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Collapse of the *f*-band in CeNi with intermediate valence of Ce

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On the basis of a narrow peaks (NP) model for the 4*f*-derived density of states (DOS) near the Fermi energy proposed by us earlier, we present a detailed description of the temperature dependences of the contribution of Ce *f*-states to the electrical resistivity, thermoelectric power, magnetic susceptibility, and electronic contribution to the specific heat for CeNi. It is shown that the dependences of the above mentioned characteristics in a wide temperature range are well described on the basis of a single narrow peak of Lorentzian shape, assuming temperature dependence of the peak parameters. At low temperatures (T < 20 K) the peak parameters are consistent with the corresponding parameters of the 4*f* DOS in the Anderson model for Kondo systems with strong orbital degeneracy of *f*-states at the characteristic temperature $T_K \approx 330$ K. At higher temperatures (T > 50 K) the best correspondence of the model to the experimental data was achieved considering a drastic reduction (collapse) by ~50 % of the width of the narrow peak for the DOS in a temperature range near $T \approx \Theta_D = 115$ K (Θ_D is the Debye temperature).

Rare earth compounds / Electronic structure of metals and alloys / Electronic transport / Kondo effect

1. Introduction

The intermetallic compound CeNi (orthorhombic structure of CrB-type, space group *Cmcm* [1]) is well known as an interesting intermediate valence (IV) system with an abnormal strong effect of electron-lattice coupling, which has been intensively investigated over the last decades [1-8]. A peculiarity of the transport and thermodynamic properties of CeNi is the appearance of additional contributions, which take maximum values at the so-called Kondo characteristic temperature T_K [1-4]. CeNi, which has a metallic ground state, has attracted special attention because of the gap-like magnetic excitation of the spectrum observed at low temperatures, similar to those typical for so-called «Kondo-insulators» [7,8]. Besides, it was found that the structure of the quasiparticle state spectrum of CeNi exhibits a number of peculiarities that are difficult to describe within the frame of existing models for systems with IV of Ce. In this context it is important to examine the structure of the quasiparticle states on the basis of investigations of the electronic transport properties, particularly sensitive to IV states of Ce.

In this paper, we present a detailed description of the main transport properties of CeNi in a wide temperature range on the base of a narrow peaks (NP) model for the density of states near the Fermi energy proposed by us earlier [9-11].

2. Method

Regarding the theory, the electronic transport properties of systems with IV of Ce have been most logically studied by means of the Anderson model [12,13]. However, it has not been possible so far to derive analytical relationships that are able to describe the behavior of systems with transport properties implying IV of Ce in a wide temperature range. This requires the development of various phenomenological approaches [9-11,14,15], based on an NP model. The band approach proposed by us earlier [9,10] seems to be the most suitable of them. According to this approach, the main contribution of the IV of Ce to the transport coefficients is determined by electron scattering at transitions from a broad *s* conduction band to a narrow *f*-band. The scattering process can be described by the relaxation time in the form

$$\tau_{sf}(E,T)^{-1} \sim g_f(E,T) R_{ph}(T), \qquad (1)$$

where $g_f(E,T)$ represents peaks of the effective density of *f*-states, the parameters of which can depend on the temperature. The function

$$R_{ph}(T) = (T/\Theta_D)^3 J_3(\Theta_D / T),$$

where Θ_D is the Debye temperature, and $J_3(\Theta_D / T)$ is a well known transport integral, which takes into account the possible phonon-induced interband *s-f* transition.

From the linearized Boltzmann transport equation, the following expressions for the electrical resistivity component and thermoelectric power connected with the IV of Ce were obtained:

$$\rho_f(T) = \frac{1}{e^2}\frac{1}{L_0(T)},\ S_f(T) = \frac{1}{|e|}\frac{L_1(T)}{L_0(T)}, \qquad (2)$$

$$L_n(T) = \int_{-\infty}^{\infty} E^n \tau_{sf}(E,T)(-\partial f(E)/\partial E)dE,\ n = 0,1,$$

where $\partial f(E)/\partial E$ is the energy derivative of the Fermi-Dirac distribution function. In the case of a representation of the quasiparticle state spectrum $g_f(E,T)$ in the form of a peak of Lorentzian shape (approximation of independent scattering on impurity *f*-centers) these transport coefficients can be written in the simple analytical forms [9,10]

$$\rho_f(T) \approx \frac{\Gamma_f(T)\cdot R_{ph}(T)}{(\pi^2/3)T^2 + \varepsilon_f(T)^2 + \Gamma_f(T)^2}, \qquad (3)$$

$$S_f(T) = \frac{2}{3}\pi^2 \frac{k_B}{|e|}\frac{T\cdot\varepsilon_f(T)}{(\pi^2/3)T^2 + \varepsilon_f(T)^2 + \Gamma_f(T)^2}, \qquad (4)$$

where ε_f is the position of the $g_f(E,T)$ peak relative to the Fermi level E_F, Γ_f is its width. Eqs. 3 and 4 satisfactorily describe the temperature dependences of the transport coefficients of the majority of the systems with IV of Ce, even without taking into account the possible temperature dependence of the parameters ε_f and Γ_f [9]. We have recently shown for systems with IV states of Ce that are sensitive to temperature [10], that a good agreement of the calculated transport coefficients with the experimental data can only be obtained when the temperature dependences of the parameters ε_f and Γ_f are taken into account. In this paper, the temperature-induced changes of the $g_f(E,T)$ peak were associated with high stabilization of the Ce^{3+} magnetic state when the temperature increases, which has been confirmed by spectroscopic measurements of *f*-state occupation [16].

Within the framework of the given model, the contributions of the *f*-states to the magnetic susceptibility $\chi_f(T)$ and electronic specific heat coefficient $\gamma_f(T)$ can be found by the relations

$$\chi_f(T) = \mu_{eff}^2 K_0(T),$$
$$\gamma_f(T) = K_2(T) - K_1(T)^2 / K_0(T) \qquad (5)$$
$$K_n(T) = \int_{-\infty}^{\infty} E^n g_f(E,T)(-\partial f(E)/\partial E)dE,$$
$$n = 0,1,2$$

where μ_{eff} is the effective magnetic moment of the cerium $4f^1$-state.

3. Results and discussion

The transport properties of the compound CeNi and its analogue with La have been partially analyzed by us earlier [9-11]. With the aim to define the contribution of Ce *f*-states to the electronic transport properties of CeNi, it was assumed that LaNi is a good analogue for the description of the corresponding properties of the so-called "background" and is "in principle" identical to CeNi without considering the involvement of *f*-electrons in forming resonance states at the energy E_F. In this case the contribution of Ce *f*-states to the total transport properties may be written as

$$X_f(T) \approx X_{Ce}(T) - X_{La}(T), \qquad (6)$$

where X_{Ce} and X_{La} denote arbitrary transport properties measured for CeNi and LaNi, respectively.

To analyze details of the fine structure of the density of states of CeNi on the basis of electronic transport properties, experimental data reported in [2,3,11] was used. Figs. 1-4 present the temperature dependences of the contribution of Ce *f*-states to the total values of the electrical resistivity (ρ_f), thermoelectric power (S_f), magnetic susceptibility (χ_f) and the Sommerfeld electronic specific heat coefficient (γ_f). For the estimations of χ_f based on data for monocrystalline samples of CeNi [3], it was assumed that the total susceptibility χ(CeNi) = ($\chi_a + \chi_b + \chi_c$)/3, where $\chi_{a,b,c}$ are the magnetic susceptibilities for the fields along the *a*-, *b*- and *c*-axis, respectively. All the dependences are characterized by one asymmetric maximum, the position of which is qualitatively determined by the values of $T_K \approx$ 150 K. Investigations of transport, magnetic, and spectral properties of CeNi indicate that the values of T_K should be in the range 150…360 K [1-5,10,11]. At $T << T_K$ the system exhibits properties typical of a Fermi liquid, but at $T > T_K$ properties of a paramagnetic substance with localized magnetic moments. This is in qualitative agreement with theoretical views on systems with IV of Ce [12].

In this approach the parameters Γ_f and ε_f are considered as the main fitting parameters in the process of correlating the calculated dependences $\rho_f(T)$, $S_f(T)$, $\chi_f(T)$, and $\gamma_f(T)$

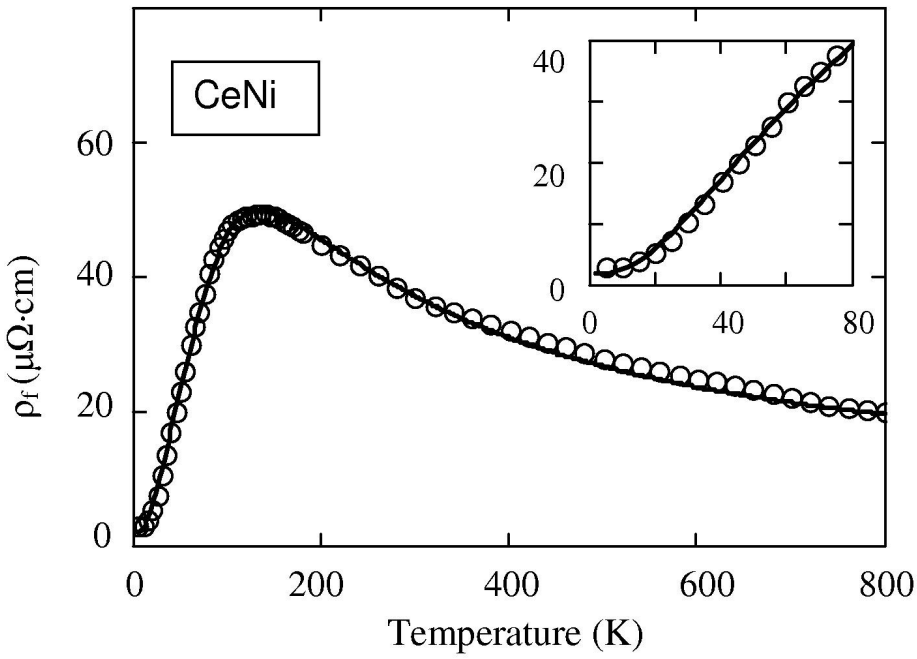

Fig. 1 Temperature dependence of the contribution of Ce *f*-states to the total electrical resistivity of CeNi (ρ_f). The solid line shows the electrical resistivity calculated from Eq. 3. The inset shows the resistivity in the low-temperature region.

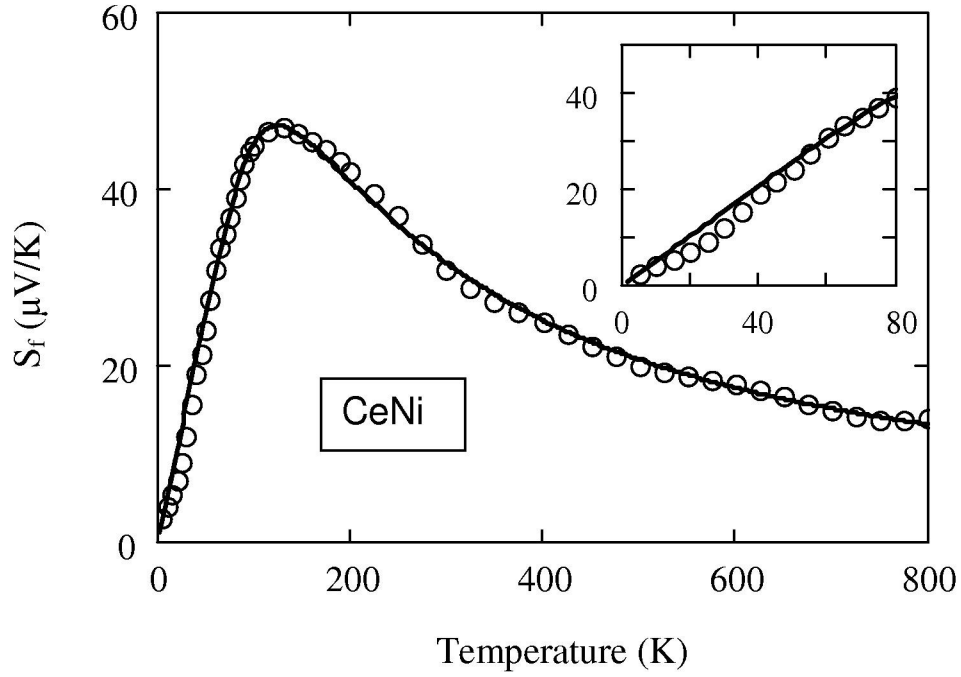

Fig. 2 Temperature dependence of the contribution of Ce *f*-states to the total thermopower of CeNi (S_f). The solid line shows the thermopower calculated from Eq. 4, imposing the best correlation of the calculations with the experimental dependence $\rho_f(T)$. The inset shows the thermopower in the low-temperature region.

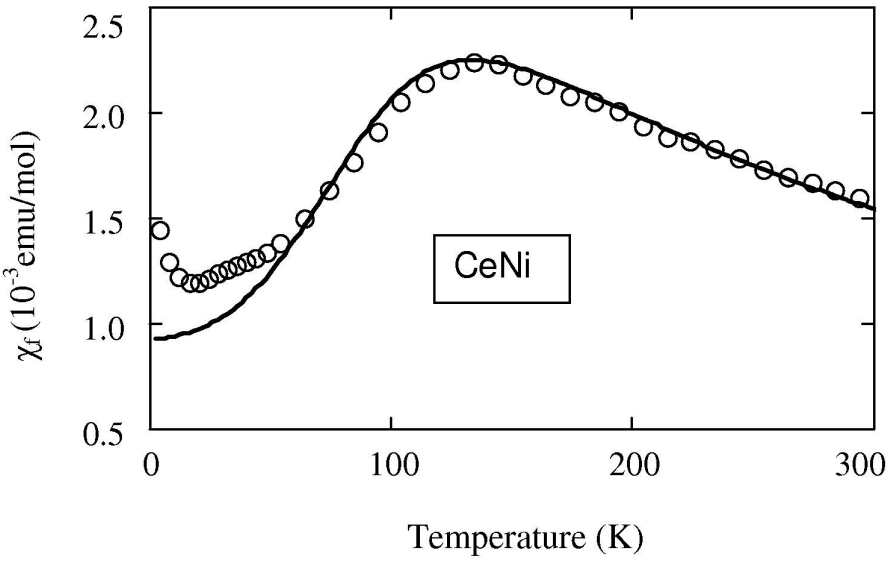

Fig. 3 Temperature dependence of the contribution of Ce *f*-states to the total magnetic susceptibility of CeNi [6] (χ_f). The solid line shows the magnetic susceptibility calculated from Eq. 5, imposing the best correlation of the calculations with the experimental dependences $\rho_f(T)$, $S_f(T)$.

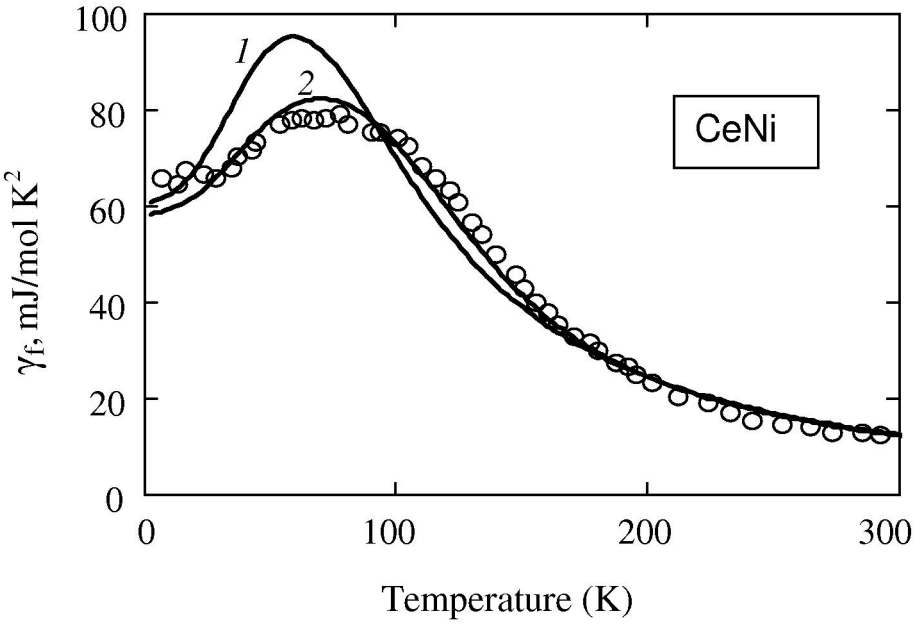

Fig. 4 Temperature dependence of the contribution of Ce *f*-states to the total electronic specific heat coefficient of CeNi [7] (γ_f). The solid lines show the electronic specific heat coefficient calculated from Eq. 5, imposing the best correlation of the calculations with the experimental dependences $\rho_f(T)$, $S_f(T)$ (line 1), and $\gamma_f(T)$ (line 2).

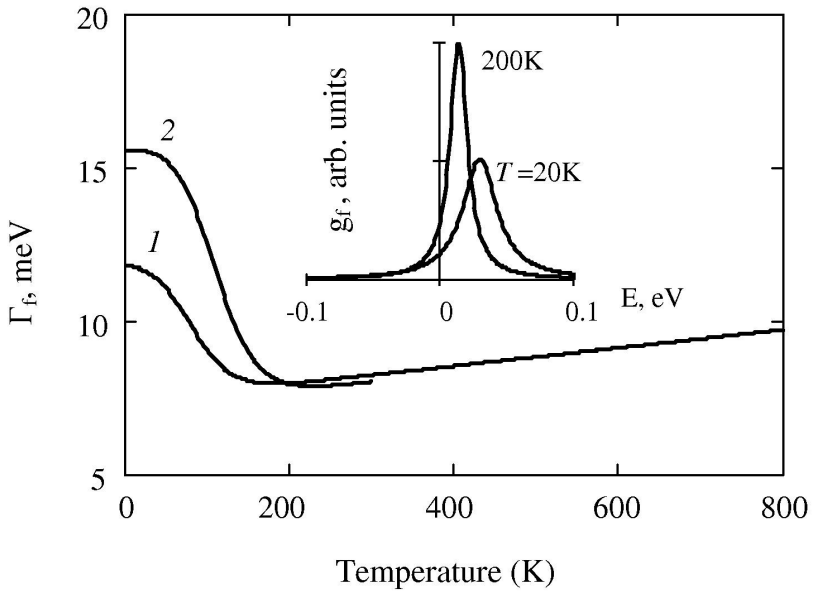

Fig. 5 Temperature dependence of the parameter Γ_f of the peak density of *f*-states, obtained imposing the best correlation of the calculations with the experimental dependences $\rho_f(T)$, $S_f(T)$ (line 1), and $\gamma_f(T)$ (line 2) for CeNi. The inset shows the peak density of *f*-states near the Fermi level (E_F = 0) calculated for two temperatures. The parameters of the peak are the same as those employed for the calculation of the temperature dependence $\gamma_f(T)$ (Fig. 4, line 2).

with the experimental ones. With the aim of obtaining a better correlation of the calculations with the experiment we used normalized values of the calculated coefficients, imposing as a condition their equality to the experimental coefficients at one point on the temperature scale. The maximum values of electrical resistivity and thermoelectric power, as well as the values of χ_f and γ_f at T = 300 K, were accepted as such points. In the calculations applying Eqs. 3 and 4 we used only two experimental values: correction for the residual resistivity $\rho_f(0)$ = 3 μΩ·cm [11] and the Debye temperature Θ_D = 115 K [5].

The results of the calculations of the transport coefficients (Figs. 1-4, solid lines) are presented for temperature-dependent parameters Γ_f and ε_f, obtained imposing the best correlation with the experiment. The best agreement with the experiment throughout the 4…800 K temperature range was realized for the dependencies $\rho_f(T)$ and $S_f(T)$, taking into account the temperature dependence of the parameter Γ_f, shown in Fig. 5. The dependence of the $\Gamma_f(T)$ to $\varepsilon_f(T)$ ratio is given by the linear relation $\Gamma_f(T)/\varepsilon_f(T) = 0.45\ (1+4\cdot10^{-4}T)$. It is well known that the relationship between the parameters ε_f, Γ_f and T_K in the single-impurity Anderson model [12] for systems with IV of Ce at low temperatures is described by the relations: $\Gamma_f/\varepsilon_f \approx \pi/N_f = 0.52$ and $T_K = \sqrt{\varepsilon_f^2 + \Gamma_f^2} \approx \varepsilon_f$, where N_f is the orbital degeneracy of the *f* states. In our case, the ratio Γ_f/ε_f increases linearly in the temperature range 4…800 K and takes the values 0.45...0.6. The parameter T_K decreases with increasing temperature, taking the values 330 K (T < 50 K) and ~200 K (T > 150 K). The temperature dependence $\Gamma_f(T)$ has a nearly jump-like character, decreasing in the temperature range 50…150 K, but exhibiting an approximately linear increase in the temperature range 200...800 K (Fig. 5, solid line 1). For the electronic specific heat coefficient γ_f the two presented curves were obtained imposing the best correlation of the calculations with the experimental dependences $\rho_f(T)$, $S_f(T)$ (Fig. 4, solid line 1), and $\gamma_f(T)$ (Fig. 4, solid line 2). The dependence $\gamma_f(T)$ is better described by a peak of density of states with a width slightly larger than Γ_f at low temperatures, but with similar character of the temperature dependence in the range T = 50…150 K (Fig. 5, solid line 2). The difference between the descriptions of $\rho_f(T)$, $S_f(T)$ and $\gamma_f(T)$ is caused by the fact that the behavior of the transport characteristics is determined by electron scattering from a broad *s*-band to a narrow, strongly correlated *f*-band. The scattering process can be described by the relaxation time (dynamic process). In the case of the electronic specific heat coefficient we

have static characteristics of the crystal electronic subsystem.

The use of temperature-dependent parameters Γ_f, ε_f allows a better fit of the theoretical curves to the experimental ones, except for the behavior of $\chi_f(T)$ in the low-temperature region ($T < 50$ K). According to magnetic susceptibility data for CeNi [1-3] and model notions of physical properties of systems with IV of Ce [17], the inconsistency between the calculated values of χ_f and the experimental ones should be connected with a possible partial manifestation of spin fluctuation coherence at the *s-f* transitions and the presence of paramagnetic impurities.

The parameters of the peak $g_f(E,T)$ at $T < 50$ K take the values $\Gamma_f \sim 12$ meV, $\varepsilon_f \sim 26$ meV, which are consistent with the corresponding parameters of the Abrikosov-Suhl resonance in Kondo systems with $T_K \approx 330$ K [17]. The transport coefficients at $T \to 0$ calculated from the given values of T_K are in good agreement with the experimental data. This means that the density of states $g_f(E,T)$ is principally of spin nature. The revealed temperature dependence of the peak is in qualitative agreement with data obtained by inelastic neutron scattering [7,8]. One of the three peaks of inelastic scattering, observed at the energy of falling neutrons $E =$ 120 meV, shows features resembling those established for the resonance peak $g_f(E,T)$. At low temperatures ($T = 12$ K) the above mentioned peak is at the energy $E = 34$ meV, which is of the same order of magnitude as the T_K value. With increasing temperature the peak narrows sharply and shifts to a region of lower energies, which is in good qualitative agreement with the temperature behavior of the parameters of the peak $g_f(E,T)$. The narrowing of the peak (~50 %, inset of Fig. 5) on approaching the values of Θ_D on the temperature scale correlates with the stabilization of Ce^{3+} states, established based on data from X-ray absorption spectroscopy [15]. Considering the fact that the *f*-electrons in CeNi are rather strongly connected with lattice vibrations [6], the reason of stabilization of the Ce^{3+} magnetic state can be a so-called polaron collapse of the *f*-band, which allows explaining a number of typical peculiarities of physical properties of systems with heavy fermions [18].

4. Conclusions

We have shown that peculiarities in the behavior of the transport coefficients of CeNi are well described within the framework of the NP model using just one peak of density of states of Lorentzian shape in the energy region E_F. At low temperatures ($T < 50$ K) the parameters of the peak are in qualitative agreement with those assumed in the Anderson model for Kondo systems with strong orbital degeneracy of *f*-states. In the 50…150 K temperature range the DOS peak undergoes a drastic reduction (collapse) of its width and shifts towards the energy E_F. This behavior may be caused by an electron-polaron effect.

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