ELECTRONIC STRUCTURE AND KINETIC-PROPERTY PECULIARITIES OF PARAMAGNETIC NICKEL

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The features of the temperature dependence of the thermal conductivity, the electrical resistance, and the Lorentz function of paramagnetic nickel are analyzed within the framework of the interband carrier-scattering model.

Nickel is one of the metals whose thermophysical properties are presently under investigation. This is largely because of the great discrepancy between the results obtained, leading to the suggestion that a number of its electronic properties (primarily the conduction) are highly sensitive to the spectrum and amount of impurities. In [1] an attempt was made to discover the most probable conductivity polytherms and Lorentz function for paramagnetic nickel that is free from the influence of impurity. By means of statistical analysis of the most reliable data from the literature and our own work, the following equations were obtained to describe the temperature dependence of the properties under consideration.

The electrical resistivity is described by

$$\rho = 7.002 + 37.597 \cdot 10^{-3} T - 3.974 \cdot 10^{-6} T^2 \ (\text{МРТзН-68}). \tag{1}$$

The correction for thermal expansion was introduced according to the data of [2].

The Lorentz function is described by

$$L \cdot 10^8 = 2.944 - 0.209 \cdot 10^{-3} T + 0.137 \cdot 10^{-6} T^2, \ [L] = \text{V}^2/\text{deg}^2. \tag{2}$$

The thermal conductivity may be calculated from these data on the basis of the well-known Wiedemann—Franz relation

$$\lambda = LT\rho^{-1}. \tag{3}$$

The temperature characteristics of the conductivity of nickel following from these equations may expediently be illustrated on a graph in the coordinates: $\tilde{L} = L(T)/L(800)$, $\tilde{\lambda} = \lambda(T)/\lambda(800)$, $\tilde{\sigma} = T\sigma(T)/(800\sigma(800))$.

It is evident from Fig. 1 that the thermal conductivity of nickel is not constant, but rises with temperature, while the Lorentz number markedly (by 17% at 800°K) exceeds the theoretical value, and there is an evident tendency to increase with temperature; the value of $\tilde{\sigma}$ differs from unity, which is what it would be if the Bloch—Grüneisen law were satisfied, and also rises with temperature. It is of interest to establish the nature of these temperature peculiarities.

One possible reason for the temperature dependence of $\tilde{\lambda}$ and $\tilde{\sigma}$ is variation in the characteristic temperature Θ_D, which, as is well known, may be related to the relative change in volume of the metal due to thermal expansion as follows

$$\Theta_D = \Theta_D^0 \left\{1 - \Gamma_0 \frac{\delta V}{V}\right\}, \tag{4}$$

where Θ_D° is the Debye temperature at a volume V_0 and Γ_0 is the corresponding Grüneisen constant. The correction $\delta\Theta = \Gamma_0 \delta V/V_0 \approx 3\Gamma_0 \delta l/l_0$, where $\delta l/l_0$ is the relative linear expansion with change in temperature, determines the temperature dependence of the thermal conductivity and the specific electrical resistivity.

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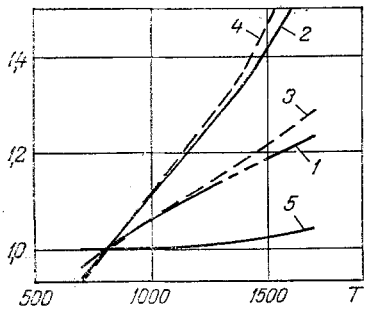

Fig. 1

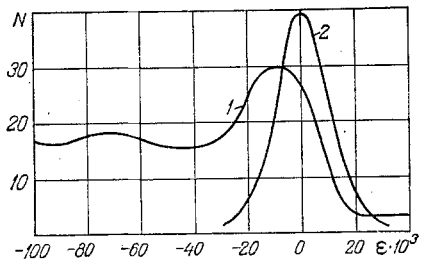

Fig. 2

Fig. 1. Polytherms of reduced critical characteristics of paramagnetic nickel: 1) $\tilde{\sigma}$; 2) $\tilde{\sigma}_V$; 3) $\tilde{\lambda}$; 4) $\tilde{\lambda}_V$; 5) $\tilde{L}$. T, °K.

Fig. 2. Total electron-state density of paramagnetic nickel according to [5]: 1) N(ε); 2) df/dε at T = 1000°K. N, states/at Ry; $\varepsilon \cdot 10^3$, Ry.

Using the data of [3] for the Grüneisen constant of nickel and the value of the thermal-expansion coefficient from [2], isochoric conductivity values have been calculated. Note that in the first approximation the given factor does not affect the Lorentz number. The data obtained are also shown in Fig. 1; the reduced conductivity at constant volume changes even more rapidly with temperature. In the temperature range 800-1600°K, the growth in $\tilde{\sigma}_V$ and $\tilde{\lambda}_V$ is $\approx 50\%$.

Nickel is a transition metal. It is natural, therefore, following Mott, to seek to explain the temperature anomalies in terms of the specific features of the electron spectrum associated with the d electrons.

Calculations of the band structure of nickel by various authors have shown that in the vicinity of the Fermi energy the electron-state-density curve has the form of an asymmetric bulge, the energy spread of which is of the order of kT in the given temperature region. This excludes the possibility of approximating the electronic spectrum by a branch of the standard d zone, and does not provide a basis for use of the correcting temperature factor found by Mott [4].

The state-density curve of paramagnetic nickel obtained in [5] is shown in Fig. 2, together with the curve of the energy derivative of the Fermi distribution. It is evident that analysis of the conductivity must be based on numerical integration, allowing all the features of the energy spectrum in the layer of electron thermal excitation to be taken into account.

If the hypothesis of constant basic-carrier velocity within the limits of the thermal layer is adopted, and their relaxation time is assumed to be inversely proportional to the d-electron state density, i.e., electron–phonon scattering from the s to the d band is assumed to be dominant, then expressions for the conductivities may be written in the form of the product of the normal conductivity with temperature-dependent factors:

$$\sigma = \sigma_0 \eta_0 (T), \tag{5}$$

$$\lambda = \lambda_0 \eta_\lambda (T), \tag{6}$$

$$\eta_0 = N_{d_0} G_0, \tag{7}$$

$$\eta_\lambda = \eta_2 (1 - G_1 G_2^{-1} G_0^{-1}), \tag{8}$$

$$\eta_2 = 3\pi^{-2} (kT)^{-2} N_{d_0} G_2. \tag{9}$$

The factors G_n, where n may take the value 0, 1, or 2, contain information on the d-band state-density curve:

$$G_n = \int_0^\infty (\varepsilon - \mu)^n N_d^{-1} (\varepsilon) \frac{\partial f}{\partial \varepsilon} d\varepsilon. \tag{10}$$

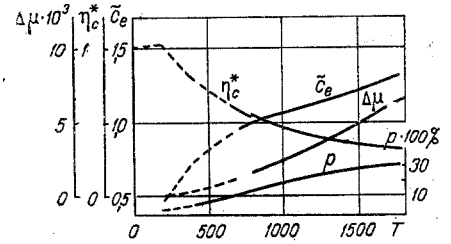

Fig. 3

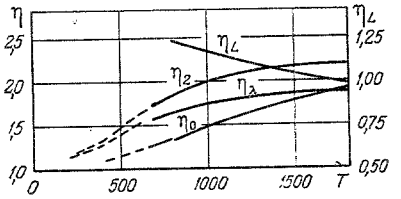

Fig. 4

Fig. 3. Thermodynamic factors of nickel. $\Delta\mu \cdot 10^3$, Ry.

Fig. 4. Transport-property correction factors for nickel.

The Fermi energy appearing in Eq. (10) depends on the temperature in view of the asymmetry of the total electron-state-density curve with respect to the Fermi level at T = 0°K.

The temperature dependence of the chemical potential may be calculated from the data of [5] on the state density; the results of the calculation are shown in Fig. 3. It is evident that when the temperature changes from 800 to 1600°K the Fermi level is shifted toward higher energy by $1.5 \cdot 10^{-3}$ and $5.4 \cdot 10^{-3}$ Ry, respectively. The dependence $\Delta\mu(T)$ is nonlinear: the weak increase in its temperature dependence reflects the involvement in the thermal excitation of d-band electron states lying a considerable distance from the Fermi energy in the region of formation of the second state-density maximum.

Results calculated for the relative change in electronic specific heat $\tilde{c}_e = c_e(T)/c_e(800)$ with temperature are also shown in Fig. 3. Note the rapid decline in the rate of increase in electronic specific heat of paramagnetic nickel occurring in the temperature range up to 1000°K. At higher temperatures, the function $c_e(T)$ is close to linear. For greater clarity, the quantity $\eta_c^* = 3c_e/(\pi^2 k^e T N_{T=0})$, showing the way in which the calculated curve deviates from the linear extrapolation from the low-temperature region, is also plotted in Fig. 3.

The results calculated for the correction factors for the transport properties are shown in Fig. 4. Here it must be emphasized that in calculating the integrals for G_n the function $N_d^{-1}(\varepsilon)$ was replaced by $(N_d(\varepsilon) + q)^{-1}$, where the parameter q, chosen arbitrarily, allowed the effect of the contribution of intraband electron—phonon scattering to be taken into account [6, 7]. Increase in q leads to decrease in the absolute value of the correcting factors and the convergence of their values.

The polytherms of $\eta(T)$ in Fig. 4 were obtained with q = 10. It follows from Fig. 4 that the electrical conductivity of paramagnetic nickel must decrease with rise in temperature at a slower rate than is indicated by the Bloch—Grüneisen law. Taking the form of the function $\eta_0(T)$ into account, it might be expected to follow a dependence of the type $(\alpha + bT - cT^2)/T$, which leads to an electrical resistivity varying as the inverse function $T/(\alpha + bT - cT^2)$. This agrees qualitatively with the experimental data in Fig. 1.

The thermal conductivity of paramagnetic nickel should rise with temperature, tending to a constant value. The first of these assertions corresponds to reality, but no slowing of the growth rate is observed. The difference in the curves of η_λ and η_0 within the framework of the given model must indicate the nature of the deviation of the Lorentz function from the standard value for a degenerate electron gas. Judging from the curve of $\eta_L(T)$, the Lorentz number of nickel at 800°K should be ≈25% higher than the theoretical value, and then begin to decrease with rise in temperature, reaching the theoretical value $2.445 \cdot 10^{-8}$ V^2/deg^2 at 1700°K. In practice (which is probably what matters most), this is not observed. The Lorentz number remains practically constant over a wide range at high temperatures.

Note that neither variation in the estimated limits of the parameter q nor taking account of the slight variations within the limits of the thermal layer of the s-band electron velocity allows these discrepancies to be explained. Thus, it must be concluded that the model of dominant s—d electron—phonon scattering, even when the real d-band state-density spectrum is taken into account, is a very coarse approximation for explaining all the high-temperature features of the transport properties of a classical transition metal such as paramagnetic nickel. For a more correct analysis, it is evidently necessary to take

into account the contribution to the conductivity of all the electron states occupying a vicinity of width ±(15-20)kT with respect to the Fermi level, allowing for effects of both intra- and interband scattering.

In the light of the foregoing, it seems worthwhile to investigate the mechanism of bipolar thermodiffusion in nickel, which may be responsible for the additional rise in thermal conductivity and the compensation of the drop in Lorentz number with rise in temperature.

NOTATION

ρ, specific electrical resistivity, $\mu\Omega\cdot$cm; T, absolute temperature, °K; L, Lorentz function; $\tilde{L}$, ratio of Lorentz function at current temperature to its value at 800°K; $\tilde{\lambda}$, ratio of thermal conductivity at current temperature to its value at 800°K; $\tilde{\sigma}$, reduced electrical conductivity; θ_D, Debye temperature; θ_D^0, Debye temperature of undeformed metal; Γ_0, Grüneisen constant; $\delta l/l_0$, relative linear expansion; η_0, η_λ, η_2, η_L, temperature factors; N_{d_0}, d-band state density at the Fermi level at T = 0°K; k, Boltzmann constant; G_n, energy integrals in the vicinity of the Fermi energy; f, Fermi—Dirac distribution function; ε, energy; c_e, electronic specific heat; N, total electron-state density at Fermi level; q, fitting parameter.

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