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Specific Heat of the Ce(Ni$_{1-x}$Cu$_x$)$_4$Mn Compounds

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Specific heat of the Ce(Ni$_{1-x}$Cu$_x$)$_4$Mn compounds has been studied. The samples are prepared by induction melting and it is found, based on the X-ray diffraction, that all the compounds keep the CaCu$_5$-type structure. This series exhibits a transition between the ferromagnetically ordered CeNi$_4$Mn and the spin-glass CeCu$_4$Mn compounds, which is well visible in the measurements of the ac susceptibility peak as a function of the magnetic field frequency and in the magnetization relaxation. In the present research we explore the behavior of the specific heat for various x. The changes of the electronic specific heat coefficient γ are determined by analysis of the low temperature part of the $C_p/T(T^2)$ dependence. We also observe that the magnetic phase transition is only detectable in the specific heat signal after extraction of the magnetic contribution of the Mn atoms. This is carried out by subtraction of the specific heat of the reference sample.

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1. Introduction

Intermetallic compounds containing Ce are known to exhibit unusual magnetic properties. The increased interest in the physical properties of the CeNi$_4$Mn compound appeared after Singh et al. [1] had suggested half-metallic properties. Later studies classified this compound rather as a semimetal [2]. In CeNi$_4$Mn the main contribution to the magnetic moment is carried by the Mn atoms. The rest of the magnetic moment is mainly due to the four Ni atoms, which together gives 1.1 μ_B/f.u., supplemented by a small contribution of the antiferromagnetically polarized Ce (-0.14 μ_B/f.u) [3].

For the CeCu$_4$Mn compound, our recent results of the AC susceptibility, field-cooled (FC) and zero-field-cooled (ZFC) DC magnetization and remanent magnetization relaxation have shown the typical spin-glass (SG) behavior [4]. The AC susceptibility measurements revealed a shift of the characteristic peak to higher temperatures with the increasing frequency. The freezing temperature T_f for the lowest value of the frequency $\omega = 10$ Hz was equal to 51.3 K. A large difference between the FC and ZFC susceptibilities was observed below the freezing temperature.

We have additionally shown that a partial substitution of Cu in the place of Ni or Nd in the place of Ce in the ferromagnetically ordered CeNi$_4$Mn compound leads also to the spin-glass-like behavior [4].

Specific heat is a unique tool for obtaining information on the magnetic properties, phase transitions and energy levels distribution. In this paper we describe our studies of C_p as a function of temperature and magnetic field for selected representatives of the Ce(Ni$_{1-x}$Cu$_x$)$_4$Mn series of compounds.

2. Experimental details

Polycrystalline samples of the Ce(Ni$_{1-x}$Cu$_x$)$_4$Mn series with $x = 0$, 0.25, 1 were prepared by the induction melting of the stoichiometric amounts of the pure elements in an argon atmosphere. The samples were turned and re-melted several times to achieve a better homogeneity.

The crystal structure was established by the powder X-ray diffraction technique, using the Co K_α radiation. All the prepared compounds crystallized in the hexagonal CaCu$_5$-type structure, space group $P6/mmm$. Ce occupies the 1a site (0, 0, 0) and Ni(1) the 2c site (1/3, 2/3, 0). Ni(2) and Mn are statistically distributed over the 3g sites (1/2, 0, 1/2).

The heat capacity measurements have been carried out using the PPMS commercial device (Quantum Design), in the temperature range 1.9–300 K by relaxation method with the two-τ model.

3. Results

The specific heat C_p/T of the Ce(Ni$_{1-x}$Cu$_x$)$_4$Mn compounds in zero magnetic field and in $H = 9$ T is represented in Fig. 1. We have not observed any real sign of the magnetic order down to 2 K and the accessible maximal value of the applied magnetic field does not change noticeably the C_p/T vs. T curves. The arrows show the characteristic temperatures (magnetic ordering

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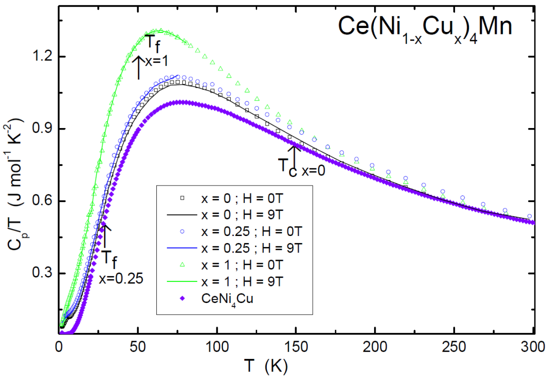

Fig. 1. The specific heat of Ce(Ni$_{1-x}$Cu$_x$)$_4$Mn compounds and the reference CeNi$_4$Cu sample as the C_p/T vs. T dependence. The open symbols and the solid lines correspond to the measurements in the external magnetic field $H = 0$ T and $H = 9$ T, respectively. The arrows show the characteristic temperatures for those compounds.

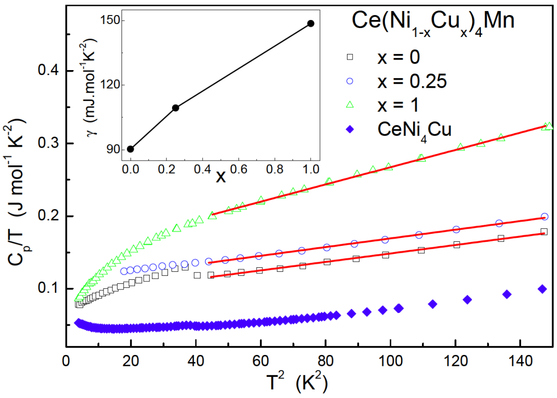

Fig. 2. Low-temperature specific heat of the Ce(Ni$_{1-x}$Cu$_x$)$_4$Mn and the CeNi$_4$Cu compounds. The lines represent the electronic contribution to the specific heat. Inset: the value of the Sommerfeld coefficient as the dependence on the copper concentration.

or the freezing temperature) obtained from the magnetic measurements [4–6].

In Fig. 1 the previous result [7] for the CeNi$_4$Cu compound is additionally presented, as it will be further used to estimate the Mn contribution to the magnetic specific heat.

In general, the specific heat of metals can be considered as the sum of the independent electronic, lattice (phonon) and magnetic contributions [8]:

$$C_p = C_{\mathrm{el}} + C_{\mathrm{ph}} + C_{\mathrm{mag}}. \tag{1}$$

The electronic specific heat is expressed as $C_{\mathrm{el}} = \gamma T$, where γ is the Sommerfeld coefficient and at low temperatures the phonon part can be approximated by the Debye law βT^3. The low temperature part of the $C_p/T(T^2)$ dependence is demonstrated in Fig. 2. The extrapolation

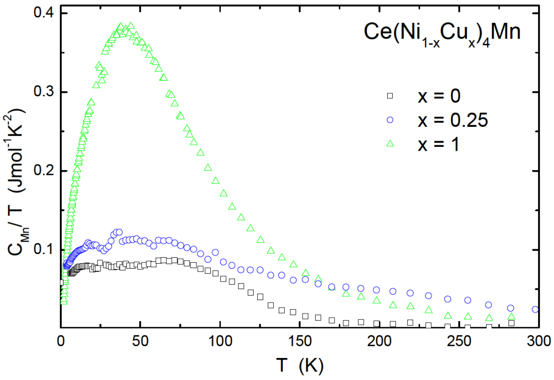

Fig. 3. The magnetic contribution to the specific heat of Ce(Ni$_{1-x}$Cu$_x$)$_4$Mn received as the difference between $C_p(T)/T$ of the Ce(Ni$_{1-x}$Cu$_x$)$_4$Mn and CeNi$_4$Cu compounds. A growth of a peak starts close to the ordering temperature ($x = 0$) and the freezing temperature ($x > 0$).

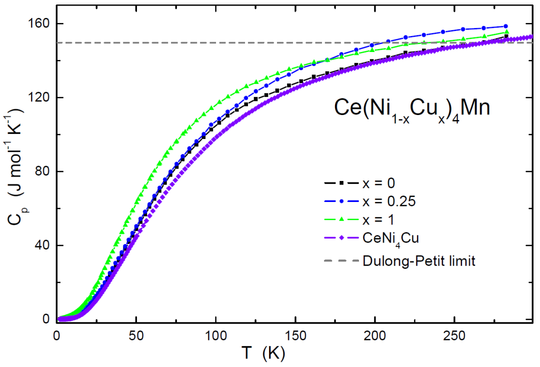

Fig. 4. Temperature dependence of the specific heat of Ce(Ni$_{1-x}$Cu$_x$)$_4$Mn and CeNi$_4$Cu compounds. The dash line represent the Dulong–Petit limit (3NR).

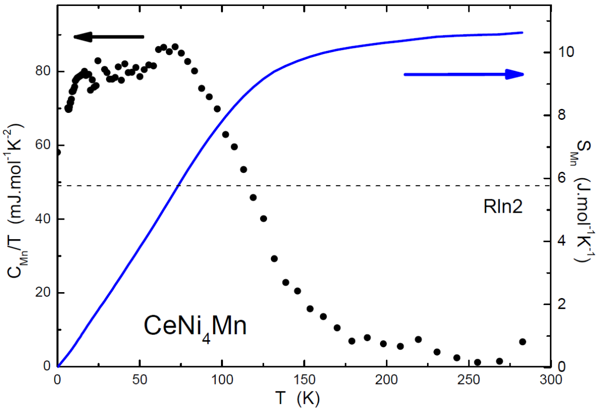

Fig. 5. Left axis: the Mn contribution to the specific heat of CeNi$_4$Mn received as the difference between $C_p(T)/T$ of CeNi$_4$Mn and CeNi$_4$Cu. Right axis: the Mn entropy S_{Mn} as a function of temperature for CeNi$_4$Mn.

to $T = 0$ K has been carried out for $T > 6$ K since slight traces of the Ce oxide can be noticed at lower temperatures. The values of the electronic specific heat coefficient derived from the extrapolation are plotted in the inset of Fig. 2 versus the concentration of the Cu atoms. The obtained large values, especially for $CeCu_4Mn$, are not a sign of a heavy fermion state but result rather from other contributions, like disorder inherent to the SG systems or crystal electric field effects.

Since the magnetic and/or SG ordering is not directly visible in the presented specific heat measurements we have used $CeNi_4Cu$ as a nonmagnetic analog [7, 9] for the $Ce(Ni_{1-x}Cu_x)_4Mn$ compounds. It means that the subtraction of the specific heat of the analog sample should enable a rough estimation of the exclusive Mn contribution: $C_p[Mn] \approx C_p[Ce(Ni_{1-x}Cu_x)_4Mn] - C_p[CeNi_4Cu]$. It is assumed that Ni does not contribute to the magnetic properties of the compounds studied and, hence, the same analog compound is used also for $x > 0$.

C_p/T of $Ce(Ni_{1-x}Cu_x)_4Mn$ after the subtraction procedure is shown in Fig. 3. It is evident even better than in Fig. 1 that there is a huge excess heat for the $CeCu_4Mn$ compound. Apart from the disorder and difference in the crystalline electric field (CEF) induced Schottky contributions, an additional source of the significant difference in the specific heat of the $CeCu_4Mn$ and $CeNi_4Mn$ compounds may be the change of the anharmonic contribution to the specific heat. As can be seen in Fig. 4, when approaching the room temperature the specific heat exceeds the Dulong–Petit limit (3NR) and this fact cannot be described within the harmonic approximation. This limit is crossed at about 270 K for $CeNi_4Mn$ and already at 230 K for $CeCu_4Mn$. The intermediate behavior for $x = 0.25$ ($CeNi_3CuMn$) indicates that the differences develop gradually with the increase of the Cu content in $Ce(Ni_{1-x}Cu_x)_4Mn$.

Figure 5 demonstrates that the magnetic contribution of Mn shows a peak at about 70 K and the entropy reaches the value of $R\ln 2$ exactly at this temperature. It is found that $CeNi_4Cu$ is not a good reference sample for the Cu-rich $Ce(Ni_{1-x}Cu_x)_4Mn$ compounds due to the excess heat, which would provide too large values of the entropy.

4. Conclusions

The first studies of the specific heat for the series of compounds $Ce(Ni_{1-x}Cu_x)_4Mn$ have been presented. In contrast to the magnetometric measurements neither the magnetic ordering temperature ($CeNi_4Mn$) nor the freezing temperature (for $x > 0$) have been visible in the direct specific heat measurements. However, it was found that the subtraction of the specific heat of the nearest acceptable nonmagnetic analog material ($CeNi_4Cu$) reveals a peak corresponding well to the magnetic contribution of manganese in $CeNi_4Mn$. Any discrepancies can result from the neglect of the Ce and Ni contributions to the magnetic properties. In spite of these assumptions the magnetic entropy of $CeNi_4Mn$ reaches the value of $R\ln 2$ close to the ordering temperature. It seems that for $x > 0$ $CeNi_4Cu$ is not a good reference sample and the crystal electric field, disorder and anharmonic contributions to the heat capacity have to be investigated.

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