

Crystal field studies on the heavy fermion compound $\text{CeNi}_8\text{CuGe}_4$

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Abstract. Substitution of nickel by copper in the heavy fermion system $\text{CeNi}_{9-x}\text{Cu}_x\text{Ge}_4$ alters the local crystal field environment of the Ce^{3+} -ions. This leads to a quantum phase transition near $x \approx 0.4$, which is not only driven by the competition between Kondo effect and RKKY interaction, but also by a reduction of an effectively fourfold to a twofold degenerate crystal field ground state. To study the consequences of a changing crystal field in $\text{CeNi}_8\text{CuGe}_4$ on its Kondo properties, inelastic neutron scattering (INS) experiments were performed. Two well-defined crystal field transitions were observed in the energy-loss spectra at 4 K. The crystal field level scheme determined by neutron spectroscopy is compared with results from specific heat measurements.

1. Introduction

The heavy fermion system CeNi_9Ge_4 exhibits an outstanding Fermi-liquid (FL) behavior with the largest value of the electronic specific heat $\Delta C/T \approx 5.5 \text{ Jmol}^{-1}\text{K}^{-2}$ ever recorded in the absence of any magnetic order [1; 2]. The crystal field (CF), investigated by single crystal susceptibility analysis, consists of a quasi-quartet ground state and one doublet at $\Delta_2 \simeq 11 \text{ meV}$ ($\simeq 128 \text{ K}$) [3]. The quasi-quartet is internally split into two doublets separated by $\Delta_1 \simeq 0.5 \text{ meV}$ ($\simeq 6 \text{ K}$). The Kondo-temperature $T_K \simeq 3.5 \text{ K}$, determined by inelastic neutron scattering (INS) studies [3], falls in the same energy-range as the splitting of the quasi-quartet ground state.

While this unusual FL behavior is mainly driven by single-ion effects [2], Ni/Cu substitution leads to antiferromagnetic order in $\text{CeNi}_8\text{CuGe}_4$ with $T_N = 175 \text{ mK}$. Profound analysis of specific heat, magnetic susceptibility and electrical resistivity of the substitution-series $\text{CeNi}_{9-x}\text{Cu}_x\text{Ge}_4$ reveals a continuous tuning of the ground state from an effectively fourfold degenerate nonmagnetic Kondo ground state in CeNi_9Ge_4 towards a magnetically ordered, effectively twofold degenerate ground state in $\text{CeNi}_8\text{CuGe}_4$ [4]. Around the critical Cu-concentration of $x \simeq 0.4$ the system exhibits quantum critical behavior with χ and $C/T \propto \ln T$ and $\rho \propto T$. Previous investigations on the system suggested, that this quantum phase transition is not only driven by the competition between Kondo-effect and RKKY interaction, but also by a reduction

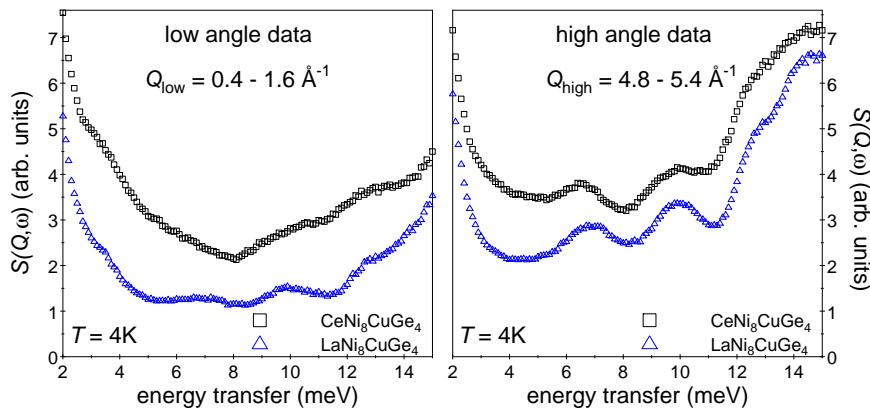


Figure 1. (Color online) Inelastic neutron scattering spectra of $\text{CeNi}_8\text{CuGe}_4$ and $\text{LaNi}_8\text{CuGe}_4$ at 4K, which were used for the phonon subtraction.

of the effective CF ground state degeneracy, caused by two or more different CF environments of the Ce^{3+} -ion [4]. To prove these suggestions, mainly based on specific heat measurements, we performed neutron scattering experiments on the compound $\text{CeNi}_8\text{CuGe}_4$ in order to study the crystal field and the disorder effects, occurring in the chemical environment of the Ce^{3+} -ion.

2. Experimental Details

The neutron scattering studies were performed at the research reactor FRM-II (Garching, Germany), where inelastic scattering studies were carried out on the time-of-flight spectrometer TOFTOF, whilst elastic scattering was studied at the high-resolution structure powder diffractometer SPODI ($\lambda = 1.5483 \text{ \AA}$). For the sample preparation several polycrystalline samples of $\text{CeNi}_8\text{CuGe}_4$ and of the nonparamagnetic reference compound $\text{LaNi}_8\text{CuGe}_4$ have been synthesized by arc melting of pure elements in a highly purified argon atmosphere. To obtain the highest possible homogeneity the samples were flipped over and remelted several times and finally annealed under vacuum for one week at 950°C . X-ray diffraction experiments showed that both $\text{CeNi}_8\text{CuGe}_4$ and $\text{LaNi}_8\text{CuGe}_4$ are single-phase materials and their structure belongs to the LaFe_9Si_4 -type (tetragonal space group $I4/mcm$) with three Ni-sites (Ni1:16*k*, Ni2:16*l*, Ni3:4*d*), one Ge (16*l*) and one Ce site (4*a*). It is evident that X-ray diffraction can not reveal any ordering of copper in the lattice due to the minute differences in the scattering factors of Ni and Cu. In order to determine which of the individual Ni-sites is preferentially substituted by Cu and to estimate the degree of Ni/Cu disorder in $\text{CeNi}_8\text{CuGe}_4$ a neutron diffraction experiment was performed at 300 K and 4 K. The compound was filled in a single-wall cylindrical vanadium container (14 mm in diameter, 0.15 mm wall thickness). The diffraction experiment showed a rather weak, but still noticeable reflection broadening over the entire Q -range. After deconvolution with the instrumental resolution function this line broadening could be assigned to a size-effect, which was best simulated with platelet-like shaped crystallites (ca. 400 \AA in diameter and surface parallel to [200]). For the localization of the copper atoms in the lattice, the occupancies of the different Ni sites were checked. As a result of the best Rietveld fit, 99% of the copper atoms could be located on the Ni1 site. This is in good agreement with bandstructure calculations based on the new full-potential augmented spherical wave method [4], which clearly show an energetic preference for a Ni/Cu substitution at the Ni1 site. We note that the replacement of the Ni1 site by Cu does not lead to any superstructural reflections, hence the local site symmetry of Ce can still be approximated by 422. Furthermore, a little excess of the occupancy on the 16*l*-place of both Ni and Ge was found, which is probably related

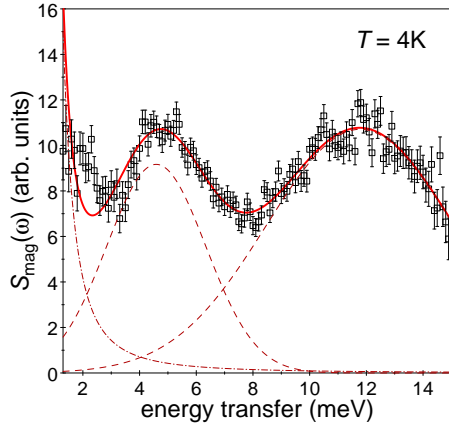


Figure 2. (Color online) Magnetic scattering function $S_{\text{mag}}(Q, \omega)$ of $\text{CeNi}_8\text{CuGe}_4$ at 4 K. The solid line represents a fit to a spectral function consisting of two Gaussians (dashed line) and one Lorentzian (dash-dotted line).

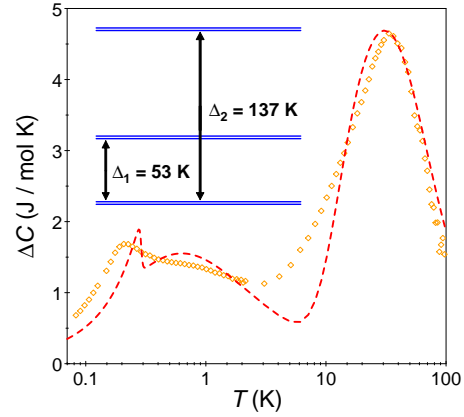


Figure 3. (Color online) The magnetic contribution of the specific heat ΔC . The dashed line is a theoretical adjustment to the data taking into account the determined crystal level scheme displayed in the insert.

to a weak static disorder existing in the material.

For the determination of the CF level scheme about 35 g of $\text{CeNi}_8\text{CuGe}_4$ were filled in a thin double-walled aluminium can mounted onto a closed-cycle refrigerator. An incident neutron energy of $E_i = 16.9 \text{ meV}$ has been chosen at a sample-temperature of 4 K. Additionally, the nonparamagnetic reference compound $\text{LaNi}_8\text{CuGe}_4$ and a vanadium standard have been measured to determine the phonon part of the scattering and the detector efficiency. The data analysis was carried out with a modified version of the program IDA written by Wuttke [5]. The main challenge in the quantitative interpretation of measured INS spectra is to derive the phonon contribution correctly, particularly in compounds, such as $\text{CeNi}_8\text{CuGe}_4$, that contains elements with large nuclear cross sections. Fig. 1 shows the inelastic scattering spectra of $\text{CeNi}_8\text{CuGe}_4$ and $\text{LaNi}_8\text{CuGe}_4$ at 4 K for low ($\langle \Theta_{\text{low}} \rangle = 20^\circ$) and high ($\langle \Theta_{\text{high}} \rangle = 125^\circ$) scattering angles with the corresponding momentum transfer ranges of $Q_{\text{low}} = 0.4 - 1.6 \text{ \AA}^{-1}$ and $Q_{\text{high}} = 4.8 - 5.4 \text{ \AA}^{-1}$ ($Q = \frac{4\pi}{\lambda} \sin \Theta$). While the scattering at high Q is almost identical in both $\text{CeNi}_8\text{CuGe}_4$ and $\text{LaNi}_8\text{CuGe}_4$, there is a discrepancy in the scattering at low Q . This clearly indicates the presence of magnetic scattering in $\text{CeNi}_8\text{CuGe}_4$, because the intensity of magnetic scattering will decrease with increasing Q following the squared magnetic form factor, $F^2(Q)$, while the intensity of phonon scattering will increase with Q as Q^2 . The observed similar scattering at high Q reflects a similar phononic scattering contribution in both compounds, as expected. To extract the magnetic signal from the large phononic background we used the different Q -dependencies as described in [6]. First, the nonparamagnetic reference compound was used to determine the ratio of the high-angle and low-angle scattering intensities. Then this ratio was used to scale the high Q to the low Q response in $\text{CeNi}_8\text{CuGe}_4$ and to subtract the phonon contribution. In Fig. 2 the corrected data, which show the magnetic scattering function $S_{\text{mag}}(\omega)$ of $\text{CeNi}_8\text{CuGe}_4$, are displayed. Two broad excitations around 4.5 meV and 12 meV are observed in the spectrum, which can be assigned to magnetic transitions. The deviation from the fit around 2 meV could be caused by disorder effects as already mentioned in [4]. In order to analyze the scattering function in a proper way, we fitted a combination of two Gaussian-functions (dashed line), representing the CF transitions, and a Lorentzian-function (dash-dotted line), describing the elastic scattering line, to our data. From the fit the values of the CF splitting $\Delta_1 \approx 4.6 \pm 0.2 \text{ meV}$ ($\approx 53 \text{ K}$) and

$\Delta_2 \approx 11.8 \pm 0.2 \text{ meV}$ ($\approx 137 \text{ K}$) can be determined. On the basis of a simple CF approach the sixfold-degenerate ground state ($J = \frac{5}{2}$) of Ce^{3+} -ions displaying a local site symmetry of 422 will split in the presence of the crystal field into three doublets. The CF level scheme can be determined as displayed in the insert in Fig. 3.

3. Discussion and conclusions

In contrast to the preliminary results published in [4], where the phonon-contribution was taken into account by a simple La-subtraction and which conclude that more than one Ce site with different environments exist, we observe only one Ce site with $\Delta_1 \approx 53 \text{ K}$ and $\Delta_2 \approx 137 \text{ K}$. In Fig. 3 an analysis of the magnetic contribution to the specific heat ΔC of $\text{CeNi}_8\text{CuGe}_4$ considering the above determined CF scheme is shown. The interplay between molecular field and Kondo effect within the doublet ground state is regarded by the resonant-level model in combination with a molecular field approach (for details see [4]). The good agreement with the experimental data supports the above described CF scheme and therefore the fact, that the system $\text{CeNi}_8\text{CuGe}_4$ exhibits only one CF environment of the Ce-atoms with the Cu-atoms localized at the Ni1 site. The deviation between the experimental data and the theoretical adjustment around 7 K could be due to a weak disorder in the Ce-environment, which can not be excluded, especially because of the observation of the additional scattering intensity in the INS spectra around 2 meV. Structural disorder can indirectly be confirmed by relatively high magnitudes of isotropic displacement parameters at 4 K as well as a weak excess occupation on Ni2 (16l) and Ni1 (16k) atomic sites.

Comparing the CF scheme with the pure Ni-compound CeNi_9Ge_4 , where the crystal field consists of a quasi-quartet ground state at around $\Delta_1 \approx 6 \text{ K}$ and one doublet at $\Delta_2 \approx 128 \text{ K}$, the substitution of Ni by Cu leads to a splitting of the quasi-quartet into a twofold degenerated ground state and a higher shifting doublet, while the excited doublet remains at almost the same energy. This reduction of the effective CF ground state degeneracy could be related to the quantum phase transition in $\text{CeNi}_{9-x}\text{Cu}_x\text{Ge}_4$. So not only the competition between Kondo effect and RKKY interaction but also the change in the CF scheme could be the driving force in this quantum critical scenario. To prove that this CF shift is a crucial tuning parameter in terms of the observed quantum critical transition, further INS experiments on other Ni/Cu-composition are in progress, to study the change of the CF scheme in detail, especially around the quantum critical transition ($x = 0.4$) itself.

4. Acknowledgments

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