LOW-TEMPERATURE SPECIFIC HEAT
OF Ce-Ni-Ge COMPOUNDS
AND THEIR NONMAGNETIC ANALOGUES *

A.P. Pikul$^a$, D. Kaczorowski$^a$, H. Michor$^b$, P. Roh$^c$
A. Czopnik$^d$, Yu. Grin$^d$, E. Bauer$^b$ and G. Hilscher$^b$

$^a$Institute of Low Temperature and Structure Research
Polish Academy of Sciences, P.O.Box 1410, 50-950 Wroclaw, Poland
$^b$Institut für Festkörperphysik, Technische Universität Wien
A-1040 Wien, Austria
$^c$Institut für Physikalische Chemie, Universität Wien, A-1090 Wien, Austria
$^d$Max-Planck-Institut für Chemische Physik fester Stoffe
01187 Dresden, Germany

(Received July 10, 2002)

The specific heat of CeNiGe$_3$, Ce$_2$Ni$_3$Ge$_5$, Ce$_3$NiGe$_2$ and Ce$_3$Ni$_2$Ge$_7$
and their isostructural analogues with La or Y was studied in the temperature range 2.5–70 K. For all the Ce-based compounds $C_p(T)$ exhibits
pronounced λ-shaped peaks at the magnetic phase transitions. In the paramagnetic range Kondo and Schottky terms notably contribute to the total
specific heat. In the ordered region, $C_p(T)$ is dominated by a spin-wave
contribution. The characteristic Kondo and RKKY energy scales in all the
compounds are estimated to be of similar magnitude.

PACS numbers: 75.20.Hr, 75.30.Mb

The recent discovery of pressure-induced superconductivity in CeNi$_2$Ge$_2$
[1] has stimulated investigations on several other phases from the ternary
Ce-Ni-Ge system. In this paper we report the results of specific heat measure-
ments carried out on CeNiGe$_3$, Ce$_2$Ni$_3$Ge$_5$, Ce$_3$NiGe$_2$ and Ce$_3$Ni$_2$Ge$_7$,
which complete our comprehensive studies on bulk magnetic [2] and elec-
trical transport [3] behaviour of these compounds. All the Ce-based phases
and their isostructural analogues with La and Y were prepared and checked
in a manner described previously [3]. The specific heat was measured in
the temperature range 2.5–70 K by employing an adiabatic step-heating
 technique.

---

$^*$ Presented at the International Conference on Strongly Correlated Electron Systems,
(SCES02), Cracow, Poland, July 10–13, 2002.

(1235)
Ce$_2$Ni$_2$Ge$_7$ and Ce$_2$Ni$_5$Ge$_5$. The arrows mark magnetic phase transitions. Insets: $C_p(T)$ vs $T^2$ for La compounds. (b), (e) Non-lattice specific heat and entropy vs $T$ (left and right axes, respectively). The dashed lines represent the electronic, Kondo and Schottky contributions. The thick solid lines are fits to Eq. (1). (c), (f) Low-temperature $\Delta C$. The solid lines are fits to Eq. (2). Insets: estimation of the Kondo temperatures according to Ref. [7] and [8].

The magnetic phase transitions in CeNi$_3$, Ce$_2$Ni$_3$Ge$_5$, Ce$_3$NiGe$_2$ and Ce$_3$Ni$_5$Ge$_7$ manifest themselves in $C_p(T)$ as pronounced $\lambda$-shaped peaks at $T_{N,C} = 5.5, 5.1, 6.2$ and 7.5 K, respectively. As an example, Fig. 1 displays the results obtained for Ce$_3$Ni$_2$Ge$_7$ and Ce$_2$Ni$_5$Ge$_5$ (the data for
CeNiGe₃ and Ce₃NiGe₂ will be given elsewhere). In the case of Ce₂Ni₃Ge₅, a subsequent order–order transition is seen at T₁ = 4.4 K in agreement with Ref. [4]. Tiny anomalies in C_p(T) at about 10 K may result from a small amount of magnetic impurity, presumably Ce₂NiGe₆ [5].

The C_p(T) curves for the La(Y)-based phases are typical for nonmagnetic metals (see Fig. 1). The experimental data below 10 K follow the dependence C_p = γT + βT³ with the Sommerfeld coefficients γ of the order of a few mJmol⁻¹K⁻² and the Debye temperatures of about 300 K. Assuming that the phonon contribution to the specific heat, C_ph, of the nonmagnetic analogues is a good approximation of C_ph in the Ce compounds, the non-lattice contribution ΔC = C_p − C_ph was extracted, as shown in Fig. 1. Then the ΔC curves were analysed in the paramagnetic region as a sum

\[ \Delta C = C_{el} + C_{K} + C_{Sch}, \]  

were the subscripts denote the electronic, Kondo and Schottky specific heat, respectively. For C_d(T) a simple proportionality C_d = γ_pT was assumed. The Kondo contribution C_K(T) with the characteristic temperature T_K was applied, as derived theoretically by Desgranges and Schotte [6]. For C_Sch(T) a doublet–doublet crystal field scheme with an energy gap ΔCEF was adopted for Ce₃Ni₂Ge₇ and Ce₂Ni₃Ge₅, because the magnitude of the magnetic entropy at 50 K is for both compounds only slightly larger than Rln2 (see Fig. 1). In the case of CeNiGe₃ a doublet–doublet scheme appeared to be not appropriate and the third doublet originated from the ⁵F₇/₂ Ce³⁺ ground multiplet was taken into account. In turn, ΔC(T) for Ce₃NiGe₂ does not reveal any dear Schottky contribution and thus the C_Sch term was neglected. Fitting the experimental specific heat curves to Eq. (1) yielded the parameters γ_p, ΔCEF and T_K given in Table I. It is worthwhile noticing that for all the compounds the values of ΔCEF and T_K are close to those estimated from the electrical resistivity data [3,4].

<table>
<thead>
<tr>
<th>Compound</th>
<th>γ_p (mJ mol⁻¹K⁻¹)</th>
<th>ΔCEF (K)</th>
<th>T_K (K)</th>
<th>γ' (mJ mol⁻¹K⁻²)</th>
<th>Δ (K)</th>
<th>A (mJ mol⁻¹K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeNiGe₃</td>
<td>45</td>
<td>116, 163</td>
<td>4.5</td>
<td>193</td>
<td>4</td>
<td>9.1</td>
</tr>
<tr>
<td>Ce₂Ni₂Ge₇</td>
<td>4</td>
<td>173</td>
<td>4.7</td>
<td>504</td>
<td>17</td>
<td>6.4</td>
</tr>
<tr>
<td>Ce₂NiGe₂</td>
<td>25</td>
<td></td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce₃Ni₂Ge₇</td>
<td>10</td>
<td>148</td>
<td>5.2</td>
<td>78</td>
<td>10</td>
<td>1.1</td>
</tr>
</tbody>
</table>

For comparison the Kondo temperatures have also been calculated from the magnetic entropy S at T_N,C [7] and the specific heat jump δC at T_N,C [8].
(see the graphical analysis of $T_K$ in Ce$_3$Ni$_2$Ge$_7$ and Ce$_2$Ni$_3$Ge$_5$, presented in the insets to Figs. 1(c) and 1(f), respectively). The values of $T_K$ derived from $S (\delta C)$ are 6.2 (3.7), 6.5 (2.2), 10 (8.4) and 14 (2.5) K for CeNiGe$_3$, Ce$_2$Ni$_3$Ge$_5$, Ce$_3$NiGe$_2$ and Ce$_3$Ni$_2$Ge$_7$, respectively. Despite some discrepancies between the values obtained by different methods it is clearly seen that in all the compounds studied the energy scales for Kondo and RKKY interactions are of similar magnitude.

In the ordered region $C_p (T)$ of an antiferromagnetic Kondo lattice is given by the formula [9]

$$\Delta C(T) = \gamma^* T + A \Delta^{7/2} T^{1/2} e^{-\Delta/T} [1 + (39/20)(T/\Delta) + (51/32)(T/\Delta)^2],$$

where $\gamma^* T$ is an electronic term, $\Delta$ is an energy gap in the spin-wave spectrum and $A$ is a constant. The least-squares fitting parameters for CeNiGe$_3$, Ce$_2$Ni$_3$Ge$_5$ and Ce$_3$Ni$_2$Ge$_7$ (ferromagnetic Ce$_3$NiGe$_5$ will be analysed separately) are given in Table I (see also the solid lines in Figs. 1(c) and 1(f)). The enhanced values of $\gamma^*$ hint at strong electronic correlations in all the compounds studied, and thus, together with the behaviour of $C_p (T)$ in the paramagnetic state, support the dense Kondo picture postulated for these ternaries in the previous studies [2–4].

The work was supported by the Austrian–Polish Scientific–Technical Exchange Program (project No. 14/2001), the Max-Planck Society and the Polish State Committee for Scientific Research (KBN) grant No. 2P03B 028 23.

REFERENCES