Intermediate valence behavior in CeCo$_9$Si$_4$

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Abstract

The novel ternary compound CeCo$_9$Si$_4$ has been studied by means of specific heat, magnetisation, and transport measurements. Single crystal X-ray Rietveld refinements reveal a fully ordered distribution of Ce, Co and Si atoms with the tetragonal space group $I4/mcm$ isostructural with other $R$Co$_9$Si$_4$. The smaller lattice constants of CeCo$_9$Si$_4$ in comparison with the trend established by other $R$Co$_9$Si$_4$ is indicative for intermediate valence of cerium. While $R$Co$_9$Si$_4$ with $R$ = Pr, ... Tb, and Y show ferromagnetism and LaCo$_9$Si$_4$ is nearly ferromagnetic, CeCo$_9$Si$_4$ remains paramagnetic even in external fields as large as 40 T, though its electronic specific heat coefficient ($\gamma \simeq 190$ mJ/mol K$^2$) is of similar magnitude as that of metamagnetic LaCo$_9$Si$_4$ and weakly ferromagnetic YCo$_9$Si$_4$.

Key words:
CeCo$_9$Si$_4$, Intermediate Valence, High Field Measurement

The ordered ternary rare-earth cobalt silicon phase with composition 1:9:4 attracted our attention mainly because of the extraordinary magnetic properties of LaCo$_9$Si$_4$ which is a strongly exchange enhanced Pauli paramagnet and exhibits an itinerant metamagnetic phase transition at about 3.5 T for $H||c$ and 6 T for $H \perp c$, which is the lowest value ever found for rare earth intermetallic compounds [1]. Related isostructural $R$Co$_9$Si$_4$ with $R$ = Pr, Nd, Gd, Dy and also Y are ferromagnetic (see Refs. [2,3]) with relatively low $T_C \sim 20 - 50$ K. This report is on the exceptional behavior of CeCo$_9$Si$_4$ among the ferromagnetic (FM) or almost FM RCo$_9$Si$_4$ compounds.

Polycrystalline samples of CeCo$_9$Si$_4$ and related RCo$_9$Si$_4$ were synthesized by induction melting of pure elements ($R$ 3N, Co 4.5N, Si 6N) under protective argon atmosphere and subsequent annealing at.
1050°C for one week. The crystal structure was determined by means of single crystal X-ray diffraction (R_{p2} = 2.3%) revealing, analogous to CeNi_{5}Si_{4} [4], a fully ordered distribution of Ce, Co and Si atoms with the LaFe_{5}Si_{4}-type [5] (space group I4/mcm). The lattice parameters are a = 7.801(1) Å and c = 11.521(2) Å at room temperature.

The comparison of the lattice parameters of RCo_{9}Si_{4} with R = La, Ce, Pr, Nd shown in Fig. 1 reveals a significant negative deviation of the CeCo_{9}Si_{4} data from the common trend. The smaller lattice constants of CeCo_{9}Si_{4} indicates an intermediate valence state in between the magnetic trivalent 4f^{3} and the non-magnetic tetravalent 4f^{4} state due to hybridization of 4f and conduction band states. Intermediate valence close to tetraivalence is corroborated by the magnetisation data shown in Fig. 2 where the Curie-Weiss component expected for Ce^{3+} ions is not observed. The dc susceptibility measurement in fact reveals an almost temperature independent paramagnetic susceptibility for CeCo_{9}Si_{4}, while LaCo_{9}Si_{4} exhibits a more pronounced temperature dependence, typical for a spin fluctuation system, and all other RCo_{9}Si_{4} are ferromagnetic below 20–50 K (see the YCo_{9}Si_{4} data shown in Fig. 2 as one example). The small off-set of the room temperature magnetic moment of CeCo_{9}Si_{4} as compared with LaCo_{9}Si_{4} and YCo_{9}Si_{4} in Fig. 2 is due to a contribution from traces of unreacted free Co which is also visible in the M(H) data (see Fig. 3). The Pauli-susceptibility χ_{0} estimated from M/H at 40 T is about 5 × 10^{-7} m^{3}/kg, slightly smaller than 8.2 × 10^{-7} m^{3}/kg given in Ref. [1] for LaCo_{9}Si_{4}.

Motivated by the metamagnetism observed for LaCo_{9}Si_{4} high-field magnetisation M(H) measurements have been carried out up to 40 T in pulsed fields (see Ref.[6] for details of the setup) on CeCo_{9}Si_{4} and LaCo_{9}Si_{4} for comparison. Apart from a small hysteresis at low fields due to the above mentioned Co impurities, CeCo_{9}Si_{4} shows a rather perfectly linear paramagnetic field dependence reaching 2 µ_{B}/f.u. at B_{max} = 40 T, whereas the magnetic moment of the field induced FM state of LaCo_{9}Si_{4} saturates already above about 8 T at approximately 1.1 µ_{B}/f.u.

The obviously more stable paramagnetic state of CeCo_{9}Si_{4} with respect to the appearance of metamagnetism is most likely due to d-band filling caused by hybridized 4f states of cerium being close to tetravalence. Thus, one expects a reduction of spin-fluctuation mass enhancement which however may be partly compensated by contributions due to Ce valence fluctuations. The latter is supported by the specific heat data (not shown) where the linear electronic specific heat coefficient of CeCo_{9}Si_{4}, the Sommerfeld value γ≃ 190 mJ/molK^{2}, is slightly lower than that of nearly magnetic LaCo_{9}Si_{4}, where γ≃ 200 mJ/molK^{2}. The comparison of the temperature dependent resistivities ρ(T), on the other hand (not shown), indicates for both a Fermi liquid behavior with ρ(T) = ρ_{0} + AT^{2}, however, with a significantly lower A-coefficient for CeCo_{9}Si_{4} as compared to LaCo_{9}Si_{4} [7].

We conclude that CeCo_{9}Si_{4} exhibits intermediate valence with Ce being close to a non-magnetic tetravalent state where 4f states hybridize with the conduction bands and thereby weaken the magnetic correlations among d-electrons as compared to other RCo_{9}Si_{4}.

References
[1] H. Michor et al., Phys.Rev. B 69 (2004) 081404(R).
[2] M. Q. Huang et al., J. Appl. Phys. 79 (1996) 5949.
[3] H. Michor et al., SCES04 (this conference).
[4] H. Michor et al., Phys.Rev. B 67 (2003) 224428.
[5] W.H. Tang et al., J. Appl. Phys. 76 (1994) 4095.
[6] D. Eckert et al., Physica B 294-295 (2001) 705.
[7] M. El-Hagary et al., to be published.