A new Kondo antiferromagnet Ce(Ni$_{0.25}$In$_{1.75}$)

H H Sung[1], H H Wu[1], K J Syu[1], W H Lee[1,3] and Y Y Chen[2]

[1] Department of Physics, National Chung Cheng University, Ming-Hsiung, Chia-Yi 621,
Taiwan, Republic of China
[2] Institute of Physics, Academia Sinica, Taipei 115, Taiwan, Republic of China

E-mail: whlee@phy.ccu.edu.tw

Abstract
We find that Ce(Ni$_{0.25}$In$_{1.75}$) crystallizes in the hexagonal AlB$_2$-type structure with lattice
parameters $a = 0.4850(5)$ nm and $c = 0.3908(5)$ nm. Magnetic susceptibility, electrical
resistivity and low-temperature specific heat data reveal that the bulk phase transition at
3.7 ± 0.2 K in Ce(Ni$_{0.25}$In$_{1.75}$) is to an antiferromagnetic state. The magnetic contribution to the
resistivity ρ_{mag} of Ce(Ni$_{0.25}$In$_{1.75}$) increases as $\ln(T)$ when temperature is lowered from room
temperature and reaches a plateau at 9 K, followed by a rapid decrease around 4 K. These
results associated with a reduction of the Ce magnetic moment and of the magnetic entropy at
T_N suggest that Ce(Ni$_{0.25}$In$_{1.75}$) could be a Kondo antiferromagnet. The Kondo temperature is
estimated to be of order 6 K.

(Some figures in this article are in colour only in the electronic version)

The low-temperature electronic, magnetic, and thermal
properties of dense Kondo systems have attracted much
interest during the past decades [1, 2]. In the course of
our search for new materials compounds, we have found that
Ce(Ni$_{0.25}$In$_{1.75}$) displays properties of both antiferromagnetic
ordering and dense Kondo systems. In this paper, we
report the crystal structure, the temperature dependence of the
magnetic susceptibility, electrical resistivity and heat capacity
of Ce(Ni$_{0.25}$In$_{1.75}$). As determined from ac susceptibility,
electrical resistivity and heat capacity measurements, the
compound Ce(Ni$_{0.25}$In$_{1.75}$) exhibits antiferromagnetic order
below 3.7 ± 0.2 K. In addition to experiments on
Ce(Ni$_{0.25}$In$_{1.75}$), electrical resistivity and heat capacity
measurements on the isostructural La(Ni$_{0.25}$In$_{1.75}$) have been
made in order to estimate the phonon contribution to the
resistivity and heat capacity of Ce(Ni$_{0.25}$In$_{1.75}$).

Polycrystalline samples investigated for this work were
synthesized by arc melting together stoichiometric amounts
of the constituent elements on a water-cooled Cu hearth
in 1 atm of ultrahigh-purity argon gas in which a Zr
button used as an oxygen getter had been previously arc
melted. The 3N purity rare-earth elements, 4N purity
nickel (Ni) and 5N purity indium (In) were purchased from
Alfa Aesar, a Johnson Matthey company. Weight losses
during arc melting were less than 0.2%. To ensure that no
impurity phase was present in the sample, each sample was
wrapped in tantalum foil, sealed under argon in a quartz
tube and annealed for four weeks at $590 \pm 20\,^\circ$C. This
heat treatment was followed by a water quench to room
temperature. Analysis of powder x-ray diffraction patterns
indicates that the samples crystallize in a hexagonal AlB$_2$-
type structure [3] with space group $P6/mmm$. No traces
of secondary phase were observed, as shown in figure 1.
One formula unit of Ce(Ni$_{0.25}$In$_{1.75}$) (or LaNi$_{0.25}$In$_{1.75}$) is
present in the unit cell. The crystallographic parameters were
determined by using the PowderCell program [4]. The lattice
parameters $a = 0.4850(5)$ nm, $c = 0.3908(5)$ nm for
Ce(Ni$_{0.25}$In$_{1.75}$) and $a = 0.4850(2)$ nm, $c = 0.3963(8)$ nm
for La(Ni$_{0.25}$In$_{1.75}$) were then obtained. In this refinement
to determine lattice parameters, only the positions of the x-
ray lines were required. A comparison of the calculated
line intensities with those established experimentally showed
reasonable agreement, especially considering the nature of
powder x-ray data for a quantitative determination of line
intensities. In this likeness, we used standard atomic positional
parameters for the atoms in the unit cell. Specifically, the rare-
earth atom was placed in the la position while the atoms Ni and
In were randomly located in the 2d position of the space group
$P6/mmm$ (D$_{6h}^1$) with the following fractional coordinates:
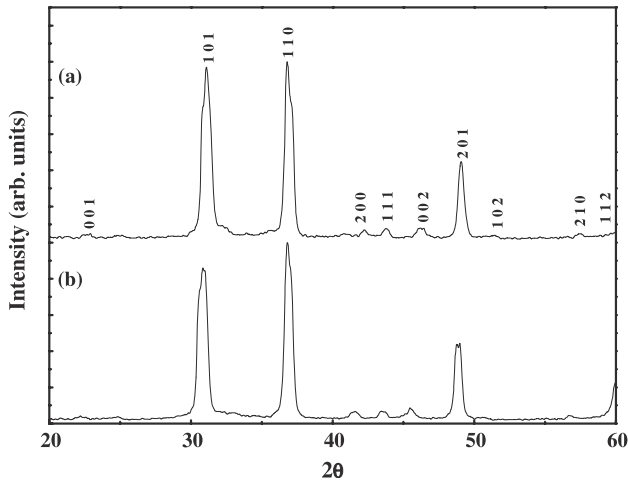
Figure 1. Room-temperature powder x-ray diffraction patterns of (a) Ce(Ni$_{0.25}$In$_{1.75}$) and (b) La(Ni$_{0.25}$In$_{1.75}$).
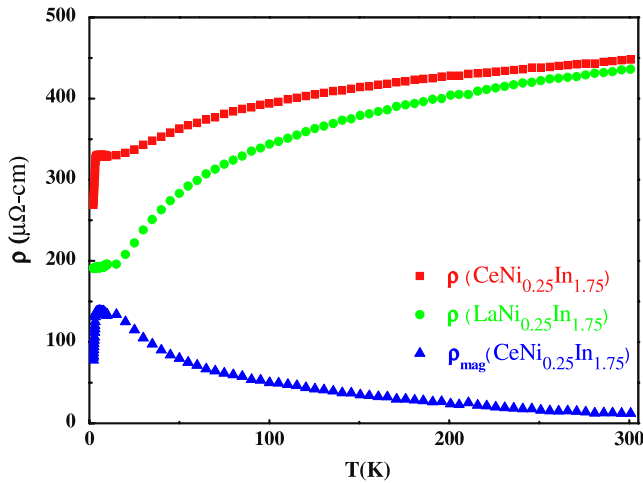
Figure 2. Resistivity versus temperature of Ce(Ni$_{0.25}$In$_{1.75}$), La(Ni$_{0.25}$In$_{1.75}$), and the difference between these two compounds from 1.8 to 300 K.
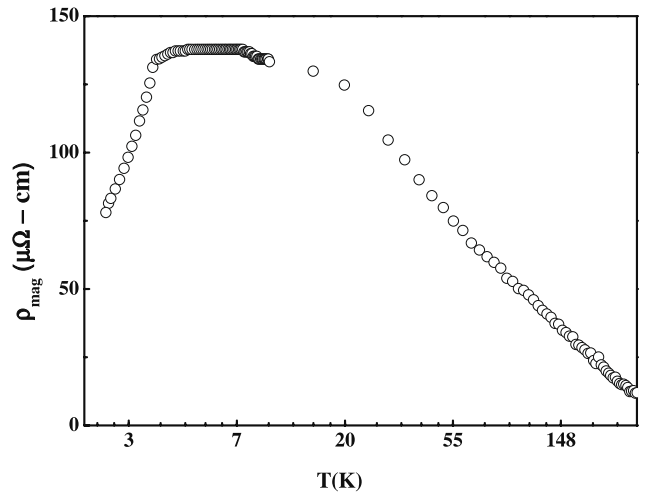
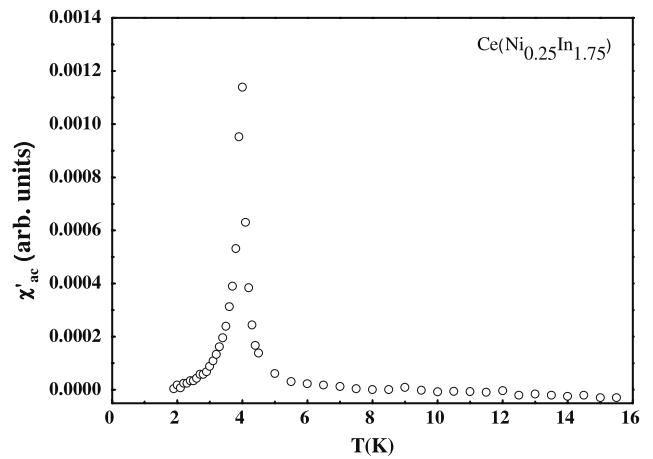**Figure 3.** Magnetic resistivity ρ_{mag} versus ln(T) of Ce(Ni$_{0.25}$In$_{1.75}$) between 1.8 and 300 K.

Figure 4. The temperature dependence of the real component of ac susceptibility for Ce(Ni$_{0.25}$In$_{1.75}$) in a driving field of 1.0 G at 1000 Hz.

Ce or La (0, 0, 0), 1/8 Ni and 7/8 In (1/3, 2/3, 1/2). The agreement of intensities indicates that no significant vacancy is present in our samples. Very interestingly, neither CeNi$_2$ (Cu$_2$Mg type) [5] nor CeIn$_2$ (CeCu$_2$ type) [6] is the parent compound of Ce(Ni$_{0.25}$In$_{1.75}$).

Dc electrical resistivity measurements were made between 1.8 and 300 K using a standard four-probe technique in a system fully automated for temperature stability and data acquisition [7]. Figure 2 displays the temperature dependence of the resistivity of Ce(Ni$_{0.25}$In$_{1.75}$), La(Ni$_{0.25}$In$_{1.75}$), and the magnetic resistivity ρ_{mag} of Ce(Ni$_{0.25}$In$_{1.75}$). The magnetic resistivity was estimated by subtracting the resistivity of isostructural La(Ni$_{0.25}$In$_{1.75}$) from that of Ce(Ni$_{0.25}$In$_{1.75}$). The data for ρ_{mag} are replotted as a function of ln(T) in figure 3. It is seen that the curve in figure 3 shows a logarithmic increase with decreasing temperature in the high-temperature region and reaches a plateau around 9 K. The ln(T) dependence in ρ_{mag} is due to the scattering processes of the conduction electrons with independent Kondo centers and is one of the

characteristic features of dense Kondo systems. Upon further cooling, ρ_{mag} decreases rapidly below ∼4 K. This decrease of ρ_{mag} may be ascribed to both the onset of coherence between Kondo states at Ce sites and the magnetic ordering, because the rapid decrease of ρ_{mag} commences near the Néel temperature T_N as determined from the ac susceptibility and the specific heat data. We must point out here that the overall $\rho_{mag}(T)$ of Ce(Ni$_{0.25}$In$_{1.75}$) is reminiscent of that of CeCu$_{1.54}$Si$_{1.46}$ [8]. However, the compound CeCu$_{1.54}$Si$_{1.46}$ has larger residual magnetic resistivity (∼150 $\mu\Omega$ cm below 3 K), because of the disorder in the Cu and Si sublattice, which weakens the coherence between Kondo states, and behaves as an incoherent Kondo system even at low temperatures.

Figure 4 presents the real part of ac susceptibility χ'_{ac} for the compound Ce(Ni$_{0.25}$In$_{1.75}$) measured in a driving field of 1.0 Oe and at a frequency 1000 Hz between 1.8 and 16 K with a commercial SQUID magnetometer. A very sharp transition from nonmagnetic to magnetic ordering is seen at 3.9 K (peak value). The data curve of the imaginary part
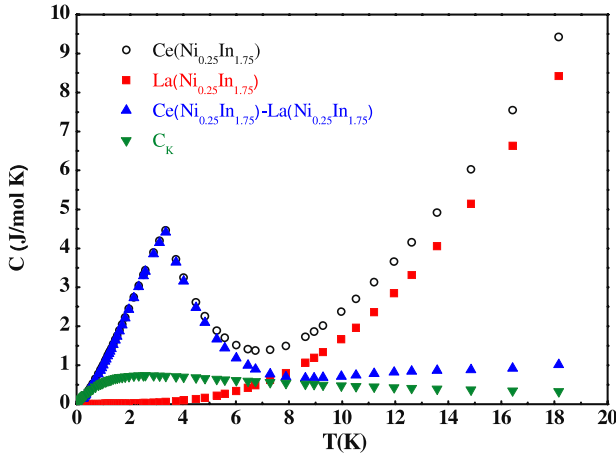
Figure 5. Heat capacity of Ce(Ni$_{0.25}$In$_{1.75}$), La(Ni$_{0.25}$In$_{1.75}$), the difference between these two compounds C_{mag} and the Kondo model fit C_K between 0.35 and 20 K. The data curve for the sample Ce(Ni$_{0.25}$In$_{1.75}$) shows a rather broad λ type of antiferromagnetic ordering peak centering at 3.6 K and a minimum around 7 K. It is implied that the inhomogeneity of the sample is due to the disordered Ni and In atoms arranged in the 2d position of the space group $P6/mmm$.

Figure 6. Specific heat divided by temperature C/T versus T^2 of Ce(Ni$_{0.25}$In$_{1.75}$) between 0.35 and 20 K; inset, C/T versus T^2 between 0.35 and 5 K.

χ_{ac}'' is not shown here because it has similar shape and its peak occurs at slightly different temperature ($\sim$3.8 K) from that of the real part χ_{ac}'. Since no frequency dependence of the position of the peak value in the $\chi_{ac}'(T)$ or $\chi_{ac}''(T)$ curve is observed, the possibility of spin-glass behavior in this compound Ce(Ni$_{0.25}$In$_{1.75}$) is excluded. In fact, the high-temperature dc magnetic susceptibility data ($T > 100$ K) can be fitted to a linear Curie–Weiss law with an effective moment of 2.6 ± 0.1 μ_B per cerium atom and a paramagnetic Curie temperature -22 K. This value of μ_{eff} is sufficiently close to the free Ce^{3+} ion value to preclude intermediate valence. Earlier experience may tell us that for a compound containing 4f light rare earth and 3d (e.g. Mn, Fe, Co, Ni) intermetallics the spins S couple anti-parallel between S_{3d} and S_{4f}. The magnetic moment, however, depends upon the coupling between S_{3d} and J_{4f}. $J = L - S$ for the light rare earths from Hund's rule and as a result J_{4f} is coupled parallel to S_{3d}. We must point out here that there seems to be not much influence of Ni on total magnetic moment in the compound Ce(Ni$_{0.25}$In$_{1.75}$), probably due to the low Ni concentration ($\sim$8.3 at.%). In fact, the low concentration of Ni in the compound La(Ni$_{0.25}$In$_{1.75}$) also shows neither magnetic order nor superconductivity above 350 mK according to specific heat measurements. It is noted here that for the higher Ni concentration compound Ce(Ni$_{0.5}$In$_{1.5}$) (or Ce$_2$NiIn$_3$) with the same AlB$_2$-type structure [9], spin-glass-like features arise below the freezing temperature $T_{sf} \sim 2.8$ K together with the Kondo and crystal field effects [10].

The low-temperature specific heat measurements were made using a thermal relaxation microcalorimeter. Detailed measurement procedures can be found in [11, 12]. As illustrated in figure 5, the heat capacity versus T data curve for the sample Ce(Ni$_{0.25}$In$_{1.75}$) measured in zero field between 0.35 and 20 K shows a λ type of antiferromagnetic ordering

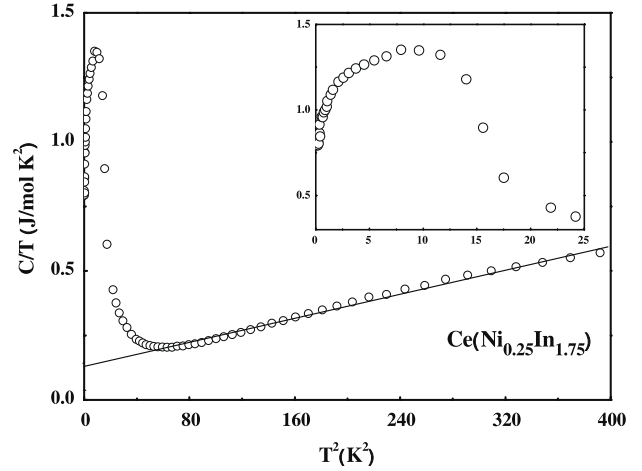peak centering at 3.6 K and a peak value approaching 4.5 J mol^{-1} formula K. The agreement of transition temperatures measured by ac susceptibility and heat capacity techniques are clear evidence of bulk antiferromagnetism in Ce(Ni$_{0.25}$In$_{1.75}$). We note here that the jump in the heat capacity is much smaller than the value 15 J mol^{-1} Ce K as expected on the basis of the mean-field theory. Two factors may affect this large reduction in heat capacity jump at the magnetic transition. One is the inhomogeneity of the sample, which results in a rather broad λ transition, due to the disordered Ni and In atoms arranged in the 2d position of the space group $P6/mmm$, and the other one is attributed to the Kondo effect. A determination of the electronic and lattice heat capacity contributions is complicated by the existence of the antiferromagnetic ordering peak. The specific heat data in the form of C/T versus T^2 for Ce(Ni$_{0.25}$In$_{1.75}$) are plotted in figure 6. It is seen that the heat capacity $C(T)$ of Ce(Ni$_{0.25}$In$_{1.75}$), in the paramagnetic state at temperatures between 8 and 20 K, can be fitted to the expression $C_n = \gamma T + \beta T^3$ by a least squares analysis, which yields a γ value of about 130 mJ mol^{-1} K^{-2} and a β value of about 1.2 mJ mol^{-1} K^{-4} or a Debye temperature $\Theta_D = 170$ K. As was previously pointed out [13], such high γ values, which exceed those of normal metals by nearly two orders of magnitude, are indications of Kondo interactions. Similar γ values have been observed in the Kondo lattice systems CeAl$_2$ [13], CeCuAl$_3$ [14], CeCu$_2$ [15], CeCu$_5$ [16], CePtSi$_2$ [17] etc. Since the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interactions are responsible for long-range magnetic ordering and the Kondo-type interactions favor a nonmagnetic ground state, the sharp drop in the $\rho_{mag}(T)$ curve that marks most of the magnetic order at low temperatures tends to obscure the Kondo maximum when $T_K \sim T_m$. Thus, as shown in figure 3, a rough estimate of Kondo temperature T_K by using the temperature of the maximum [18] in the $\rho_{mag}(T)$ curve should occur between 4 and 9 K for the compound Ce(Ni$_{0.25}$In$_{1.75}$). Another estimation comes from the low-temperature heat capacity data [19, 20]. As depicted in figure 5, we mark the low-temperature magnetic

contribution as $C_{mag} = C_{tot} - C_{ph} - C_{cryst} = C_K + C_{AF}$. The C_{cryst} term can be neglected because no Schottky type anomaly in the specific heat data is seen below 20 K for the compound $Ce(Ni_{0.25}In_{1.75})$. This Kondo model fit leads to $T_K = 6$ K, which is consistent with the estimate based on magnetic resistivity data. Using numerical integration, we estimate the magnetic entropy as a function of temperature from $S_M = \int_0^T (C_{mag}/T) \, dT$. The magnetic entropy $S_M(T_N)$ associated with a modulated magnetic structure for $Ce(Ni_{0.25}In_{1.75})$ is only 62% of $R \ln(2)$, corresponding to a reduction of 38% of the cerium moment. The temperature at which $S_M = R \ln 2$ is 14 K, in good agreement with estimates of the Kondo temperature for this material.

In conclusion, the intermetallic compound $Ce(Ni_{0.25}In_{1.75})$, which crystallizes in the AlB_2-type structure, exhibits antiferromagnetic order below $T = 3.7 \pm 0.2$ K. This compound is found to be a Kondo lattice compound with $T_K \sim 6$ K from the unusual resistivity and specific heat data.

Acknowledgment

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