Kondo lattice behaviour of $CeNi_9Si_4$

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Abstract

We have studied the crystal chemistry, thermodynamic and transport properties of ternary compounds RNi$_9$Si$_4$ with R = La and Ce. The Rietveld refinement of the X-ray diffraction pattern revealed a tetragonal crystal structure (space group $I4/mcm$) that is derived from the cubic $NaZn_{13}$ structure type. In the case of $CeNi_9Si_4$ resistivity, magnetic susceptibility and specific heat measurements reveal Kondo-lattice behaviour with a T^2 temperature dependence of the electrical resistivity, an enhanced Pauli susceptibility $\chi_0 = 5 \times 10^{-3}$ emu/mol and a Sommerfeld value $\gamma = 155\,(5)$ mJ/molK^2. The magnetic susceptibility and specific heat contribution is well described by the Coqblin-Schrieffer model with a fully degenerate $J = 5/2$ ground state and a characteristic temperature $T_0 \simeq 180$ K. $LaNi_9Si_4$ exhibits simple Pauli paramagnetic, metallic behaviour with a Sommerfeld value $\gamma = 33$ mJ/molK^2.

Key words: Kondo effect; ternary compounds; magnetic susceptibility; specific heat

We report on the physical properties of novel fully ordered compounds RNi$_9$Si$_4$ with R = La and Ce. A related phase is the partially disordered tetragonal compound $Ce_2Ni_{17}Si_9$ reported by Bodak [1] which has its own structure type (space group $I4/mcm$) that is derived from the cubic $NaZn_{13}$-type. A neutron diffraction study [2] on $Ce_2Ni_{17}Si_9$ reported a strong site preference of Si to one particular lattice site being fully occupied by Si and partial occupation of another particular lattice site which is primarily occupied by Ni.

Polycrystalline samples RNi$_9$Si$_4$ (R = La, Ce) were prepared by induction melting of the elements (Ce and La better than 99.9%, Ni and Si with 5N) under protective argon atmosphere and subsequent annealing at 990°C for one week. The phase purity and composition of the samples was confirmed by electron microprobe and X-ray diffraction studies. Rietveld refinements were performed on X-ray Guinier image plate data obtained from a flat powder specimen in transmission mode employing the FullProf98 program. Dc susceptibility and specific heat were measured with a SQUID magnetometer and with an adiabatic step heating calorimeter, respectively.

The Rietveld refinement of the X-ray powder diffraction data of single phase RNi$_9$Si$_4$ indicates a fully ordered arrangement of the R = Ce and La, Ni and Si

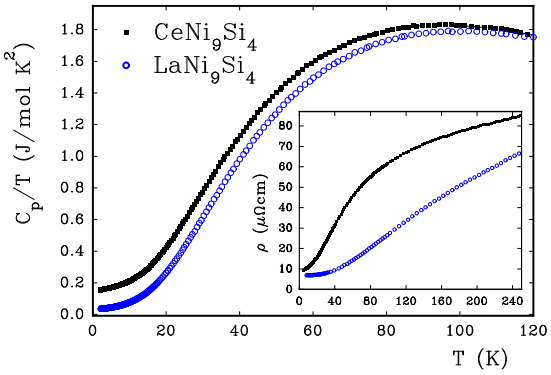

Fig. 1. The specifc heat $C_p(T)$ of $CeNi_9Si_4$ and $LaNi_9Si_4$; the inset shows the electrical resistivities $\rho(T)$.

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atoms in the sites of the space group I4/mcm with $a = 7.842$ Å, $c = 11.446$ Å and $a = 7.868$ Å, $c = 11.467$ Å, respectively. The existence of an ordered 1-9-4 phase is corroborated by a one order of magnitude lower residual resistivity of the stoichiometric RNi$_9$Si$_4$ samples compared to specimens prepared by the same procedure but with slightly off-stoichiometric Ni/Si composition as e.g. CeNi$_{8.8}$Si$_{4.2}$.

The specific heat $C_p(T)$ of CeNi$_9$Si$_4$ and LaNi$_9$Si$_4$ shown in Fig. 1 as C/T vs. T reveals a significant enhancement of the T-linear contribution $\gamma = 155\,(5)\,\mathrm{mJ/molK^2}$ of CeNi$_9$Si$_4$ compared to $\gamma = 33\,(2)\,\mathrm{mJ/molK^2}$ of LaNi$_9$Si$_4$. This observation is in line with the resistivity behaviour shown in the inset of Fig. 1, where CeNi$_9$Si$_4$ exhibits a temperature dependence typical for a Kondo lattice with a T^2 dependence: $\rho(T) = \rho_0 + AT^2$ for $T < 20\,\mathrm{K}$ yielding $A \sim 0.017\mu\Omega\mathrm{cm/K^2}$, and an in-coherent Kondo regime at elevated temperatures. The resulting Kadowaki-Woods ratio $A/\gamma^2 \sim 10^{-6}\mu\Omega\mathrm{cm(molK/mJ)^2}$ is of similar magnitude as that of some Yb Kondo-lattice compounds e.g. YbCu$_4$Ag and d-metals [3], but significantly smaller than the typical $10^{-5}\mu\Omega\mathrm{cm(molK/mJ)^2}$ of many Ce and U compounds. The larger Kadowaki-Woods ratio of the latter systems compared to CeNi$_9$Si$_4$ may be attributed to stronger RKKY interactions which is plausible because of the low fraction Ce-ions in the 1-9-4 compound.

For a direct comparison of the thermodynamic behaviour of CeNi$_9$Si$_4$ with the thermodynamic equations of the Coqblin-Schrieffer (CS) model [4] solved by Rajan [5] we show in Fig. 2 the magnetic contribution $\Delta C_p(T)$ to the specific heat of CeNi$_9$Si$_4$ (open circles; obtained by subtracting the specific heat of the non-magnetic reference LaNi$_9$Si$_4$) and the solid line corresponds to the result of the CS model for a 6-fold degenerate ground state ($J = 5/2$) with a characteristic temperature $T_0 = 178\,\mathrm{K}$. The latter is the only free

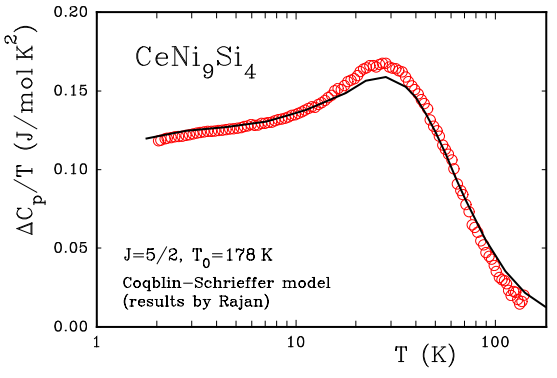

Fig. 2. The magnetic specifc heat contribution $\Delta C_p(T)$ of CeNi$_9$Si$_4$; the solid line corresponds to the Coqblin-Schrieffer model for a 6-fold degenerate ground state with the characteristic temperature $T_0 = 178\,\mathrm{K}$.

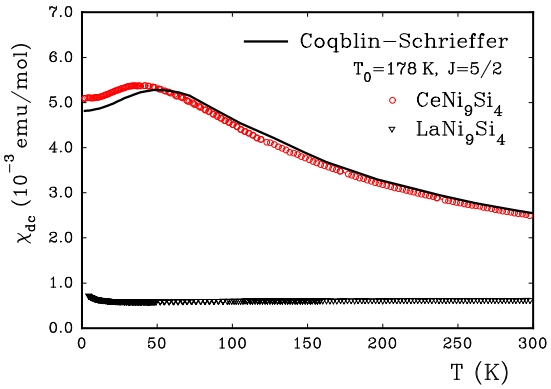

Fig. 3. The dc magnetic susceptibility of $\chi(T)$ of CeNi$_9$Si$_4$ and LaNi$_9$Si$_4$ measured at 1 T; the solid line corresponds to the Coqblin-Schrieffer model for a 6-fold degenerate ground state with $T_0 = 178\,\mathrm{K}$.

parameter which accounts for the energy scale of the Kondo interaction and has been determined by a simple fit to the experimental data.

The dc magnetic susceptibility $\chi(T)$ of CeNi$_9$Si$_4$ and LaNi$_9$Si$_4$ shown in Fig. 3 reveals simple Pauli paramagnetic behaviour with $\chi_0 \simeq 0.6 \times 10^{-3}$ emu/mol for LaNi$_9$Si$_4$ and a typical *heavy electron* type weakly temperature dependent magnetic susceptibility with $\chi_0 \simeq 5 \times 10^{-3}$ emu/mol for CeNi$_9$Si$_4$. The solid line in Fig. 3 again shows the result of the CS model for a 6-fold degenerate ground state with $T_0 = 178\,\mathrm{K}$. The Wilson ratio $R = \chi/\gamma \simeq 2$ agrees with the value expected for Ce^{3+}. The rather good agreement between the experimental data, the specific heat and the magnetic susceptibility of CeNi$_9$Si$_4$ with the degenerate CS model which does not account for any crystalline electric field (CEF) effects indicates that the overall CEF splitting of the Ce^{3+} ground multiplet is smaller than the characteristic energy scale T_0.

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