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# Specific heat in $CeNi_4Cu$ and $YbNi_4Cu$

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**Abstract**

The temperature dependence of specific heat for the compounds $CeNi_4Cu$ and $YbNi_4Cu$ is analysed. These studies are supported by magnetic susceptibility and x-ray photoemission spectroscopy measurements. The scheme of the energy levels created by the splitting due to the crystal electric field is determined from the Schottky contribution to the specific heat. Anomalies observed at low temperatures are discussed in the framework of heavy-fermion/Kondo physics. It is found that an external magnetic field has a strong influence on the low temperature part of the specific heat.

## 1. Introduction

Specific heat is a unique tool for obtaining information on magnetic properties, phase transitions and energy level distribution. This technique has appeared to be exceptionally useful in studies on such materials as superconductors, heavy fermions and ferromagnets. It also enables an additional verification for the presence of the non-Fermi-liquid behaviour or quantum critical phenomena [1–5].

In this paper the investigations of the specific heat of $CeNi_4Cu$ and $YbNi_4Cu$ are presented and supported by the magnetic susceptibility and x-ray photoemission spectroscopy (XPS) measurements. Both the cerium-based and ytterbium-based compounds are of special interest because of their unstable valence state. In the case of Ce there is a nearly empty 4f shell, and for Yb a nearly full 4f shell; therefore, Yb is a hole counterpart of Ce. These features may lead to hybridization effects, which manifest themselves in phenomena like Kondo lattice and heavy-fermion behaviour. We determine the electronic and phonon contributions to the specific heat and discuss the observed anomalies in the context of the possible presence of such effects.

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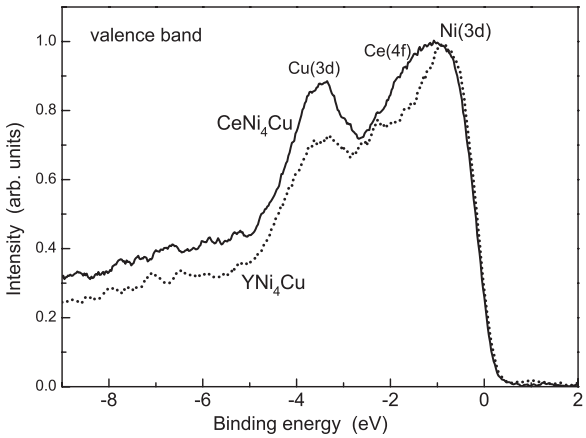


**Figure 1.** XPS valence band of $CeNi_4Cu$. For the sake of comparison the spectrum of nonmagnetic $YNi_4Cu$ is also displayed.

## 2. Experimental details

The polycrystalline $RNi_4Cu$ compounds (R = Ce, Yb) were prepared by induction melting of the constituent elements under an argon atmosphere [6].

The specific heat was measured from pumped helium up to room temperature employing the quasi-adiabatic method and using a specific heat option of the Quantum Design PPMS system.

The x-ray photoemission spectra were obtained using the Al K$\alpha$ source (1487.6 eV) with a Physical Electronics PHI 5700/660 XPS Spectrometer.

Measurements of the dc susceptibility were carried out on a MagLab2000 instrument providing magnetic field up to 9 T and temperatures down to 2 K.

## 3. Magnetic and spectroscopic properties

The crystallographic structure of $RNi_4Cu$ is of the hexagonal $CaCu_5$-type, space group $P6/mmm$. R occupies the 1a site $(0, 0, 0)$ and Ni(1) the 2c site $(1/3, 2/3, 0)$. Ni(2) and Cu are statistically distributed over the 3g sites $(1/2, 0, 1/2)$. The typical lattice constants are $a = 4.8468$ Å and $c = 4.0028$ Å (for $YbNi_4Cu$).

Our previous studies on $CeNi_4Cu$ has revealed its paramagnetic properties with $\mu_{\mathrm{eff}} = 0.9\ \mu_{\mathrm{B}}$/f.u. and $\theta = -11.7$ K [6]. The resistivity behaviour resembles a Kondo impurity system with a minimum of $\rho(T)$ at about 12 K. This reduced effective magnetic moment (in comparison with the theoretical value of 2.54 $\mu_{\mathrm{B}}$) suggests the possibility of a mixed valence state. This is verified by the XPS measurements of the Ce(3d) spectrum.

Figure 1 shows the valence band of $CeNi_4Cu$ in comparison with a result for the nonmagnetic $YNi_4Cu$. Yttrium provides a negligible contribution to the valence band; therefore, a few general conclusions can be derived based on the difference between the two spectra. It is seen that there is a contribution of the Ce($4f^1$) state between 1–2 eV below $E_{\mathrm{F}}$. In addition, the Cu(3d) peak seems to differ for the two compounds. The proximity of the Ce(4f) peak to the Fermi level promotes the possibility of the mixed valence behaviour. This can be estimated quantitatively by analysis of the core Ce(3d) spectrum within the confines of the Gunnarsson and Schönhammer (G–S) model [7–9] if apart from the main

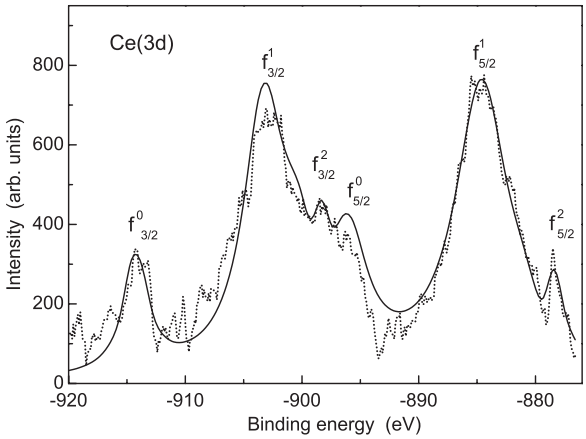


**Figure 2.** Ce(3d) spectrum of $CeNi_4Cu$. The solid line represents a multi-peak fit.

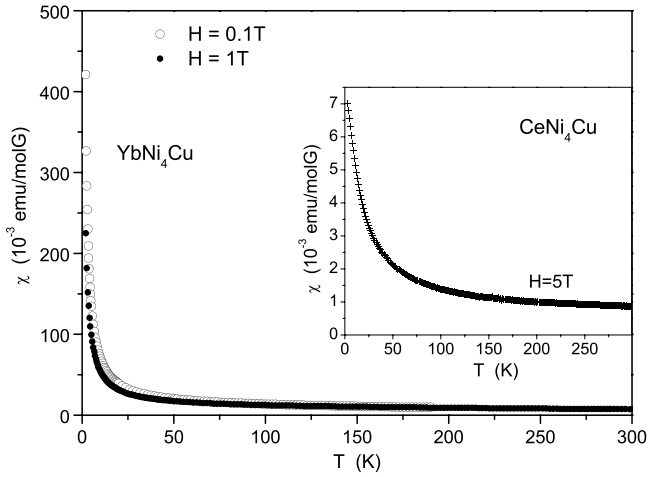


**Figure 3.** Magnetic susceptibility of $YbNi_4Cu$ and $CeNi_4Cu$ (inset).

peaks, additionally, the appropriate satellites are noticeable (figure 2). From the intensity ratios $r = I(f^2)/[I(f^1) + I(f^2)]$ and $r_0 = I(f^0)/[I(f^0) + I(f^1) + I(f^2)]$ one can deduce the hybridization parameter $\Delta \approx 20$ meV and the f-occupancy $n_f \approx 0.8$.

From our XPS studies of the valence band of $YbNi_4Cu$ we have found that it does not exhibit a mixed valence state [10]. This compound seems to be dominated by the $Yb^{3+}$ configuration, which has been additionally confirmed by the full value of the effective magnetic moment $\mu_{eff} \approx 5\ \mu_B$/f.u. The paramagnetic Curie temperature is equal to $-195$ K, which suggests the presence of antiferromagnetic correlations; however, down to 2 K this compound does not order magnetically. As one can see in figure 3, the magnetic susceptibility is large at $T \to 0$ K, which may be due to the creation of heavy fermions. The increase of the applied magnetic field from 0.1 T up to 1 T causes a significant decrease of the susceptibility. This could be due to lowering of the Néel temperature but the specific heat studies discussed in the next section do not support this explanation. The magnetic susceptibility of $CeNi_4Cu$ is much lower, but nevertheless still significant (see the inset of figure 3).

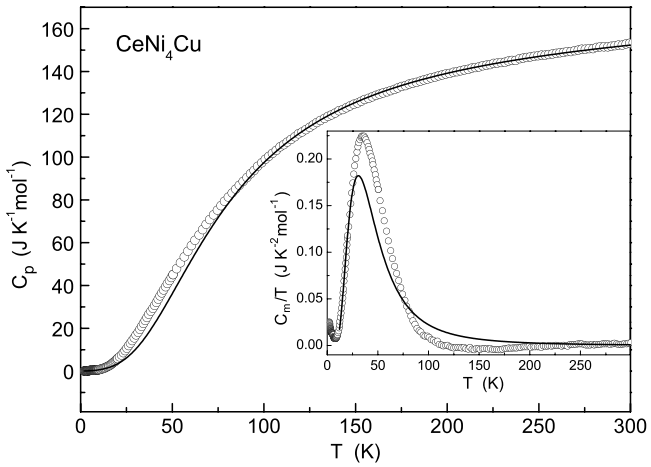


**Figure 4.** Temperature dependence of the specific heat of $CeNi_4Cu$, fitted using equation (1). Inset: the magnetic contribution to the specific heat obtained by subtracting the phonon and electronic contributions. The solid line is the $C_m/T$ versus $T$ fit with equation (2).

## 4. Specific heat

Figure 4 shows the temperature dependence of the specific heat for $CeNi_4Cu$. To get the magnetic contribution due to the Ce ions the electronic and the phonon contributions have to be subtracted. To perform this there are two approximations, which are usually used. First, one can refer to a nonmagnetic analogue, e.g. La- or Y-based compound [11]. The second possibility consists in looking for an optimal fit to the standard formulae describing the electronic and the phonon contributions. Here, the second approach is employed. The solid line in figure 4 presents a fit of $C_p(T)$ by the standard formula:

$$C_p(T) = \gamma T + \frac{9NR}{1-\alpha T}\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{(e^x-1)^2} \tag{1}$$

where the first and the second term correspond to the electronic and the phonon contribution, respectively. $N = 6$ is the number of atoms in the formula unit and $x = \hbar\omega/k_B T$. At the higher temperatures the specific heat can take values over the Dulong–Petit limit; therefore, a small anharmonic correction, $\alpha$, has been included in equation (1) [12].

The obtained values of the parameters are: the Debye temperature $\Theta_D = 320$ K, the electronic specific heat coefficient $\gamma = 25$ mJ K$^{-2}$ mol$^{-1}$, and $\alpha = 8 \times 10^{-5}$ K$^{-1}$.

A similar analysis has been carried out for $YbNi_4Cu$ (figure 5), yielding $\Theta_D = 302$ K, $\gamma = 10$ mJ K$^{-2}$ mol$^{-1}$ and $\alpha = 35 \times 10^{-5}$ K$^{-1}$.

The insets of figures 4 and 5 display the difference between the measured values of the specific heat and the estimated electronic and phonon contributions for $CeNi_4Cu$ and $YbNi_4Cu$, respectively. This magnetic part is plotted as $C_m/T$ versus $T$, which facilitates the determination of the entropy just by integration of the underlying area. The values of the entropy obtained by integrating up to room temperature are relatively small, reaching about 10 J K$^{-1}$ mol$^{-1}$ for both compounds, which means that no more than only the three lowest doublets are populated at room temperature. A system of discrete levels results from the removal of the degeneracy of the ion's $(2J + 1)$-fold degenerate energy level by the crystal electric field (CEF). The subsequent thermal population of the energy levels leads to a maximum in the specific heat known as the Schottky anomaly. This peak of $C_m/T$ versus $T$

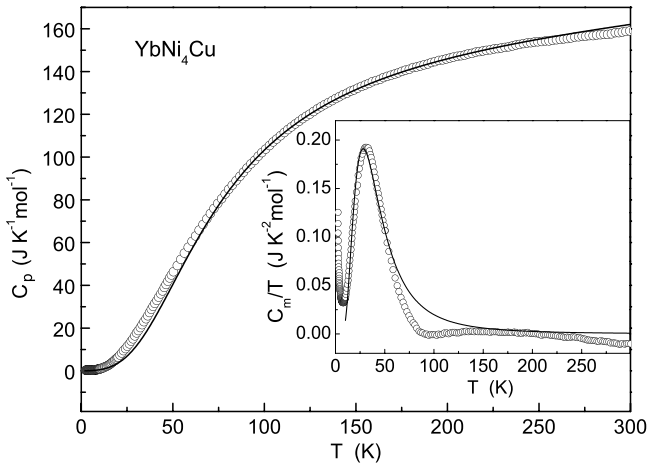


**Figure 5.** Temperature dependence of the specific heat of $YbNi_4Cu$, fitted using equation (1). Inset: the magnetic contribution fitted with equation (2).

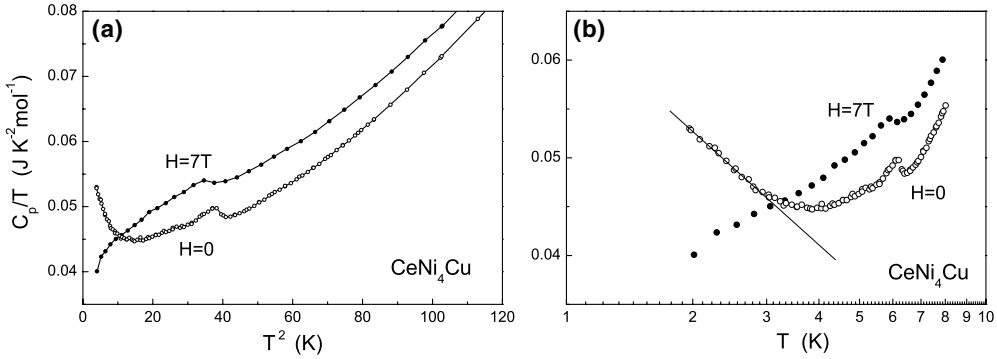


**Figure 6.** $CeNi_4Cu$: (a) $C_p/T$ versus $T^2$, (b) $C_p/T$ versus $T$ at low temperatures and logarithmic scale of temperature.

can be reproduced by the following formula [13]:

$$C_{\mathrm{Sch}}(T) = \frac{R}{T^2}\left[\frac{\sum_{i=0}^{n-1}\Delta_i^2 \mathrm{e}^{-\Delta_i/T}}{\sum_{i=0}^{n-1}\mathrm{e}^{-\Delta_i/T}} - \left(\frac{\sum_{i=0}^{n-1}\Delta_i \mathrm{e}^{-\Delta_i/T}}{\sum_{i=0}^{n-1}\mathrm{e}^{-\Delta_i/T}}\right)^2\right] \tag{2}$$

where $n$ denotes the number of the energy levels and $\Delta_0 = 0$.

For $Ce^{3+}$ ions the 4f levels split into three doublets ($n = 3$) or a doublet and quartet in hexagonal or cubic symmetry, respectively. For our hexagonal compounds the first case should be realized, but based on the fit presented in the inset of figure 4 the latter level arrangement occurs. The quartet is separated by 105 K from the ground state doublet (assumed to be at 0 K).

For Yb the $J = 7/2$ multiplet splits into four doublets ($n = 5$) but the $C_m/T$ versus $T$ dependence is best refined (inset of figure 5) with three doublets: $\Delta_0 = 0$, $\Delta_1 = 85$ K and $\Delta_2 = 113$ K; this is additionally justified by the small value of the overall entropy.

In figures 6 and 7, $C_p/T$ versus $T^2$ is plotted because it enables an easy estimation of the electronic specific heat coefficient. Both $CeNi_4Cu$ and $YbNi_4Cu$ show an interesting behaviour at low temperatures. For $CeNi_4Cu$ a very small λ-type anomaly is observed (figure 6), like

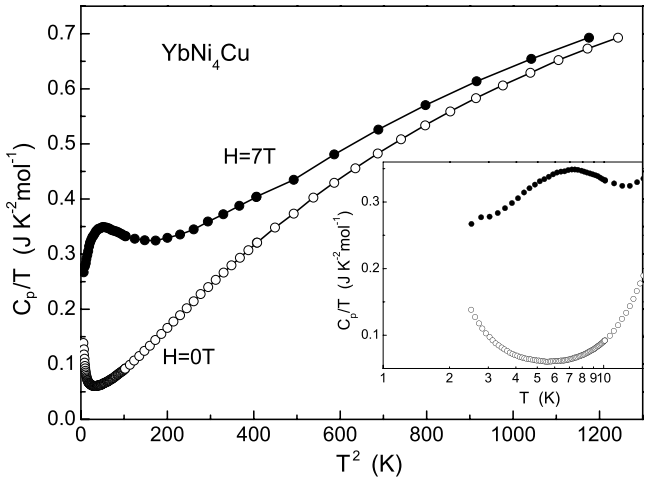


**Figure 7.** $C_p/T$ versus $T^2$ for $YbNi_4Cu$. Inset: $C_p/T$ versus $T$ at low temperatures.

in the case of the previously studied $CeNi_4Al$ compound [14]. Below this anomaly an upturn of the $C_p/T$ versus $T^2$ dependence occurs. After application of the external magnetic field of 7 T the anomaly is smaller and it hardly changes position—it shifts to lower temperatures only by about 0.25 K. However, the lowest temperature part changes dramatically; i.e., the sudden increase of $C_p/T$ below 3 K is now converted to a more rapid decrease. A possible explanation is that the peak at 6 K corresponds to a small amount of antiferromagnetic phase. The Néel temperature can decrease with magnetic field, but the observed shift of the anomaly towards lower temperatures is relatively small. However, the peak can also appear because of a small number of Ce ions in wrong crystallographic positions and characterized by a good localization of the magnetic moments, leading to a Kondo impurity-like behaviour [11], which requires the presence of antiferromagnetic correlations. The paramagnetic Curie temperature is $\theta = -12$ K [6], which provides a rough estimation of the Kondo temperature $T_K = |\theta|/2 = 6$ K [15], being in good coincidence with the specific heat anomaly position. The upturn below 3 K fulfils a logarithmic law (figure 6(b)); therefore, it may be connected with a non-Fermi-liquid behaviour at the lowest temperatures [16]. The effect of the magnetic field is to recover the Fermi-liquid state.

In the case of $YbNi_4Cu$ a similar field effect is observed (figure 7); however, lower temperatures would be required to verify a logarithmic divergence. Moreover, the applied magnetic field not only causes a switch between the increasing/decreasing heat but also reveals a maximum at about 7 K. Our previous magnetometric investigations have not shown any evidence of a transition to a magnetically ordered state; hence the origin of the field-induced peak is not clear. Nevertheless, the main effect of the magnetic field is, like for $CeNi_4Cu$, to destroy the (presumable) non-Fermi-liquid state.

The sudden increase of $C_p/T$ observed for both compounds below 3 K is probably reminiscent of heavy-fermion physics. The large values of the low temperature magnetic susceptibility (figure 3) corroborate such a suspicion.

## 5. Conclusions

The research on the $CeNi_4Cu$ and $YbNi_4Cu$ compounds presented has revealed that both materials show a tendency to the heavy-fermion state below about 3 K. This is deduced based

on the significant increase of $C_p/T$ and large values of the magnetic susceptibility at low temperatures. A strong influence of the magnetic field on the specific heat below 3 K has been observed.

For $CeNi_4Cu$ an anomaly in $C_p/T$ is found at 6 K, which may be due to the antiferromagnetic correlations promoting a Kondo effect.

The analysis of the Schottky peak appearing in the magnetic part of the specific heat has provided the scheme of the energy levels being a result of the splitting by the crystal's electric field. Instead of the three doublets expected for Ce in a hexagonal compound, a quartet separated by 105 eV from the ground state doublet has been determined. For Yb, three doublets with $\Delta = 0$, 85 and 113 K have been obtained.

## Acknowledgment

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