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Electronic transport properties of $R_xY_{1-x}Ni_5Ge_3$ (R = Ce, Yb) with R elements in Kondo state

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The results of an investigation of electrical resistivity ρ and thermoelectric power S are presented for the solid solutions $Ce_xY_{1-x}Ni_5Ge_3$ ($x \leq 0.5$) and $Yb_xY_{1-x}Ni_5Ge_3$ ($x = 0, 0.5$) in the temperature range 4-400 K. The overall shape of the $\rho(T)$ and $S(T)$ dependences observed for the Ce- and Yb-containing alloys is typical for paramagnetic intermetallics exhibiting a combined effect of Kondo and crystal field (CF) interactions with a low single-ion Kondo temperature T_K, which is generally much lower than the overall CF splitting. The single-ion Kondo interaction does not vary when the Y sublattice is diluted with Ce (T_K ~ 60-80 K). For the Yb-containing alloy, the dependences typical for a Kondo-impurity ground state with T_K < 5 K were observed.

Rare earth compounds / Electronic transport / Kondo effects / Crystal fields

1. Introduction

Ternary rare earth metal-nickel-germanium systems have attracted considerable interest in recent years because of their peculiar crystal structures and greatly varying physical properties [1-3]. Systematic studies of isothermal sections of the phase diagrams of *R*–Ni–Ge systems show the formation of RNi_5Ge_3 intermetallic compounds with YNi_5Si_3-type structure (space group *Pnma*) [4,5]. The peculiarity of this structure type is the formation of one-dimensional -*R*- chains along [010]. The short Y-Y distances in the chain, equal to ~3.9 Å, in the YNi_5Ge_3 compound indicates the existence of Y-Y bonds, while the distance between the chains is above 5.6 Å. Thus, the RNi_5Ge_3 compounds constitute a perspective object for the investigation of real low-dimensional Kondo-systems based on the valence unstable elements Ce or Yb.

According to literature data [5,6], no Ce-containing compound with YNi_5Si_3-type structure is formed in the ternary Ce-Ni-Ge system. In the case of Yb-Ni-Ge a compound with YNi_5Si_3-type structure exists, but the magnetic susceptibility, specific heat, and electrical resistivity do not indicate any Kondo-effect, and the $YbNi_5Ge_3$ compound is antiferromagnetic at T < 2.7 K [7]. The formation of Kondo state Ce- and Yb-ions in the YNi_5Ge_3-type crystal matrix may be possible as the result of atomic substitutions in the *R*-sublattice.

In this paper we present data from a study of electrical resistivity, ρ, and thermoelectric power, S, in the temperature range 4-400 K for the solid solutions $R_xY_{1-x}Ni_5Ge_3$ (R = Ce, Yb) with the R elements in Kondo state.

2. Experimental details

Polycrystalline samples were prepared by arc-melting the elemental components of the ideal composition under argon atmosphere. The purity of the starting materials was 99.9% for Y, Ce, and Yb, 99.99% for Ni, and 99.999% for Ge. Weight losses after melting were generally less than 0.5 mass%. The arc-melted buttons were homogenized by annealing in evacuated quartz tubes under vacuum at 1070 K for 800 h. The purity of the obtained samples was checked at room temperature by powder X-ray diffraction using a DRON-2.0 diffractometer with Fe *K*α-radiation.

Table 1 Lattice parameters (a, b, c) and unit-cell volumes (V) for $R_xY_{1-x}Ni_5Ge_3$ (R = Ce, Yb) solid solutions (YNi_5Si_3-type structure, space group *Pnma*).

Compound	a, Å	b, Å	c, Å	V, Å^3
$YbNi_5Ge_3$	18.982(8)	3.830(1)	6.779(4)	492.8
$Yb_{0.5}Y_{0.5}Ni_5Ge_3$	19.05(1)	3.849(2)	6.787(3)	496.9
YNi_5Ge_3	19.108(7)	3.864(4)	6.773(4)	500.1
$Ce_{0.1}Y_{0.9}Ni_5Ge_3$	19.11(1)	3.878(3)	6.787(4)	502.8
$Ce_{0.2}Y_{0.8}Ni_5Ge_3$	19.124(9)	3.887(2)	6.795(3)	505.0
$Ce_{0.3}Y_{0.7}Ni_5Ge_3$	19.151(8)	3.893(2)	6.790(2)	506.2
$Ce_{0.5}Y_{0.5}Ni_5Ge_3$	19.18(1)	3.901(3)	6.791(3)	507.9

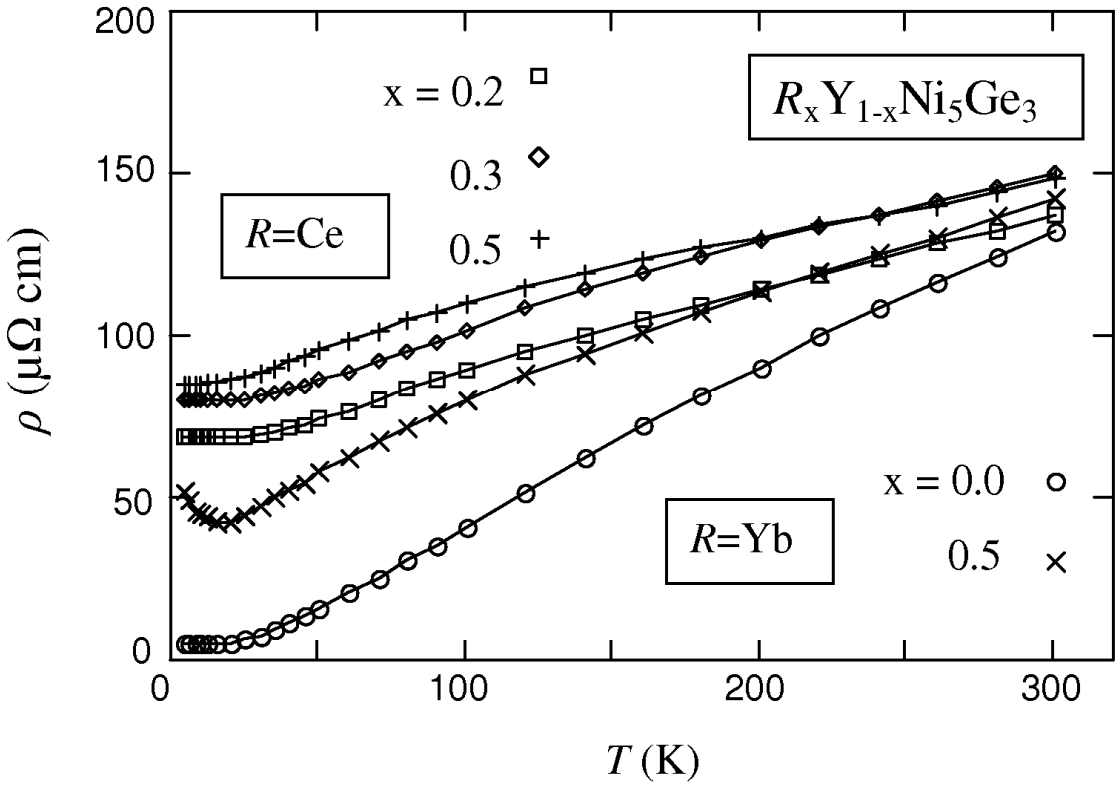

Fig. 1 Electrical resistivity of $R_xY_{1-x}Ni_5Ge_3$ (R = Ce, Yb) as a function of temperature.

The lattice parameters determined for the $R_xY_{1-x}Ni_5Ge_3$ (R = Ce, Yb) solid solutions are listed in Table 1.

The electrical resistivity was obtained by the standard four-probe *dc* technique. The thermoelectric power was measured by a differential method with a temperature gradient of 2-4 K using pure copper as reference material.

3. Results and discussion

The temperature dependence of the resistivity, $\rho(T)$, of $R_xY_{1-x}Ni_5Ge_3$ (R = Ce, Yb) is displayed in Fig. 1. The curves resemble those of the electrical resistivity of intermetallic compounds exhibiting spin fluctuations due to Kondo interactions [8]. The $\rho(T)$ plot for YNi_5Ge_3 adequately corresponds to the ordinary Bloch-Grüneisen relation. The value of the Debye temperature, Θ_D, derived for YNi_5Ge_3 by a least-squares fitting procedure, is ~250 K. Data on YNi_5Ge_3 were recorded in order to estimate the phonon contribution to the resistivity of the Ce(Yb)-containing samples. The temperature dependence of the magnetic contribution to the total resistivity, ρ_m, which can be estimated using the equation $\rho_m = \rho(R_xY_{1-x}Ni_5Ge_3) - \rho(YNi_5Ge_3)$, is shown in a semilogarithmic representation in Fig. 2. The overall shape of the $\rho_m(T)$ plots for the Ce(Yb)-containing samples appears to be typical for Kondo-impurity and crystal field (CF) interactions [9,10]. The regions of $-\ln(T)$ dependence were analyzed in terms of the theory developed by Cornut and Coqblin [9]. According to them, the combined influence of Kondo-impurity and CF

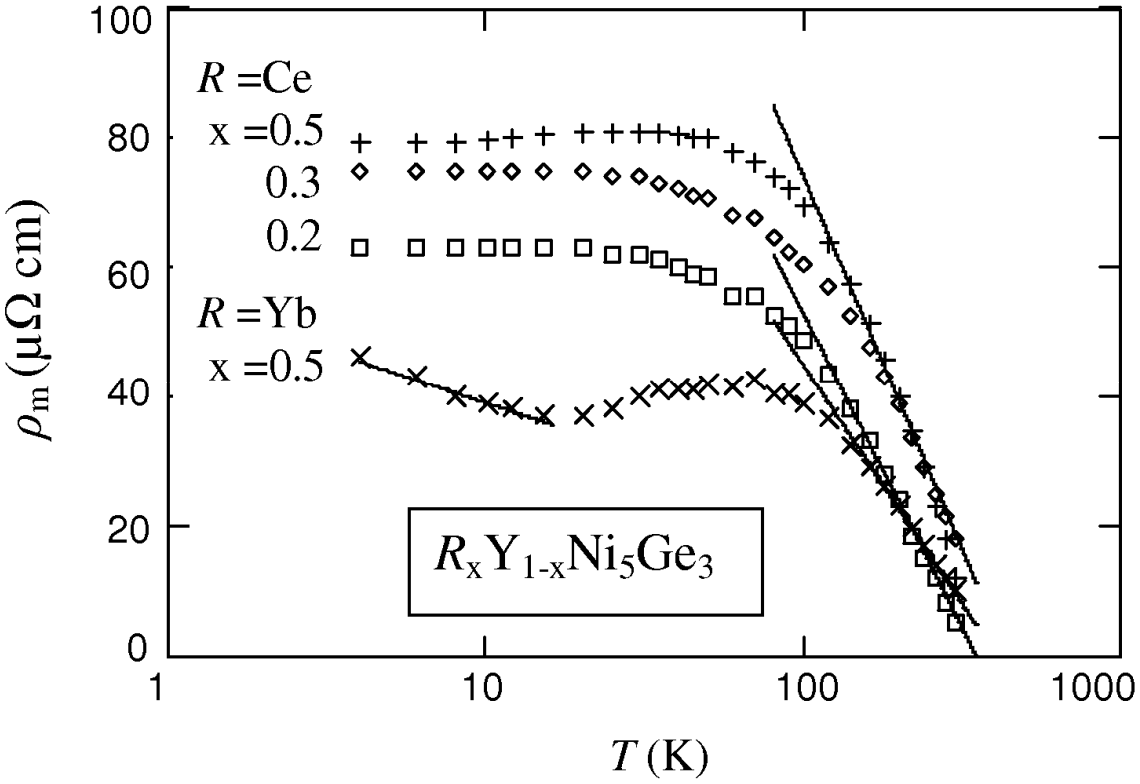

Fig. 2 Temperature dependence of the magnetic contribution to the total electrical resistivity of $R_xY_{1-x}Ni_5Ge_3$ (R = Ce, Yb) in a semilogarithmic scale.

interactions on the electrical properties of Ce(Yb)-containing intermetallic compounds results in a magnetic contribution to the total electrical resistivity, which can be expressed as:

$$\rho_m(T) = A + BN(E_F)J^3\frac{\alpha_i^2-1}{2j+1}\ln T\,, \qquad (1)$$

where J is the s-f exchange integral, α_i stands for the effective degeneracy of the crystal field 4f level, j is the total angular momentum of the Ce^{3+} (Yb^{3+}) ions, $N(E_F)$ is the electronic density of states at the Fermi energy, and A and B are constants defined in [9]. From Eq. (1) it can be seen that the ratio of the logarithmic slopes of the high- and low-temperature resistivities is determined exclusively by the α_i parameters. In the case of Ce^{3+} ions experiencing an orthorhombic crystal-field potential, the six-fold degenerated ground multiplet $^2F_{5/2}$ is split into three doublets. Therefore, for well separated crystal-field levels one can expect two regions of –ln(T) dependence of the resistivity. However, only one region of –ln(T) dependence is observed in Fig. 2. Such a behavior of $\rho_m(T)$ is characteristic of Kondo systems with $T_K \sim \Delta_1$, where Δ_1 is the energy of the first excited CF doublet. The insignificant variation of the slope of the linear segment of $\rho_m(T)$ for different amounts of atomic substitution Y → Ce shows the relative stability of the Kondo interaction energy ($JN(E_F)$ ~ const) with respect to variations of the Ce concentration. As it can be seen from Fig. 2, $\rho_m(T)$ reveals saturation at low temperature (ρ_m ~ const for T < 60-80 K). According to the theoretical description of the transport properties of Kondo systems [9,10], this indicates a nonmagnetic ground state of Kondo-impurity type with $T_K \approx$ 60-80 K for the $Ce_xY_{1-x}Ni_5Ge_3$ alloys. In the case of the $Yb_{0.5}Y_{0.5}Ni_5Ge_3$ compound there are two regions of logarithmic dependence of the resistivity. According to the theory [9], the change in the slope of the linear segments is associated with a change in the population of the sublevels formed by partial removal of the degeneracy in the ground state of the Yb^{3+} ion (ground multiplet $^2F_{7/2}$) under the influence of the crystal field when T increases. Considering the limits $T << \Delta$ and $T >> \Delta$ (where Δ is the total crystal field splitting), the ratio of the slope of the linear segment at low temperature to that of the linear segment at high temperature is given by $v = (\alpha_l^2-1)/(\alpha_h^2-1)$, where α_l and α_h denote the effective degeneracies of the crystal-field levels at low and high temperature, respectively. In a crystal field with orthorhombic symmetry, the 4f level of the Yb^{3+} ion splits into four sublevels with degeneracy α = 2. On examining all the possible transitions in such a crystal field, we obtained the following values for v: 0.20 (α_l = 2, α_h = 4), 0.09 (α_l = 2, α_h = 6), 0.05 (α_l = 2, α_h = 8), 0.43 (α_l = 4, α_h = 6), 0.24 (α_l = 4, α_h = 8), and 0.56 (α_l = 6, α_h = 8).

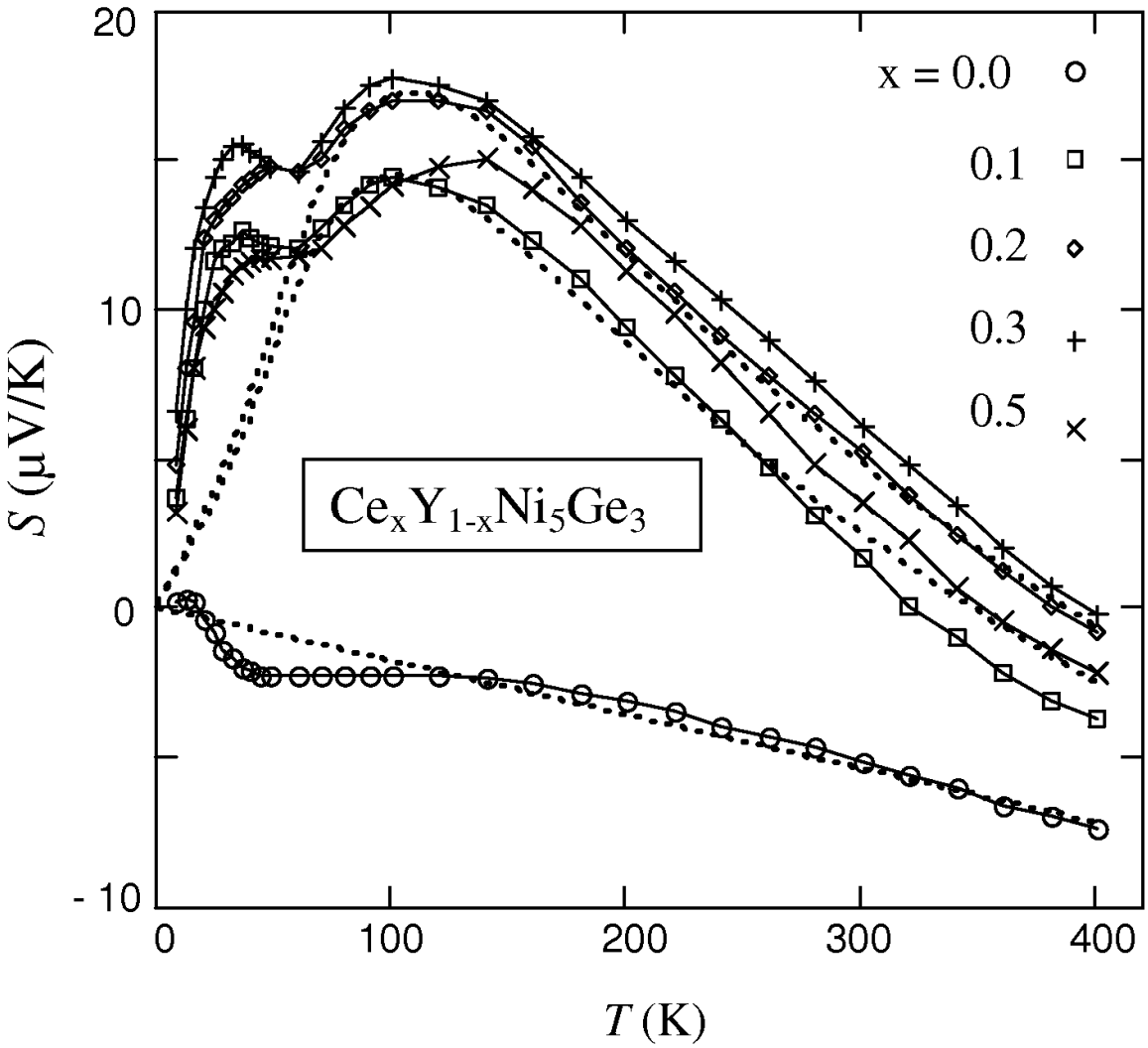

Fig. 3 Thermoelectric power of $Ce_xY_{1-x}Ni_5Ge_3$ as a function of temperature. The dotted lines show fittings according to Eq. (4).

The experimental value v = 0.21 corresponds to a scheme where the 4*f* level splits in the doublet ground and the first excited states (α_l = 2, α_h = 4). Thus, we may assume that the two linear segments are related to Kondo scattering of charge carriers, predominantly in the doublet at temperatures T < 60 K and in the four-fold degenerate 4*f* level for T > 80 K. The existence of CF effects in the Kondo scattering mechanism with a doublet ground state of the 4*f* level was confirmed by measurements of magnetic and specific heat properties for $YbNi_5Ge_3$ [7]. The absence of saturation of $\rho_m(T)$ at low temperature indicates small values of the Kondo temperature for the ground state doublet, T_K < 5 K.

Figs. 3 and 4 show the thermoelectric power, S, of samples $R_xY_{1-x}Ni_5Ge_3$ (R = Ce, Yb) as a function of temperature. For YNi_5Ge_3 $S(T)$ shows a behavior typical for nonmagnetic intermetallic compounds. It can be assumed that the thermoelectric power of YNi_5Ge_3 is qualitatively described in phonon and diffusion terms. At low temperature the phonon-drag contribution is proportional to T^3 and changes at higher temperatures to $1/T$, hence giving rise to the formation in $S(T)$ of an extremum at ~$0.2\Theta_D$, where Θ_D is the Debye temperature [11]. For YNi_5Ge_3 Θ_D estimated from resistivity measurements is 250 K, which is consistent with the minimum observed in $S(T)$ near 50 K. The phonon drag peak of about -2 $\mu V/K$ near 50 K is superposed upon the diffusion term having a slope of about -1.8×10^{-2} $\mu V/K^2$ (Fig. 3, dotted straight line).

The $S(T)$ plots for $Ce_xY_{1-x}Ni_5Ge_3$ have two broad peaks near T_{Smax1} = 30-40 K and T_{Smax2} = 100-140 K and stay positive up to 300 K. The temperature position of the peak S_{max1} is not sensitive to the Ce content, but the position of the peak S_{max2} moves to higher temperatures with increasing Ce concentration. In the case of $Yb_{0.5}Y_{0.5}Ni_5Ge_3$, $S(T)$ takes negative values in the range of measurements with a minimum at T_{Smin} = 56 K. Such a behavior at temperatures $T > T_K$ can be qualitatively described in the framework of models [12-14] that take into account a Kondo

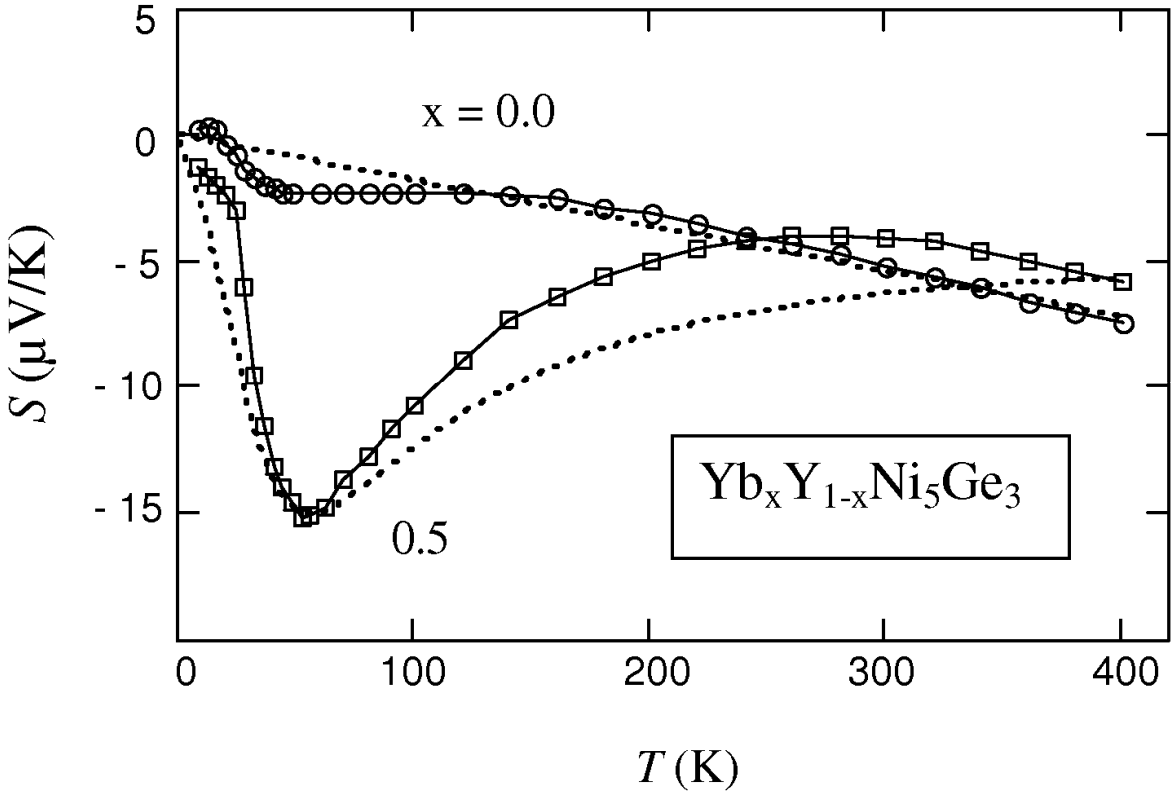

Fig. 4 Thermoelectric power of $Yb_xY_{1-x}Ni_5Ge_3$ as a function of temperature. The dotted lines show fittings according to Eq. (4).

effect in the presence of a CF effect. In [12,13] it was shown that characteristic maxima or minima on $S(T)$ for Ce- or Yb-containing intermetallic systems strongly depend on the CF splitting. This anomaly appears at around $T_{Smax,min} \sim \Delta/3$ (where Δ is the effective overall CF splitting). Taking into consideration that the CF factor is essential to describe the behavior of $S(T)$, one can approximately estimate the thermoelectric power for a two-level CF scheme splitting [14]. The absence of data on a number of microscopic parameters defining the interaction in these systems motivates the use of a simplified equation for the magnetic contribution to the overall thermoelectric power:

$$S_f = \frac{k_B}{|e|}\rho_0 \frac{S_\Delta}{R_\Delta} G_1(\Delta,0) \sim G_1(\Delta,0), \qquad (2)$$

where $\rho_0 S_\Delta/R_\Delta$ is a dimensionless quantity, which is described in [14], $k_B/e \approx 86$ μV/K. The function $G_1(\Delta,0)$ can be expressed in the form:

$$G_1(\Delta,0) = \frac{\Delta}{T}\left[1 + \frac{\Delta}{2\pi T}\,\mathrm{Im}\,\psi'\left(i\frac{\Delta}{2\pi T}\right)\right] \equiv \Phi_4\left(\frac{\Delta}{2\pi T}\right), \qquad (3)$$

$$\Phi_4(x) = \pi \int_0^\infty \frac{\sin(xt)}{2\sinh^2(t/2)}\left[\frac{t}{2}\coth\left(\frac{t}{2}\right) - 1\right] dt\,,$$

where ψ' is the derivative of the psi-(digamma-) function. The temperature dependence of the thermoelectric power for the $R_xY_{1-x}Ni_5Ge_3$ samples may be described by the expression:

$$S(T) = C_1 T + C_2 G_1(\Delta,0), \qquad (4)$$

where C_1 and C_2 are temperature-independent parameters that determine the strength of the contributions arising from the nonmagnetic Mott-type and magnetic scattering processes, respectively. Simulations of $S(T)$ (dotted lines) for Ce- and Yb-containing alloys are shown in Figs. 3 and 4. These curves were computed on the basis of Eq. (4) by fitting the calculated parameters $S_{max2}(S_{min})$ and $T_{Smax2}(T_{Smin})$ to experimental ones. The best agreement between calculation and experiment at temperatures $T > T_K$ was obtained for C_1 = -2.7×10^{-2}, -2.8×10^{-2}, and -5.4×10^{-3} μV/K^2, C_2 = 18.8, 22.0, and -16.3 μV/K, Δ = 370, 390, and 180 K for $Ce_{0.1}Y_{0.9}Ni_5Ge_3$, $Ce_{0.2}Y_{0.8}Ni_5Ge_3$, and $Yb_{0.5}Y_{0.5}Ni_5Ge_3$, respectively. Analogous calculations for the remaining $Ce_xY_{1-x}Ni_5Ge_3$ alloys gave CF parameters of Δ = 420 and 450 K for the concentrations x = 0.3 and 0.5, respectively. The calculated $S(T)$ dependences are in better agreement with the experiment for the Ce-containing than for the Yb-containing alloys. This may be an indication of the somewhat limited application of the doublet-quartet CF splitting scheme to the 4*f* level of the Yb^{3+} ion. The observed values of Δ for the Ce-containing alloys correspond

qualitatively to the change of the lattice parameters and unit-cell volumes, which suggest an increase of the chemical pressure for the atomic substitution Ce → Y.

According to the model proposed in [12,13], Eq. (4) describes the main high-temperature features of Ce and Yb intermetallics. In the low temperature region $T << \Delta$ the principal contribution to the overall thermoelectric power of the alloys is the Kondo-type interaction of the conduction electrons with the localized magnetic moments of the ground state doublets, which are well described by the single-impurity Anderson model [14,15]. Depending on the values of a number of parameters the thermoelectric power can show a minimum or a maximum at the temperature $T \sim T_K/2$. In the case of the $Ce_xY_{1-x}Ni_5Ge_3$ alloys maxima were observed at T = 30-40 K, which suggests characteristic temperatures T_K of ~60-80 K. In the case of the $Yb_{0.5}Y_{0.5}Ni_5Ge_3$ alloy a similar estimation of T_K is questionable, since positive contribution to the thermoelectric power at T = 20 K needs additional studies.

Conclusions

Bases on the transport properties of $R_xY_{1-x}Ni_5Ge_3$ alloys studied here one can conclude that Ce- and Yb-ions in the YNi_5Ge_3 crystal matrix reach the state of Kondo-impurity with T_K substantially smaller than the overall CF splitting of the 4*f* level. The detection of low-dimensional Kondo-lattice effects requires additional studies of the transport properties at lower temperatures and larger concentrations of Ce- and Yb-ions.

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