Effect of a transition to a mixed-valence state on the specific heat of the compound $Ce(Cu_{1-x}Ni_x)_5$

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Measurements of the low-temperature specific heat of the intermetallic compounds $Ce(Cu_{1-x}Ni_x)_5$ ($0 \leqslant x \leqslant 0.8$) in magnetic fields $B = 0$–8 T reveal a peak due to localized f electrons of cerium ions. The position of this peak depends on x and B. At $x \geqslant 0.6$, the peak is not observed; this result is interpreted as evidence that the cerium ions go into a mixed-valence state.

A transition to a mixed-valence state is customarily associated with the delocalization of an f electron. In this letter we report an effort to determine the nature of the transformation of the "magnetic" contribution to the specific heat from the 4f-electron localized states of Ce^{3+} ions upon a transition of this sort, for the particular case of $Ce(Cu_{1-x}Ni_x)_5$. As has been shown elsewhere,[1,2] this compound undergoes an electronic phase transition near $x \cong 0.5$, from a state in which cerium has an integer valence, $+3$ ($x < 0.5$), to a mixed-valence state ($x > 0.5$).

The specific heat of polycrystalline samples of $LaCu_5$, $LaNi_5$, and $Ce(Cu_{1-x}Ni_x)_5$ ($x = 0$, 0.2, 0.4, 0.6, and 0.8) is measured in an adiabatic calorimeter[3] ($T = 2$–70 K) in an external magnetic field $B = 0$–8 T. The samples are produced by arc melting.[4] The "magnetic" contribution is defined as the difference between the specific heats of $Ce(Cu_{1-x}Ni_x)_5$ and $La(Cu_{1-x}Ni_x)_5$ samples. The latter is found through a linear interpolation of the values measured for $LaCu_5$ and $LaNi_5$. The temperature dependence of the magnetic contribution to the specific heat of these samples in fields $B = 0$ and 8 T is shown in Fig. 1.

Here are the basic results for $T < 20$ K:

1) The "magnetic"contribution to the specific heat, $\Delta C_m(T)$, is observed only for samples with $x \leqslant 0.4$. For $CeCu_5$ the shape of the peak is similar to that of a Schottky anomaly with a peak temperature $T_m \approx 3$ K (Fig. 1a). For samples with $x = 0.2$ and $x = 0.4$, we observe only a "high-temperature tail" of the anomaly in the temperature interval studied. This result is evidence that T_m decreases with increasing x. An increase in the external field B causes an increase in T_m.

2) In a given field, the values of T_m for the $CeCu_5$ sample are higher than the values of T_m for the samples containing nickel. In the samples with $x = 0.2$ and $x = 0.4$ the values of T_m in a magnetic field $B = 8$ T are approximately the same, and the curves of $\Delta C_m(T)$ differ only in amplitude (Fig. 1b).

3) The specific heat of samples with $x \geqslant 0.6$ does not contain a magnetic contribution and does not depend on the magnetic field.

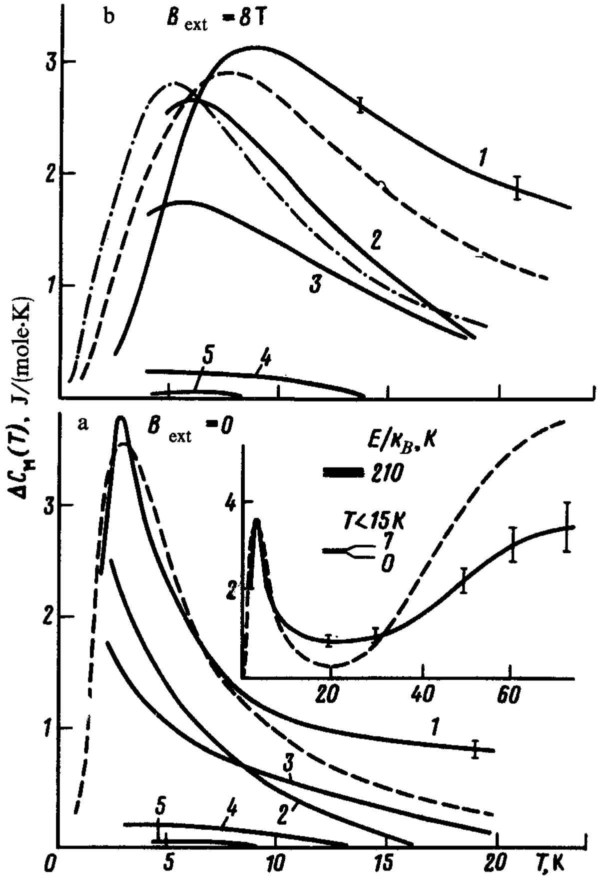

FIG. 1. Magnetic contribution to the specific heat, $\Delta C_m(T)$, for $Ce(Cu_{1-x}Ni_x)_5$ samples in various magnetic fields: 1—$x = 0$; 2—$x = 0.2$; 3—$x = 0.4$; 4—$x = 0.6$; 5—$x = 0.8$. Dashed curves) Calculated Schottky anomaly corresponding to a splitting $\Delta E = 7$ K of the doublet $|\pm 1/2\rangle$ in $CeCu_5$ (Ref. 4) with $B_{eff} = 4$ T, perpendicular to the crystallographic z axis; dot-dashed curves) $\Delta C_m(T)$ from the Zeeman splitting of the doublet $|\pm 1/2\rangle$ ($B_{eff} = 0$). The inset shows an experimental curve of $\Delta C_m(T)$ for $CeCu_5$ along with the theoretical curve, calculated on the basis of the level scheme of Ref. 4.

A qualitative explanation of these results can be offered on the basis of the arguments proposed in Ref. 4. It is assumed that the inequality $E_{CF} \ll E_{ff} > E_{sf}$ holds for $CeCu_5$, where E_{CF} is the energy of the interaction of the Ce^{3+} ion with the crystal electric field, E_{ff} is the energy of the Ruderman-Kittel-Kasuya-Yosida ion-ion exchange interaction, and E_{sf} is the energy of the interaction of the f electron of the cerium ion with conduction electrons. In this case the ground state of the Ce^{3+} ion in the crystal electric field of $CeCu_5$, the Γ_7 doublet $|\pm 1/2\rangle$, splits at low temperatures ($T \lesssim 10$–20 K; see the inset in Fig. 1) under the influence of the effective internal field B_{eff}, which is apparently due to the onset of short-range correlations in the magnetic moments as a result of an ion-ion exchange interaction. This effect is manifested in the specific heat as an anomaly with $T_m \simeq 3$ K and with an entropy $\approx R \ln 2$ ($T \lesssim 20$ K) at $B = 0$. The other levels of the Ce^{3+} ion in the crystal electric field (Γ_8, Γ_9) lie about 200 K above the ground state Γ_7, according to neutron data,[1)] and they begin to affect the specific heat only at $T > 25$ K (see the inset in Fig. 1). An external magnetic field B increases the splitting of the doublet Γ_7, causing an increase in T_m and a change in the amplitude of the anomaly. (It should be noted that Kondo anomalies are substantially wider than Schottky anomalies with the same value of[7] T_m and are suppressed by an external magnetic field.)

Increasing the Ni concentration in $Ce(Cu_{1-x}Ni_x)_5$ is known[5] to promote an increase in E_{sf} and a transition (at $x > 0.5$) to a mixed-valence state; i.e., we have $E_{sf} > E_{ff}$ at $0.5 < x < 1$. This result means that as x is increased from 0 to 0.5 the effectiveness of the exchange interaction of neighboring ions is reduced; i.e., there is a decrease in V_{eff}, and there is a corresponding shift of T_m to a lower temperature (Fig. 1a). For samples with $x = 0.2$ and $x = 0.4$, a field $B = 8$ T is apparently sufficient to completely suppress the ion-ion interaction: The value of T_m in this case is determined primarily by the Zeeman splitting of the $|\pm 1/2\rangle$ doublet in the external magnetic field (Fig. 1b). This interpretation agrees with the suggestion that the ion-ion interaction is of an antiferromagnetic nature. The absence of a contribution of f electrons to the specific heat at $x \geqslant 0.6$ agrees with the interpretation that there is a transition of cerium ions (at $0.4 < x < 0.6$) from a state with a rather well-localized f electron and an integer valence to a state with a partial delocalization or a mixed-valence state. Here the degrees of freedom of the f electron that can absorb an energy $\sim k_B T$ in the temperature range under study are suppressed, and the "magnetic" contribution to the specific heat correspondingly vanishes (the energy of the interconfigurational fluctuations in a mixed-valence state is generally[6] $\gtrsim 100$ K). The decrease in the amplitude of the magnetic contribution to the specific heat and also the blurring of the anomaly that occurs to some extent as x approaches 0.5 can be attributed to a gradual decrease in the lifetime of the f electron in the localized state because of an increase in E_{sf} and to local concentration fluctuations in the sample.

Our qualitative analysis of the experimental data does not explain certain details. For example, the curve of $\Delta C_m(T)$ in $CeCu_5$ is slightly narrower than the corresponding curve for a Schottky anomaly, and there are differences in the theoretical and experimental behavior of T_m as a function of B. To explain these features, it will be necessary to pursue the study of the sf and ff interactions, in particular, to study the question of the existence of a magnetic order in the absence of an external magnetic field.

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[1)]The parameters of the crystal electric field at the Ce^{3+} ion in $CeCu_5$ are $B_2^0 = 10.3$ K and $B_4^0 = -0.49$ K.

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