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Electronic transport properties modeling of compounds with temperature unstable valence of Ce

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Results of measurements of a thermoelectric power component (S_f) and electrical resistivity (ρ_f) connected with the temperature unstable valence of Ce are presented for compounds CeNi, CeNi₂ and CeNi₂Si₂ in the temperature range 4-800K. It is shown that dependences $S_f(T)$ and $\rho_f(T)$ are well described in the narrow peak model of the density of f -states of the Lorentz shape, which is situated near the Fermi level. The peak's width depends on temperature and is defined by characteristic Kondo temperature.

Transport properties of metallic compounds containing Ce with unstable f -electrons attract the increased attention during recent decades. This applies particularly to the coefficient of diffusive thermoelectric power S and electrical resistivity ρ , which are characteristics the most sensitive to peculiarities of the near Fermi states' spectrum.

It is known that transport characteristics of systems with Ce can be described in the relaxation time approximation with allowing for the exchange scattering of conduction electrons on local f -states [1, 2]. However, with detailed consideration of a number of important factors, such as the f-states orbital degeneracy, crystal field-split f -states, the f -states hybridization with band electrons, many-body effects connected with f-f electron correlation effects etc., one cannot succeed in obtaining the general solution of the transport coefficients behavior problem in the wide temperature range. All this contributed to development of a number of phenomenological approaches for description of transport properties of such systems [3-6]. The band approach [5] proposed by us earlier seems as the most suitable of them. We have assumed there that the main contribution into the transport coefficients is determined by electron scattering on transitions from a wide s -conduction band to a narrow,

strongly correlated f -band with density of states $g_f(E)$ of the Lorentz shape. Scattering process can be described by the relaxation time in the form of

$$\tau_{sf}(E, T)^{-1} \sim g_f(E) \phi(T). \quad (1)$$

Function $\phi(T)$ ensures the linear increase of electric resistivity in the case of simple metals according to the Bloch-Gruneisen law.

Contribution of such transitions to transport coefficients in the approximation of independent scattering on f -centers can be written as [6, 7]

$$S_f(T) = \frac{2}{3} \pi^2 \frac{k_B}{|e|} \frac{T \cdot T_K}{(\pi^2/3)T^2 + (1 + \pi^2/N_f^2)T_K^2}, \quad (2)$$

$$\rho_f(T) = \frac{\rho_f(0) \cdot \phi(T)}{(\pi^2/3)T^2 + (1 + \pi^2/N_f^2)T_K^2}, \quad (3)$$

where N_f - is the orbital degeneration of f -states, $\rho_f(0)$ - residual resistivity. Recently, we have shown [8] that good agreement of thermoelectric power curves calculated by formula (2) with experimental data can be obtained only when temperature dependence of parameter T_K is taken into account. This especially holds true for systems with the IV states of Ce, which are sensitive to temperature.

In this paper, we present results of comparison of dependences $S_f(T)$ and $\rho_f(T)$, calculated by formulas (2) and (3) for CeNi, CeNi₂ and CeNi₂Si₂ compounds with temperature unstable valence state of Ce, with experimental data.

When calculating f -states contribution to total thermoelectric power and electrical resistivity, we assumed that $S_f(T) \approx S_{Ce}(T) - S_{La}(T)$ and $\rho_f(T) \approx \rho_{Ce}(T) - \rho_{La}(T)$, where S_{Ce} , S_{La} and ρ_{Ce} , ρ_{La} denote thermoelectric power and electrical resistivity of a compound with Ce and corresponding to it isostructural analog with La. Because of special sensitivity of thermoelectric power to parameters of the density of states fine structure, detailed concordance of calculation with experiment was carried out only for the $S_f(T)$ component. Values of S_f calculated by equation (2) were normalized by coefficient $p = S_{fmax,exp}/S_{fmax,calc}$, where $S_{fmax,exp}$ and $S_{fmax,calc}$ denote the maximal values of experimental and calculated thermoelectric power. Parameter p takes into account the discrepancy between experimental and calculated values of $S_f(T)$, caused by not allowing in (2) for the concentration of scattering f -centers and presence of other scattering mechanisms in compound under study [5]. Dependences $T_K(T)$, obtained as a result of such concordance, were used for assessment of $\rho_f(T)$, normalized by coefficient $q = \rho_{fmax,exp}/\rho_{fmax,calc}$ ($\rho_{fmax,exp}$ and $\rho_{fmax,calc}$ denote maximal values of experimental and calculated electric resistivity), and some other crystal's physical characteristics.

Temperature dependences of the f -states of Ce contribution to total thermoelectric power (S_f) for compounds CeNi, CeNi₂ and CeNi₂Si₂, based on the data [7, 9-11], are presented in Fig.1. According to spectroscopic measurements [12], transition of Ce from a state with strongly mixed valence ($Ce^{3.2+}$) to almost magnetic one (Ce^{3+}) is observed in CeNi in the temperature range 80-600K. Similar decrease of the Ce valence (~ 0.1 -0.2) takes place in the case of CeNi₂ and CeNi₂Si₂ reaching state of $Ce^{3.1+}$ at $T=1000$ K [12, 13]. Apparently, typical features of the $S_f(T)$ dependence for the compounds in question are presence of asymmetric maximum (qualitatively $S_f \sim T$ at $T < T_{Sfmax}$ and $S_f \sim T^{-1}$ at $T > T_{Sfmax}$) and certain deviation from linear behavior $S_f = aT$ at low T with the occurrence of positive curvature. A good agreement of the calculated thermoelectric power (Fig. 1, solid curve) with experiment is reached when temperature dependence of parameter T_K is considered. In the low temperature

range ($T < T_{Smax}$), parameter T_K increases sharply until values $T_K \approx (2-6) T_{Sfmax}$. Linearity of dependence $S_f(T)$ at $T < T_{Sfmax}$ frequently observed in such systems [14, 15] is achieved only at $T_K = \text{const}$ according to equation (2). Such dependence is shown for CeNi₂Si₂ (Fig.1, dotted)

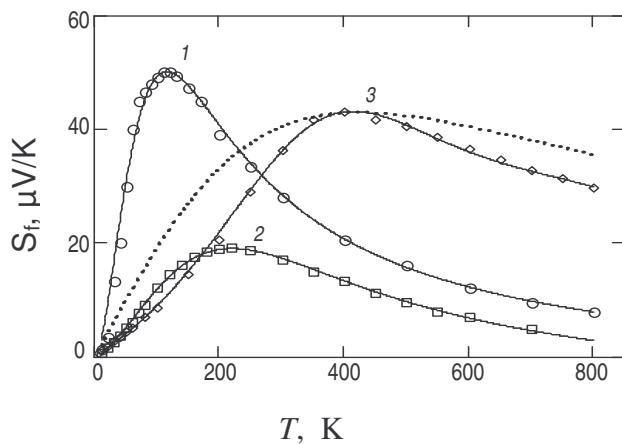


Figure 1. Temperature dependences of the contribution of Ce *f* states to the total thermopower of CeNi (1), CeNi₂ (2) and CeNi₂Si₂ (3). Solid lines plot thermopower calculated from Eq. (2) in suggestion temperature dependence of parameter T_K and $T_K = \text{const}$ (dotted curve).

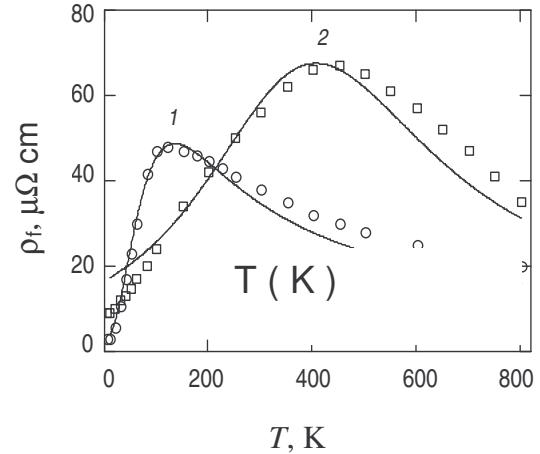


Figure 2. Temperature dependences of the contribution of Ce *f* states to the total electric resistivity of CeNi (1) and CeNi₂Si₂ (2). Lines plot calculated dependences according to Eq. (3).

curve calculated at $T_K=680\text{K}$). Appearance of positive curvature on the dependence of $S_f(T)$ in the low temperature range and corresponding increase of T_K allow coordinating parameters of resonant structure $g_f(E)$ with main thermodynamic properties of crystals.

It is well known [14] that the majority of thermodynamic properties of systems with the IV of Ce are satisfactorily described within the framework of a single impurity Anderson model with allowing for strong orbital degeneration

$$\chi(0) = \mu^2 n_f(0) / 3T_K \quad (4)$$

and

$$\gamma(0) = \pi^2 k_B^2 n_f(0) / 3T_K, \quad (5)$$

where $\mu^2 = g_J^2 J(J+1) \mu_B^2$, $n_f(0)$ - electronic population of *f*-states of Ce at low temperatures. To assess the low temperature values of T_K we use known data [12] for population of *f*-states of Ce in CeNi ($n_f(0)=0.86$) determined at $T=80\text{K}$. To deduct contributions of *d*-states of Ni to the values of coefficients $\gamma(0)$ u $\chi(0)$, it is possible to use similar data for LaNi. According to data [16, 17], $\gamma(0)=65 \text{ mJ mol}^{-1}$ (CeNi), 5 mJ mol^{-1} (LaNi); $\chi(0)=2.2 \cdot 10^{-3} \text{ emu mol}^{-1}$ (CeNi), $0.2 \cdot 10^{-3} \text{ emu mol}^{-1}$ (LaNi). After substitution of the data presented in equations (4) and (5), we obtain $T_K=350$ и 390 K correspondingly. Results of assessment of T_K are in a good agreement with those determined by means of thermoelectric power at the low temperatures (we obtain $T_K=360 \text{ K}$ at $T=15 \text{ K}$). Similar assessment carried out for CeNi₂ in [18] gives $T_K=1500 \text{ K}$, which is also in fair agreement with our calculations (we obtain $T_K=1460 \text{ K}$ by the thermoelectric power data at $T=15 \text{ K}$). For the case of CeNi₂Si₂, reliable assessment of T_K by other methods is unknown for us. Found by us value $T_K=1850 \text{ K}$ at $T=15 \text{ K}$ is presented wholly acceptable.

The experimental and calculated (solid curves) dependences of the component $\rho_f(T)$ normalized by coefficient q are shown in Fig. 2. Calculation of $\rho_f(T)$ was carried out by equation (3) with use dependence $T_K(T)$ found. The best agreement between calculation and experiment is reached when the function in formula (1) has form of $\phi(T) \sim T$ for CeNi and $\phi(T) = \text{const}$ in the case of CeNi₂Si₂. This fact agrees with anomalously strong interaction of electron system with lattice vibrations revealed previously [19]. In the case of CeNi₂Si₂, type of behavior of $\rho_f(T)$ corresponds to Mott scattering on s-f-transitions under allowing for the temperature narrowing of the density of states $g_f(E)$ peak.

By total set of data presented, one can conclude that transport properties of compounds with the temperature unstable IV of Ce are described satisfactorily within the framework of the simple model of narrow peak of density of states of Lorentz form with allowing for its narrowing caused by stabilization of the Ce³⁺ states as the temperature increases. Differences in the character of temperature dependences of electric resistivity are probably caused by relationship between T_K and the Debye temperature T_D . In the temperature range with $T_K \gg T_D$, the electron-phonon scattering of charge carriers does not manifest itself on the $\rho_f(T)$ behavior.

Such scattering mechanism is important in description of the temperature behavior of electric resistivity of systems with the IV of Ce, when the relationship $T_K \approx T_D$ holds true.

REFERENCES

1. A.K. Bhattacharjee, B. Coqblin, Phys. Rev. B 13 (1976) 3441.
2. D.L. Cox, N. Grewe, Z. Phys. B – Cond. Matter. 71 (1988) 321.
- A. Freimuth, J. Magn. Magn. Mater. 68 (1987) 28.
3. G.S. Garde and J. Ray, Phys. Rev. B 51 (1995) 2960.
4. R.V. Lutsiv, M.D. Koterlyn, Fiz. Tverd. Tela. 25 (1983) 2484.
5. M.D. Koterlyn, O.I. Babych, R.I. Yasnitskii, Fiz. Tverd. Tela. 44 (2002) 792.
6. M.D. Koterlyn, O.I. Babych, R.V. Lutsiv, V.V. Nemoshkalenko, L.I. Nikolajev and A.V. Jushchenko. Preprint inst-ta metallofiziki AN USSR, Kijev, 1986.
7. M.D. Koterlyn, R.I. Yasnitskii, G.M. Koterlyn, B.S. Morokhivskii, J. Alloys Comp. 348 (2003) 52.
8. R.V. Lutsiv, M.D. Koterlyn, O.I. Babych, Fiz. Tverd. Tela. 26 (1984) 1781.
9. E.M. Levin, R.V. Lutsiv, L.D. Finkelshtein, N.D. Samsonova, R.I. Yasnitskii, Fiz. Tverd. Tela. 23 (1981) 2401.
10. M.D. Koterlyn, R.V. Lutsiv, R.I. Yasnitskii, Ukr. Fiz. Jurn. 29 (1984) 1587.
11. A.E. Sovestnov, V.A. Shaburov, J.A. Markova, E.M. Savitskii, O.D. Chistjakov and T.M. Shkatova, Fiz. Tverd. Tela. 23 (1981) 2827.
12. M.N. Groshev, M.D. Koterlyn, E.M. Levin, R.V. Lutsiv, N.M. Miftahov, Yu.P. Smirnov, A.E. Sovestnov, A.V. Tyunis, V.A. Shaburov, R.I. Yasnitskii, S.M. Kuzmina, V.I. Petrova and V.A. Tyukavin, Fiz. Tverd. Tela. 28 (1986) 2711.
13. N.E. Bickers, D.L. Cox, and J.W. Wilkins, Phys. Rev. B 36 (1987) 2036.
14. K.H. Fischer, Z. Phys. B.-Cond. Matter. 76 (1989) 315.
15. D. Gignoux, F. Givord, R. Lemaire and F. Tasset, J. Less-Common. Met. 94 (1983) 165.
16. Y. Isikawa, K. Mori, A. Fujii and K. Sato, J. Phys. Soc. Jap. 55 (1986) 3165.
17. A.P. Murani, R.S. Eccleston, Phys. Rev. B 53 (1996) 48.
18. E.S. Clementyev, M. Braden, V.N. Lasukov, P.A. Alekseev, J.-M. Mignot, I.P. Sadikov, A. Hiess and G. Lapertot, Physica B: Cond. Matter. 259-261 (1999) 42.