eff} were calculated from the Curie–Weiss constant. For all the solid solutions under study the μ_{eff} values are very close to $2.54\mu_B$ found for cerium in the pure Ce metal. Resistivity studies on the $Ce_{1-x}La_xNiAl_4$ alloy system illustrate the transition from the Kondo regime ($x = 0.0$) to the single-ion Kondo regime ($0.05 \leq x \leq 0.8$). The substitution of Ce by La reduces the electronic heat capacity coefficient γ values from 154 mJ/mol K^2 for $CeNiAl_4$ to 4.8 mJ/mol K^2 for $LaNiAl_4$. At low temperatures γ value depends strongly on the temperature range used for the extrapolation.

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1. Introduction

The anomalous nature of *f* electrons in the compounds and alloys of lanthanides is affected not only by the distance between the atoms, but also by the electronic structure of the neighbors. A strong interaction between the 4*f* electrons and conduction electrons is competitive for both intra-atomic (correlation effects) and inter-atomic interactions. These impacts lead to the emergence of such phenomena as the Kondo effect, heavy fermions, mixed valence, spin fluctuations and unusual magnetic orderings. The occurrence of these phenomena depends primarily on the location of the level of 4*f* electrons relative to the Fermi level, hence it is important to know the band structure of the compound. In contrast to the well-localized 4*f* electrons of heavy rare earths, in the Ce compounds a high degree of hybridization with the conduction electrons occurs, which can cause delocalization of the 4*f* states. Depending on the strength of the hybridization and the position of the 4*f* level in respect to the Fermi level, these compounds may exhibit a different type of properties.

Previously, $CeNiAl_4$ was reported to crystallize in the orthorhombic $YNiAl_4$-type structure (space group *Cmcm*) and to exhibit properties typical of a Kondo lattice or heavy fermion system [1–4]. The magnetic susceptibility that follows the Curie–Weiss law in the range 30–250 K suggests a localized 4*f* electron character [3]. The electrical resistivity $\rho(T)$ shows a Kondo-like logarithmic increase down to a maximum at $T = 100$ K and then a steep decrease towards low temperature. This behaviour indicates that the resistivity is caused by the Kondo effect [3]. The thermoelectric power (TEP) of $CeNiAl_4$ is positive over the whole temperature range. The electrical resistivity and thermopower data are characteristic of the Kondo lattice. The thermoelectric measurements allowed us to locate the 4*f* peak slightly above the Fermi level. The TEP and magnetic measurements provide Kondo temperature $T_K = 40$ K and 33 K, respectively, in good agreement with that deduced from the C_p data (37 K). A large electronic specific heat coefficient $\gamma = 154$ mJ/mol K^2 is observed at minimum of the C_p/T vs. T^2 dependence. Extrapolation of the lowest temperatures range of $C_p/T(T^2)$ yields the γ value of 0.5 J/mol K^2. In combination with the thermoelectric power and resistivity data, a heavy fermion state is confirmed in $CeNiAl_4$. Recently the effect of Y dilution in $CeNiAl_4$ was also investigated [5].

The present paper concerns on the properties of the $Ce_{1-x}La_xNiAl_4$ system studied by the magnetic susceptibility, electrical resistivity and specific heat measurements.

2. Experimental

The $Ce_{1-x}La_xNiAl_4$ compounds were prepared by induction melting of the stoichiometric amounts of the constituent elements in a water-cooled boat, under an argon atmosphere. The ingot was inverted and remelted several times to ensure homogeneity. The unit cell volume V for $Ce_{1-x}La_xNiAl_4$ increases with increasing the La concentration.

Heat capacity measurements were performed by PPMS commercial device (Quantum Design) in the temperature range 1.9–300 K by relaxation method using the two-τ model. The magnetic susceptibility and the magnetization curves were measured also on the PPMS system. The electrical resistivity was measured on a bar-shaped sample using a standard four-probe technique.

* Corresponding author. Tel.: +48 61 8695 129; fax: +48 61 8684 524.
E-mail address: falkowski@ifmpan.poznan.pl (M. Falkowski).

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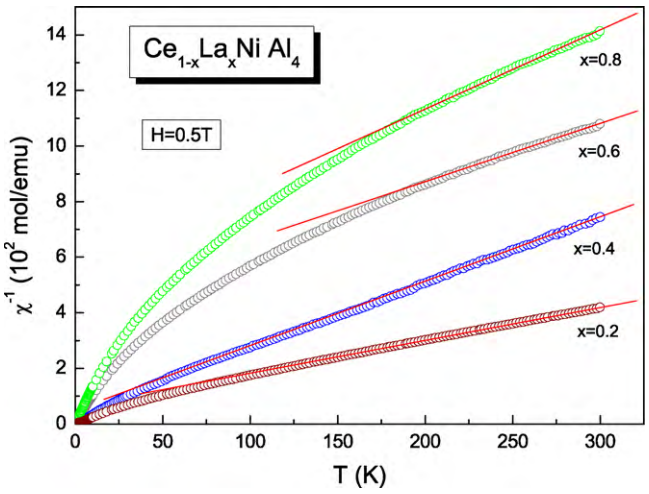

Fig. 1. Inverse magnetic susceptibility $\chi^{-1}(T)$ of the $Ce_{1-x}La_xNiAl_4$ compounds.

3. Results and discussion

Fig. 1 shows the temperature dependence of the inverse magnetic susceptibility $\chi^{-1}(T)$ for various compositions of $Ce_{1-x}La_xNiAl_4$ measured in an applied field of 0.5 T. Typically, the susceptibility of cerium compounds in the paramagnetic region follows the Curie–Weiss behavior $\chi(T) = C/(T - \theta_p)$. Here C is the effective Curie constant of the Ce ions and θ_p is the paramagnetic Curie temperature. The resulting values of μ_{eff} and $-\theta_p$ are given in Table 1. For $CeNiAl_4$ above about 30 K, $\chi^{-1}(T)$ follows the Curie–Weiss law with the effective magnetic moment $\mu_{eff} = 2.45\mu_B$/f.u. and the paramagnetic Curie temperature $\theta_p = -66$ K [4]. For all the solid solutions under study the μ_{eff} values calculated from the Curie–Weiss constant are very close to the value of $2.54\mu_B$ found for cerium in the pure Ce metal. Values of the paramagnetic Curie temperatures θ_p vary in an irregular manner across the alloy series. This anomalous result is likely due to different degrees of preferred crystalline orientation in the different alloy samples. However, the general tendency is that θ_p increases with x, which results from the transition to the single-ion Kondo regime for $x > 0.0$. For many cerium compounds, substitution of Ce by La leads to a decrease of both the Kondo temperature (due to the lattice expansion) and the magnetic transition temperature (due to the dilution), which in turn can lower the overall value of θ_p. Large negative values of paramagnetic Curie temperature indicates on the existence of a strong negative interaction between the 4*f* spins of electrons and the conduction electrons. The slight deviation of μ_{eff} from the free Ce^{3+} value is ascribed to the effect of crystal electric field (CEF).

Since $CeNiAl_4$ is a Kondo lattice (as inferred from the thermal variation of its resistivity, discussed below) there is a contribution to negative θ_p from the Kondo interaction.

The magnetic field dependence of magnetization of $Ce_{0.2}La_{0.8}NiAl_4$ and $Ce_{0.8}La_{0.2}NiAl_4$ for different temperatures is presented in Fig. 2a and b. The temperature evolution of these curves confirms the absence of magnetic ordering down to 2 K.

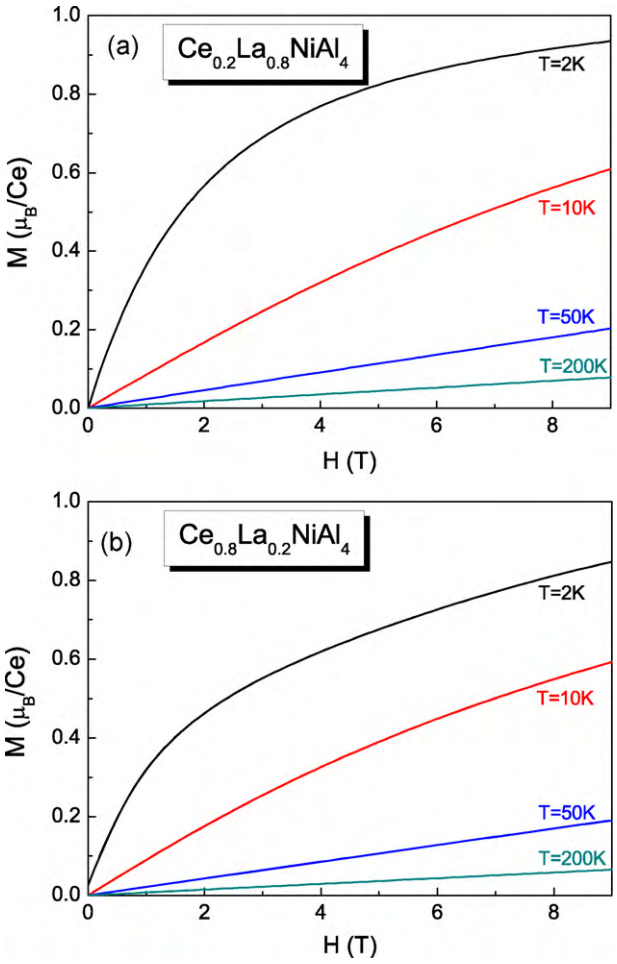

Fig. 2. The magnetic field dependence of magnetization for $Ce_{0.2}La_{0.8}NiAl_4$ and $Ce_{0.8}La_{0.2}NiAl_4$ at different temperatures.

The isothermal magnetization per Ce ion of selected $Ce_{1-x}La_xNiAl_4$ at 2 K, measured up to 9 T is shown in Fig. 3. At $T = 2$ K and at the maximum applied field of 9 T, the magnetization M decreases marginally from $0.93\mu_B$/f.u. for $Ce_{0.2}La_{0.8}NiAl_4$ to $0.84\mu_B$/f.u. for $Ce_{0.8}La_{0.2}NiAl_4$. Saturation moments at $H = 9$ T are much smaller than the theoretical values calculated for the free Ce^{3+} ion. The effect can be attributed to the important role of crystal electric fields.

The $\rho(T)$ measurements as a function of temperature for the $Ce_{1-x}La_xNiAl_4$ compounds are shown in Fig. 4, which illustrates a transition from the Kondo dense regime ($x = 0.0$), through the single-ion Kondo regime ($x \geq 0.05$), to the metallic behavior ($x = 1.0$). The $\rho(T)$ for the parent compound $CeNiAl_4$ shows a Kondo-like logarithmic increase down to a maximum at $T_{max} = 100$ K and then a steep decrease towards low temperatures. In the dense

Table 1
The Weiss constants θ_p and the effective magnetic moment μ_{eff} obtained by fits of the Curie–Weiss relation to the data in Fig. 1. Values of A and c_K are extracted from fits with Eq. (1) shown by solid line in Fig. 5. These results correspond to measurements for x changing by 0.2 for $Ce_{1-x}La_xNiAl_4$.

x	θ_p (K)	μ_{eff} (μ_B/f.u.)	Fitted range (K)	A ($\mu\Omega$ cm)	c_K ($\mu\Omega$ cm)	γ (mJ/mol K^2)
0.0	−66	2.45	30–250	400.6	61	154
0.2	−48	2.61	70–300	37.4	1.8	52
0.4	−35	2.58	50–300	40.4	1.5	22
0.6	−171	2.46	150–300	42.9	2.0	12
0.8	−184	2.42	170–300	33.2	1.4	8

Values of θ_p and μ_{eff} for $CeNiAl_4$ are taken from Ref. [4].

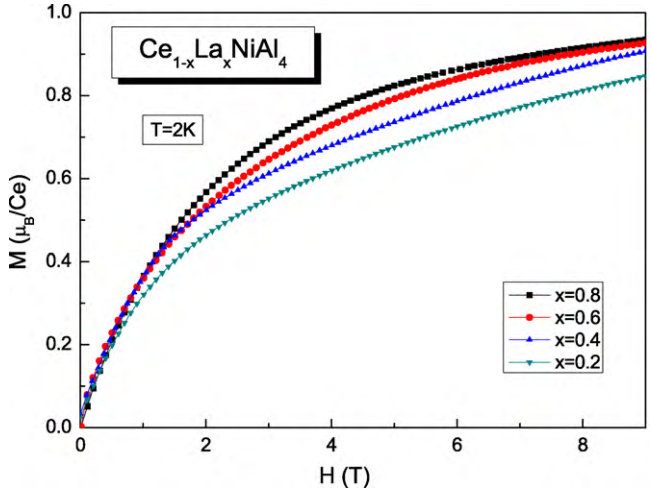

Fig. 3. The isothermal magnetization per Ce ion for $Ce_{1-x}La_xNiAl_4$ alloys at 2 K.

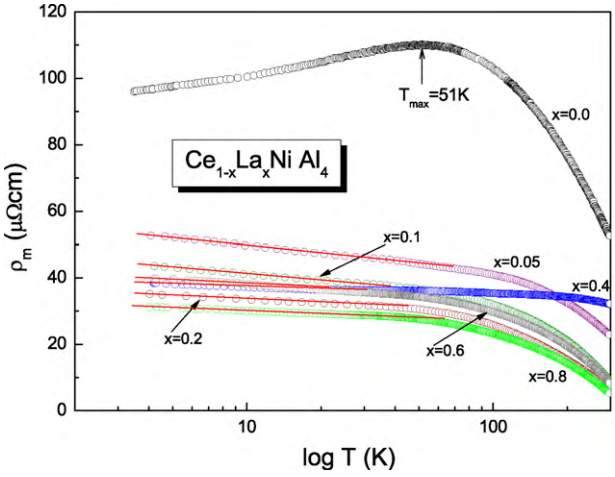

Fig. 5. Temperature dependence of the magnetic contribution $\rho_m(T)$ to the electrical resistivity of $Ce_{1-x}La_xNiAl_4$.

Kondo regime, single-ion Kondo scattering dominates at higher temperatures and $\rho(T)$ curves initially display a logarithmic upturn upon cooling. Subsequently $\rho(T)$ goes through a maximum at temperature T_{max} as a result of coherence effects. The linear region at low temperatures ($T < 20$ K) may reflect a non-Fermi liquid behavior, which has also been deduced from electron resonance studies [6]. For larger value of x a peak was not observed in the temperature range of our investigations. In fact the $\rho(T)$ behavior for the alloys with $x \geq 0.05$ resembles rather a single-ion Kondo behavior. For the La substituted samples the resistivity $\rho(T)$ passes through a Kondo minimum around 25 K, followed by a logarithmic increase at lower temperatures. $LaNiAl_4$ exhibits normal metallic behavior with a residual resistivity of 25 μΩ cm [3]. A completely different behavior occurs in the $Ce_{1-x}Y_xNiAl_4$ compounds [5]. This follows from the fact that the atomic radius of cerium is bigger than the radius of yttrium. As a consequence, unit cell volume V decreases, which moves the maximum in the resistivity towards higher temperatures. This behavior is consistent with the compressible Kondo lattice (CKL) model [7–9]. For $Ce_{1-x}Y_xNiAl_4$ system the crossover from the Kondo dense regime to the single-ion Kondo behavior was observed for $x \geq 0.6$ [5].The critical concentration of the Kondo lattice system over which we observe the coherence effect depends on the concentration of f-moments $(1 - x)$ and the number of the delocalized electrons per unit cell [10–14]. Such a critical concentration is connected with a change in the f-electron density of states from a two-peak density distribution for the coherent state to a single-peak density distribution for the incoherent state [10,11].

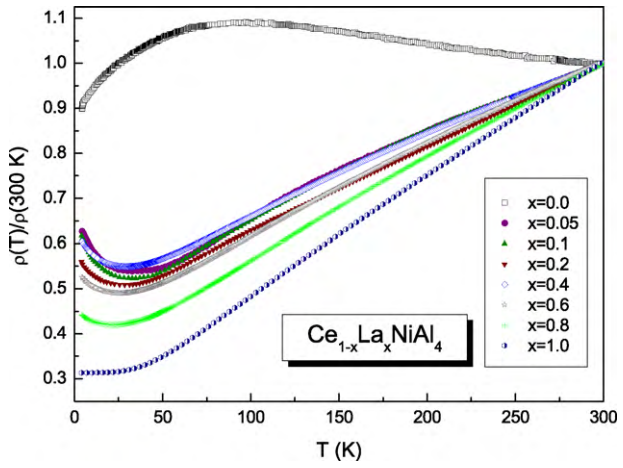

Fig. 4. Plot of $\rho(T)/\rho(300\,K)$ vs. temperature illustrating the evolution from the Kondo lattice regime, through the single-ion Kondo regime to the metallic behaviour.

The magnetic contribution $\rho_m(T)$ to the resistivity is obtained by subtracting the phonon resistivity as given by experimental resistivity results for the $LaNiAl_4$ compound $\rho_m(T) = \rho[CeNiAl_4(T)] - \{\rho[LaNiAl_4(T)] - \rho[LaNiAl_4(T = 0)]\}$. The magnetic resistivity for compositions $0.0 \leq x \leq 1.0$ of the $Ce_{1-x}La_xNiAl_4$ system is shown in Fig. 5 for the whole temperature range studied.

All the solid solutions for $0.05 \leq x \leq 0.8$ exhibit a logarithmic increase in $\rho_m(T)$ at low temperatures (Fig. 5) as expected for the single-ion Kondo systems. This is shown by the solid line least-squares fits of the equation:

$$\rho_m(T) = A - c_K \ln T \quad (1)$$

to the experimental data. A coefficient A obtained from the fits includes in addition to a temperature independent Kondo contribution that due to defects. This parameter is different for each of the samples. Values A and c_K are given in Table 1.

The analysis of magnetic resistivity revealed that only $CeNiAl_4$ shows clearly a maximum ($T_{max} = 50$ K) typical of the Kondo lattice with the logarithmic dependence above it. The $\ln T$ dependence in $\rho_m(T)$ is due to the scattering processes of the conduction electrons with independent Kondo centers and is one of the characteristic features of the Kondo lattice systems. For all other compounds a change in the slope visible at higher temperatures is rather due to the variation in the Mott KT^3 and the phonon contributions.

Fig. 6 presents the temperature dependence of the specific heat of the $Ce_{1-x}La_xNiAl_4$ compounds. As expected, there is no evidence for magnetic ordering in the studied temperature range. However, due to the anomalous behavior at low temperatures the γ value depends strongly on the temperature range used for the extrapolation. To consider the low temperature range we take just the value at the minimum, which provides $\gamma \sim 154$ mJ/mol K^2 for $CeNiAl_4$ [4]. The present results confirm that this compound is a heavy fermion. The value of the electronic specific heat coefficient leads to a value of the Kondo temperature $T_K = 37$ K using the relation $T_K = (0.68 \times R/\gamma)$. Thus, there are no differences in the value of T_K estimated from different definitions. The corresponding value of γ for $LaNiAl_4$ is 4.8 mJ/mol K^2 [4]. Now, turning to the influence of La substitution on the heavy fermion behaviour, it is found that γ decreases with increasing dilution of the Ce sublattice (see inset in Fig. 6 and Table 1).

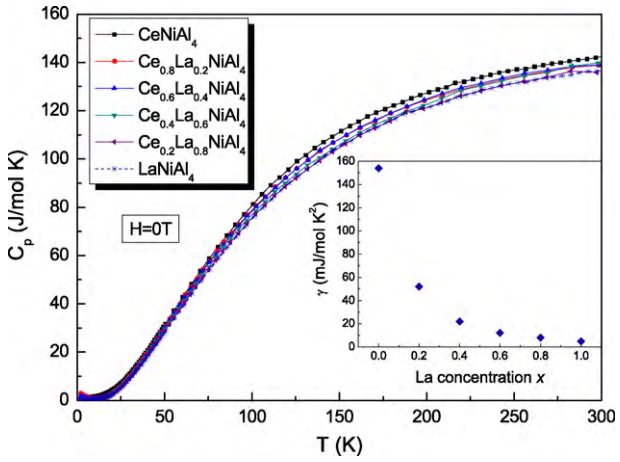

Fig. 6. Temperature dependence of the specific heat of selected $Ce_{1-x}La_xNiAl_4$ compounds. Inset: the electronic specific heat coefficient γ for $Ce_{1-x}La_xNiAl_4$.

4. Conclusions

The results of magnetic susceptibility, heat capacity and electrical resistivity measurements for the pseudo-ternary solid solutions $Ce_{1-x}La_xNiAl_4$ have been presented and show a strong dependence on x. The experimental value of μ_{eff} is close to a free Ce^{3+} ion value of $2.54\mu_B$ indicating the presence of well localized magnetic moments. At low temperatures the $\chi^{-1}(T)$ curve deviates from the straight-line behaviour, which is due to the effects of the crystal electric field.

The $\rho(T)$ measurements as a function of temperature illustrate a transition from the Kondo dense regime ($x = 0.0$) through the single-ion Kondo regime ($0.05 \leq x \leq 0.8$) to the metallic behavior ($x = 1.0$). While the $LaNiAl_4$ reference sample exhibits a typical metallic Bloch-Grüneisen behavior, $CeNiAl_4$ represents a classical Kondo lattice. All the alloys for $0.05 \leq x \leq 0.8$ exhibit a logarithmic increase in $\rho_m(T)$ at low temperatures as expected for the single-ion Kondo systems.

At low temperatures the electronic heat capacity coefficient γ value depends strongly on the temperature range used for the extrapolation. In comparison with $CeNiAl_4$ the substitution of Ce by La reduces the γ values from 154 mJ/mol K^2 for $CeNiAl_4$ to 4.8 mJ/mol K^2 for $LaNiAl_4$.

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