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Antiferromagnetic behavior in CeCo_9Ge_4

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Abstract. We investigate the novel intermetallic ternary compounds $R\text{Co}_9\text{Ge}_4$ with $R = \text{La}$ and Ce by means of X -ray diffraction, susceptibility and specific heat measurements. CeCo_9Ge_4 crystallizes in the space group $I4/mcm$ and is characterized by the coexistence of two different magnetic sublattices. The Ce-based sublattice, with an effective moment close to the expected value for a Ce^{3+} -ion, exhibits a magnetically ordered ground state with $T_N = 12.5$ K. The Co-based sublattice, however, exhibits magnetic moments due to itinerant $3d$ electrons. The magnetic specific heat contribution of the Ce-sublattice is discussed in terms of a resonance-level model implying the interplay between an antiferromagnetic phase transition and the Kondo-effect and an underlying Schottky-anomaly indicating a crystal field level scheme splitting into three twofold degenerated micro states ($\Delta_1 = 69$ K, $\Delta_2 = 133$ K).

1. Introduction

Cerium based intermetallic compounds of the tetragonal $\text{Ce}T_9X_4$ (T : transition metal, X : Group 14 element) family exhibit a rich variety of ground states, such as unprecedented Fermi-liquid (FL) behavior in CeNi_9Ge_4 ($\gamma = C/T \approx 5.5 \text{ Jmol}^{-1}\text{K}^{-2}$) [1; 2], model type Kondo-lattice behavior in CeNi_9Si_4 [3] and valence fluctuations in CeCo_9Si_4 [4; 5]. The most outstanding feature of CeNi_9Ge_4 is the approximate scaling of the magnetic specific heat and susceptibility contributions within the Ce-content in the solid solution $\text{Ce}_{1-y}\text{La}_y\text{Ni}_9\text{Ge}_4$. This indicates that the huge Sommerfeld coefficient γ is mainly due to a single-ion effect [2] caused by an effectively fourfold degenerate ground state in CeNi_9Ge_4 [6]. To gain insight into the spin fluctuation dynamics and to study the influences of the crystal electrical field (CEF) of the ground state of CeNi_9Ge_4 , substitution experiments on the ligand sites are a valuable tool.

Control of hybridization strength, between the $4f$ electrons and the conduction electrons was achieved by a systematic Ni/Cu substitution in $\text{CeNi}_{9-x}\text{Cu}_x\text{Ge}_4$. As a result a quantum critical phase (QCP) transition at $x = 0.4$ is induced. This QCP transition is not only driven by the competition between Kondo-effect and RKKY interaction, but also by a continuous reduction of the effective crystal field ground state degeneracy from non-magnetic fourfold in CeNi_9Ge_4 towards a magnetically ordered twofold one in $\text{CeNi}_8\text{CuGe}_4$ [6].

The consequences of a Ni/Cu substitution which lead to a continuous increase of the d -electron density of state at the Fermi-level have been studied already [6]. In this paper, however, we analyzed the reverse scenario to identify the consequences of a decreasing d -electron count. CeCo_9Ge_4 seems to be a suitable candidate for this study.

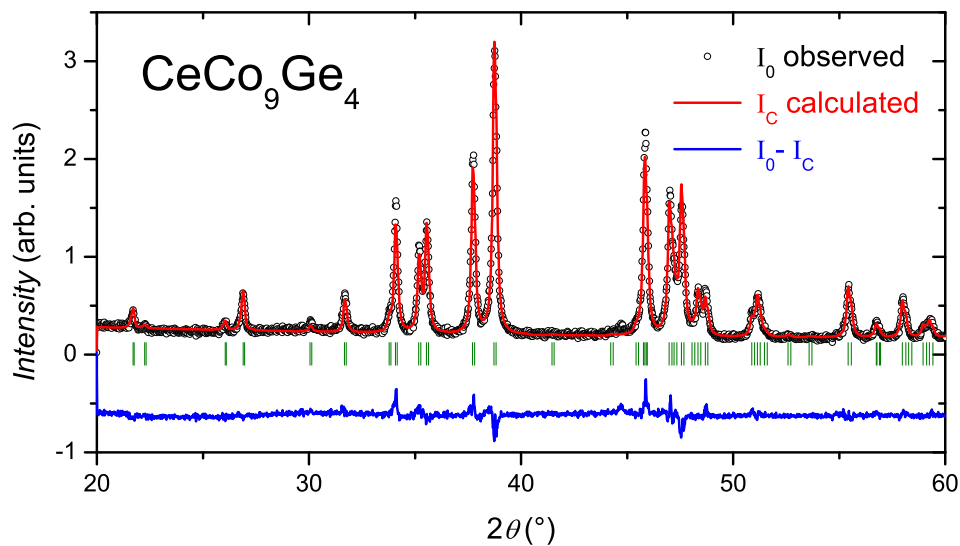


Figure 1. X-ray powder diffraction pattern of annealed CeCo_9Ge_4 . Included is a calculated fit (Rietveld refinement) to the data, the difference between fit and data, and ticks indicating Bragg peak positions.

2. Sample Preparation and Structural Characterization

Polycrystalline samples with nominal compositions of CeCo_9Ge_4 and LaCo_9Ge_4 were prepared by a two-step-arc-melting-procedure of the pure elements (Ce: 4N, La: 3N8, Co: 4N8, Ge: 5N) under a protective argon atmosphere. To obtain the highest possible homogeneity, the samples were turned upside-down, remelted several times and finally annealed in evacuated quartz glass tubes for two weeks at 950°C . The weight losses of both samples after annealing were less than 0.5% of the total mass.

Phase purity and crystal structure analysis were performed by means of X-ray powder diffractometry at room temperature. Rietveld analysis of the X-ray data confirmed that both samples crystallize in the tetragonal LaFe_9Si_4 -type [7] (space group $I4/mcm$) structure. Here, the rare-earth elements (Ce, La) occupy the crystallographic $4a$ sites, while the Ge atoms are situated on the $16l$ and the transition elements are distributed over the $16k$, $16l$ and $4d$ sites. The high quality of the refinement ($R_f = 6.51$) is reflected in the rather featureless difference plot in Fig. 1 for observed and calculated Bragg intensities in CeCo_9Ge_4 . The resulting lattice parameters for CeCo_9Ge_4 ($a = b = 7.9809(1)\text{\AA}$ and $c = 11.8825(7)\text{\AA}$) and for LaCo_9Ge_4 ($a = b = 7.9827(8)\text{\AA}$ and $c = 11.8743(7)\text{\AA}$) reveal a volume increase of about 8.0% and 6.6% in comparison to isostructural CeCo_9Si_4 and LaCo_9Si_4 [5], respectively. This pronounced volume expansion might not only arise from differences in the (ionic) radii of Si versus Ge. An additional volume increase may be due to a change of the Ce-valence from mixed-valence- (CeCo_9Si_4 [4]) to a dominant Ce^{3+} -state in CeCo_9Ge_4 .

3. Magnetic Measurements

The temperature dependence of the DC magnetic susceptibility $\chi(T)$ of CeCo_9Ge_4 and LaCo_9Ge_4 is shown in Fig. 2 between 2 K and 400 K in an external field of 0.5 T. Above 200 K the susceptibilities follow a modified Curie-Weiss type law, $\chi(T) = C/(T - \Theta_{\text{CW}}) + \chi_0$ (see insert Fig. 2). From the Curie constants C the effective magnetic moments $\mu_{\text{eff}} = 5.21\mu_{\text{B}}$ and $4.54\mu_{\text{B}}$ were determined for the Ce- and La-compounds, respectively. For CeCo_9Ge_4 these results lead to two different magnetic sublattices, one is based on the local magnetic moments of the Ce^{3+} -

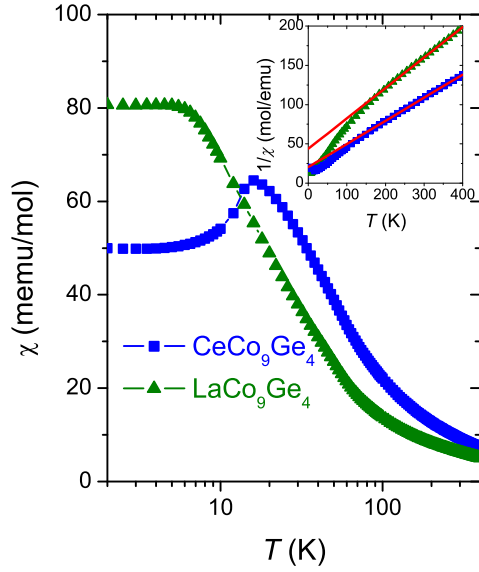


Figure 2. The magnetic *DC* susceptibility χ versus T of CeCo_9Ge_4 and LaCo_9Ge_4 measured in an external field of 0.5 T. Inset: Inverse magnetic *DC* susceptibility $1/\chi$ versus T of CeCo_9Ge_4 (squares) and LaCo_9Ge_4 (triangles). The solid lines are fits based on a modified Curie-Weiss type law, $\chi(T) = C/(T - \Theta_{\text{CW}}) + \chi_0$.

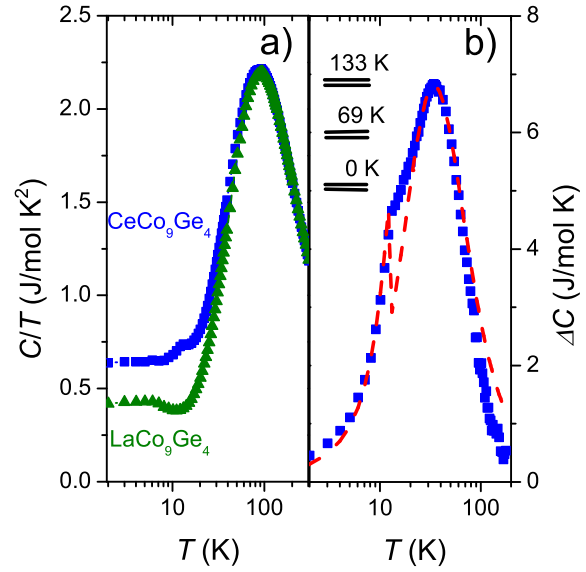


Figure 3. a) The temperature dependent specific heat divided by the temperature C/T of CeCo_9Ge_4 and LaCo_9Ge_4 . b) The magnetic contribution of the specific heat ΔC of CeCo_9Ge_4 . The dashed line represents a theoretical adjustment to the data taking into account the resonant-level model [9] and a Schottky anomaly.

ion with $\mu_{\text{eff}} = \sqrt{\mu_{\text{eff}}^2(\text{CeCo}_9\text{Ge}_4) - \mu_{\text{eff}}^2(\text{LaCo}_9\text{Ge}_4)} = 2.56\mu_{\text{B}}$, and the second one corresponds to the Co sublattice yielding a μ_{eff} of $4.54\mu_{\text{B}}$. Assuming the presence of Co^{2+} -ions displaying a $3d^7$ configuration, the determined effective moment for the Co sublattice implies that only one Co-site exhibits a magnetic moment. This assumption leads to a saturation magnetization of $3\mu_{\text{B}}$ around 3 T at 2 K, which is in contrast to a slightly convex magnetization curve found in LaCo_9Ge_4 with $M(7\text{ T}) = 0.76\mu_{\text{B}}$. A similar behavior is observed in the related novel 1-9-4 compound LaCo_9Si_4 [8], where a strong Stoner-enhanced Pauli paramagnetism is discussed. For LaCo_9Ge_4 the low-temperature flattening of the susceptibility ($T < 7\text{ K}$) corroborates the itinerant scenario. Furthermore, the low temperature susceptibility χ for CeCo_9Ge_4 reveals a maximum around 14 K, indicating an antiferromagnetic phase transition with $T_{\text{N}} = 12.5\text{ K}$.

4. Specific Heat Measurements

The temperature dependent specific heat $C(T)$ divided by temperature of CeCo_9Ge_4 and LaCo_9Ge_4 between 2 K to 300 K is displayed in Fig. 3a. Besides the high temperature regime of the specific heat, which is dominated by phonon contributions $C(T)/T$ of CeCo_9Ge_4 exhibits also a pronounced anomaly at 12.5 K indicating a phase transition to an ordered magnetic state, in good agreement with the $\chi(T)$ data. By contrast $C(T)$ of LaCo_9Ge_4 does not feature any evidence of magnetic order but a small increase below 10 K in correspondence to the observed flattening in $\chi(T)$.

Due to the fact, that itinerant $3d$ magnetism is presented in both samples, it is difficult to quantify the linear Sommerfeld coefficient γ . In order to disregard this effect and to eliminate the phonon contribution, we subtracted the total specific heat of the isostructural LaCo_9Ge_4

sample from the Ce compound. As a result we obtained the magnetic contribution of the specific heat ΔC of the Ce subsystem pictured in Fig. 3b. From a $\Delta C/T$ over T^2 plot a Sommerfeld coefficient $\gamma \approx 200 \text{ mJmol}^{-1}\text{K}^{-2}$ is extracted, yielding a Kondo-temperature of $T_K = 0.68R/\gamma = 28 \text{ K}$, where R is the gas constant. This pronounced Kondo-contribution at low temperatures can be described utilizing the resonant-level model [9] in combination with a molecular field approach to account for long-range magnetic order (see, e.g., [6]). The results of these calculations qualitatively reproduce the evolution of the magnetic specific heat anomaly ($T_N = 12.5 \text{ K}$) and the Kondo-contribution of CeCo_9Ge_4 (see dashed line in Fig. 2b). The exchange interaction J and the Kondo-temperature T_K , obtained from the resonant-level model, are 65 K and 32 K in good agreement with the T_K -value obtained from the γ -value. In addition, at high temperatures the specific heat data can be well described by a Schottky anomaly resulting from a CEF effect of the $J = 5/2$ state of the Ce^{3+} -ion. The Schottky maximum can be fitted using a crystal-field level scheme with energies levels separations of $\Delta_1 = 69 \text{ K}$ and $\Delta_2 = 133 \text{ K}$. The entropy calculation from $\Delta C/T$ nearly tends above 130 K towards the expected value of $R \ln 6$, characteristic for a sixfold degenerated system.

5. Conclusion

The influence of the observed volume expansion of about 1.2% as well as the reduction of the d -electron count compared to CeNi_9Ge_4 was investigated using susceptibility and specific heat measurements. We have found a coexistence of two magnetic sublattices in CeCo_9Ge_4 . While the Ce-sublattice is characterized by an antiferromagnetic ordered Kondo-lattice ($T_N = 12.5 \text{ K}$) with a Sommerfeld value of $\gamma \simeq 200 \text{ mJ/mol K}^2$ and a Kondo-temperature of $T_K = 32 \text{ K}$, the Co-sublattice reveals $3d$ itinerant paramagnetism. In addition, the Ni/Co exchange leads to a shift of the CEF levels. The isostructural compound LaCo_9Ge_4 is, due to the missing magnetic rare-earth sublattice, an ideal system to study the role of itinerant magnetism in CeCo_9Ge_4 and will be subject of future investigations.

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