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TRANSITION FROM KONDO-LATTICE TO INTERMEDIATE VALENCE STATE IN $Ce(Cu_{1-x}Ni_x)_5$ COMPOUNDS

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A number of studies on the temperature dependence of the magnetic susceptibility[1-4], thermopower[4,5,6], electroresistivity[4], the absorption[2] and of the shift[7] of x-ray lines of cerium in the intermetallic compounds $Ce(Cu_{1-x}Ni_x)_5$ have shown that with increasing nickel concentration, the cerium ion undergoes a transition from the trivalent stable state in $CeCu_5$ to the "strong" intermediate valence state in $CeNi_5$.

The purpose of the present paper is the study of this transition by measuring the low temperature specific heat capacity, the magnetic susceptibility and neutron inelastic magnetic scattering. The susceptibility was measured in each point of the temperature for several values of the external field. In order to avoid the influence of the impurities, the measured susceptibility was extrapolated to the infinite value of the field ($\chi = f(1/H)$). The reciprocal susceptibility vs temperature for four values of concentration $x=0.0$, 0.4, 0.5, 0.6 is shown in fig.1. For $0.0 \leqslant x \leqslant 0.4$ susceptibility follows a typical Curie-Weiss law with an effective moment for Ce ion of $\sim 2.5\ \mu_B$ very close to the value of the free ion magnetic moment Ce^{+3} $\mu = 2.54 \mu_B$. With increasing Ni concentration, the linear dependence χ^{-1} on the temperature disappears and the susceptibility decreases. This behavior of the

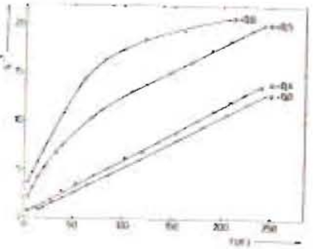

Fig.1 Temperature dependence of the reciprocal magnetic susceptibility of $Ce(Cu_{1-x}Ni_x)_5$ compounds for $x=0.0$, 0.4, 0.5, 0.6. χ^{-1} in 10^{-4} g/emu units.

susceptibility for various concentration points out a transition of $Ce(Cu_{1-x}Ni_x)_5$ into an intermediate valence state in the range of $0.4 \leqslant x \leqslant 0.6$, which agrees with the results of papers[1-7].

In fig.2 we give the experimental temperature dependence of the specific heat for several concentrations. The copper substitution for nickel in $Ce(Cu_{1-x}Ni_x)_5$ compounds, leads to a decrease of the specific heat. In the investigated temperature range the specific heat is mainly attributed to the contribution of 4f and conduction electrons as a result of the comparison with the specific heat of the isostructural compounds $LaNi_5$ and $LaCu_5$. For

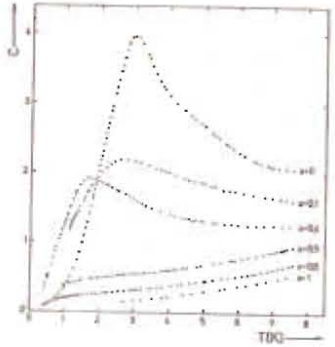

Fig.2 Specific heat capacity vs temperature for $Ce(Cu_{1-x}Ni_x)_5$ at $x=0.0$, 0.1, 0.4, 0.5, 0.6, 1.0. C in J/mol·K units. Experimental points for $x=0.0$: after [8].

$0.0 \leqslant x \leqslant 0.1$ the specific heat maximum strongly decreases (about twice). A small decrease of this maximum ($\sim 10\%$) is observed in the range of $0.2 \leqslant x \leqslant 0.4$ and furthermore a strong decrease is revealed for x between 0.4 and 0.5 (about six times).

To discuss the measured specific heat results, we shall start with the main results of our previous work[8] on $CeCu_5$ compound: $CeCu_5$ undergoes an antiferromagnetic transition for T=3K, it appears as a system which displays a competition between the antiferromagnetic exchange and Kondo scattering of the conduction electrons on the 4f moments. An analysis of the inelastic neutron scattering measurements[8] indicates that the first excited level $\Gamma_9\ |\pm 3/2\rangle$ of Ce^{+3} ion lies at the distance $\Delta = 17.5$meV above the ground level $\Gamma_7\ |\pm 1/2\rangle$. The inelastic neutron scattering and specific heat of $CeCu_5$ permitted to establish a relation between Δ, J (antiferromagnetic exchange constant) and T_K (Kondo temperature): $\Delta > J > T_K k_B$. When copper is substituted by nickel, for $0.0 \leqslant x \leqslant 0.1$ the 4f level approaches the Fermi level that leads to an increase of Kondo scattering and to suppression of the antiferromagnetic order. Hence, the drastic decrease of the specific heat maximum for x between 0.0 and 0.1 is apparently connected with the decrease of the magnetic contribution. The further process of transition to the intermediate valence state with increasing Ni concentration ($x > 0.4$) leads to a continous disappearance of the hump of the specific heat and as is seen in fig.2 it takes place mainly in the concentration range of $0.4 < x < 0.6$.

Fig.3 is a plot of C/T as a function of T^2. The electron conduction contribution was determined by extrapolation to T=0. In the same figure it may be also seen the Kondo scattering contribution, given by the logarithmic increase with temperature dec-

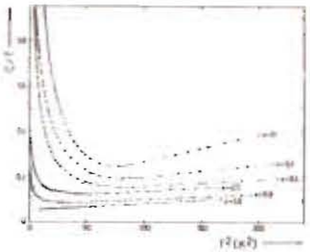

Fig.3 Dependence C/T on T^2 of $Ce(Cu_{1-x}Ni_x)_5$ compounds. Dotted line: extrapolation to T=0. C/T in $J/mol \cdot K^2$ units.

rease as it is expected for the trivalent Kondo systems /9/. For $CeNi_5$ the Kondo scattering increasing of C/T on T^2 is missed and the temperature dependence of the specific heat is very like to the corresponding behavior of the isostructural compound $LaNi_5$ /10/. Fig.4 shows the linear term γ of the specific heat in $Ce(Cu_{1-x}Ni_x)_5$ as a function on nickel concentration. Becomes relevant a decrease of the electron density of states at the Fermi level for the transition from concentrated Kondo system to the intermediate valence

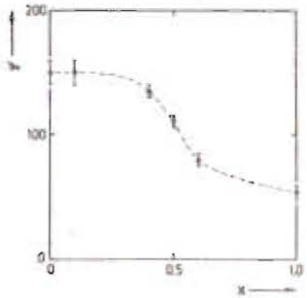

Fig.4 The linear term γ of the specific heat vs nickel concentration on $Ce(Cu_{1-x}Ni_x)_5$ compounds. γ in $mJ/mol\,K^2$ units.

state in $Ce(Cu_{1-x}Ni_x)_5$ for $0.4 < x < 0.6$. It should be noted that, by comparing the results of $Ce(Pd_{1-y}Ag_y)_3$ /11/ with those of the present work and of /4/ we may infer an analogous situation: in both the cases, for a change from a Kondo regime to one of intermediate valence, a maximum of the magnetic contribution value in electroresistivity ρ_M and a smooth decrease of γ were observed. The behavior of ρ_M, γ and of low temperatures susceptibility (χ) as a function of the number of 4f electrons (n_f) has been discussed in the theoretical papers /12,13/. There was predicted a monotonous decrease of ρ_M, γ and χ for n_f between 1 and 0, that qualitatively agrees with the experimental results obtained for γ and χ in the present work.

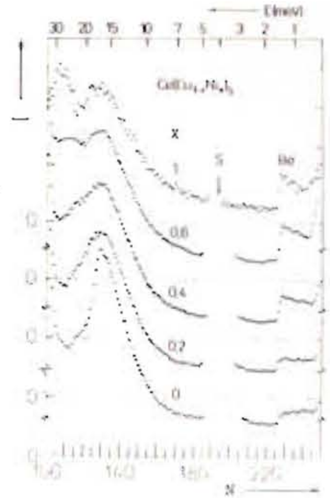

Fig.5 TOF spectra of inelastically scattered neutrons on $Ce(Cu_{1-x}Ni_x)_5$. Be' - beryllium filter precut-off, S - the peak given by the specific work at pulsed reactor IBR-30, ε - energy transfer in meV, N - channel number (channel width 64 μsec), I - intensity in arbitrary units.

The inelastic neutron scattering experiments were carried out with a time of flight (TOF) spectrometer in inverted geometry with a beryllium filter in front of the detector at the IBR-30 pulsed reactor of JINR - Dubna. In fig.5 we show the spectra on $Ce(Cu_{1-x}Ni_x)_5$ for x=0.0, 0.2, 0.4, 0.6 at the temperature of T=10K and for x=1.0 at T=30K. The spectrum from the $CeCu_5$ sample shows a peak at the energy transfer of 17.5meV caused by a crystal field transition. For the substitution of Cu by Ni, at x=0.2 this peak disappears. The spectrum of the $CeNi_5$ sample is very similar to that of $LaNi_5$ which offers only the pure nuclear scattering. The disappearance of magnetic peak due to substitution of Cu for Ni, may be caused by two reasons: the substitutional disorder (SD), which leads to a random crystalline field distribution, and the increase of s-f interaction which broadened the crystal field levels. The measurements on the $Pr(Cu_{1-x}Ni_x)_5$ compounds, where all the variations of the spectra with increasing x were induced by SD (the weak and independent on x s-f exchange), showed that the main factor which determined the variation of the magnetic excitation spectra, at least for small x ($x < 0.4$), was SD. Because most of the macroscopic properties depend upon the relation between Δ , J and T_K /14/, which should be changed by SD, these macroscopic properties are strongly influenced by SD.

CONCLUSION

The successive substitution of Cu for Ni in $Ce(Cu_{1-x}Ni_x)_5$ responsible for the growing hybridization of the 4f electron with the conduction electrons leads to a monotonous decrease of the electronic specific heat coefficient γ .

The strong decrease of γ in the concentration range of about x=0.5 indicates a continuous transition from the concentrated Kondo system to state of intermediate valence. A resonance behavior in the density of electronic states accompanied with such a transition /4/ was not observed from specific heat measurements.

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Горемычкин Е.А. и др. E14-85-789
Исследование перехода от состояния концентрированной кондо-системы к состоянию с переменной валентностью в ряду $Ce(Cu_{1-x}Ni_x)_5$

Проведены измерения магнитной восприимчивости, низкотемпературной части удельной теплоемкости и неупругого рассеяния тепловых нейтронов на непрерывном ряде твердых растворов $Ce(Cu_{1-x}Ni_x)_5$ для $0,0 \le x \le 1,0$. Наблюдаемое уменьшение восприимчивости и удельной теплоемкости при увеличении концентрации никеля позволило сделать выводы о характере перехода от состояния концентрированной кондо-системы, при x=0,0 к состоянию с промежуточной валентностью при x=1,0.

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Goremychkin E.A. et al. E14-85-789
Transition from Kondo-Lattice to Intermediate Valence State in $Ce(Cu_{1-x}Ni_x)_5$ Compounds

Measurements of the magnetic susceptibility, the low temperature specific heat capacity and the inelastic neutron scattering have been carried out on the continuous solid solution $Ce(Cu_{1-x}Ni_x)_5$, $0 \le x \le 1$. The anomalous decrease of the susceptibility and of the specific heat capacity with the nickel concentration allows one to conclude from the Kondo-lattice system at x=0 to the intermediate valence system with x=1.

The investigation has been performed at the Laboratory of Neutron Physics, JINR.

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