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Phenomenological functions for description of temperature dependences of thermal conductivities and specific resistances of solid metals from the main subgroups Ia–Va of the Periodic system

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Expressions for functions approximating experimental data on temperature depend-ences of thermal conductivities and specific resistances of 17 metals from the main subgroups Ia–Va of the Periodic system of D.I. Mendeleev are proposed. They allow not only to calculate the specified properties of metals, but also to predict, in particu-lar, the peak of thermal conductivity of calcium in the vicinity of absolute zero. The mathematical model does not describe the nonlinear behavior of the specific electrical resistance of barium, so a separate function is proposed to describe it. It is shown that the Wiedemann–Franz–Lorentz law is not fulfilled even approximately at temperatures below the Debye temperature for each metal. On between the Debye temperature and the melting point of the metal, it is satisfied when the dimensionless Lorentz number is approximately equal to one.

Keywords: thermal conductivity, specific electrical resistance, approximation, metal, main sub-group.

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1. Introduction

Wide use of metals in various branches of human activity attracts researches permanent attention to their properties for long time period. Development of new highly intelligent technologies requires not only creation of tabulated data bases, but also use of analytical relationships between the characteristics of metals and external parameters.

Currently in solid state physics the electron-phonon model of metals predominates. But in theory of thermal properties (Einstein, Debye models and their modifications [1–4]) it does not comply at temperatures above 300 K with determined experimental data [5–12] being in agreement with modern data bases on thermophysical properties of substance [13]. In particular, the model forecasts that temperature curve of thermal capacity will reach the horizontal straight line corresponding to Dulong–Petit law. Unlike the theory the experiment demonstrates further rise of thermal capacity with temperature increasing for a series of metals. Besides, the model does not explain the presence of features on the thermal capacity curve in form of step changes of the base line, peaks and pits. Their presence and physical nature were described in model of the two-phase system [14–16].

A similar picture is observed when describing the temperature dependences of thermal conductivity and resistivity of metals. Drude–Lorentz theory of free electrons (see for example [17,18]) and its modification by Sommerfeld explained Ohm, joule–Lenz, Wiedemann–Franz–Lorenz laws and other effects in metals [19–22]. But presentation, e. g., of thermal conductivity of sample as two terms linked with contributions of free electrons and lattice oscillations, does not result in relationships describing the test data. Use of the methods of Fermi-Dirac quantum mechanics and statistics to describe the behavior of free electrons shows that as they approach the absolute zero on the Kelvin scale, their energy below a certain threshold temperature remains constant. This means the possibility to observe in the experiment the residual values of thermal conductivity and resistivity of some metals upon reaching the temperature $T = 0\,\mathrm{K}$.

One of the methods describing the experimental data is search of the approximation functions [23], this corresponds to the present paper task. Besides, for solid metals from main subgroups Ia–Va of Mendeleev Periodic System it is necessary to check execution of Wiedemann–Franz law on thermal conductivity λ $[\mathrm{W/(m \cdot K)}]$ link with resistivity σ $[\Omega^{-1} \cdot \mathrm{m}^{-1}]$, and to determine type of thermal dependence of Lorentz number Lo $[\mathrm{W \cdot \Omega/K^2}]$. Presence of analytical expressions removes some negative statements of authors [24] on impossibility to forecast the thermal and electrical conductivities of the alloy as per known characteristics of components, and on use of unreasonable assumptions.

2. Functions describing thermal conductivity and resistivity of metals of main subgroups Ia–Va

The main subgroups Ia–Va of the Periodic System of D.I. Mendeleev comprise the following metals: Ia — lithium Li, sodium Na, potassium K, rubidium Rb, ce-

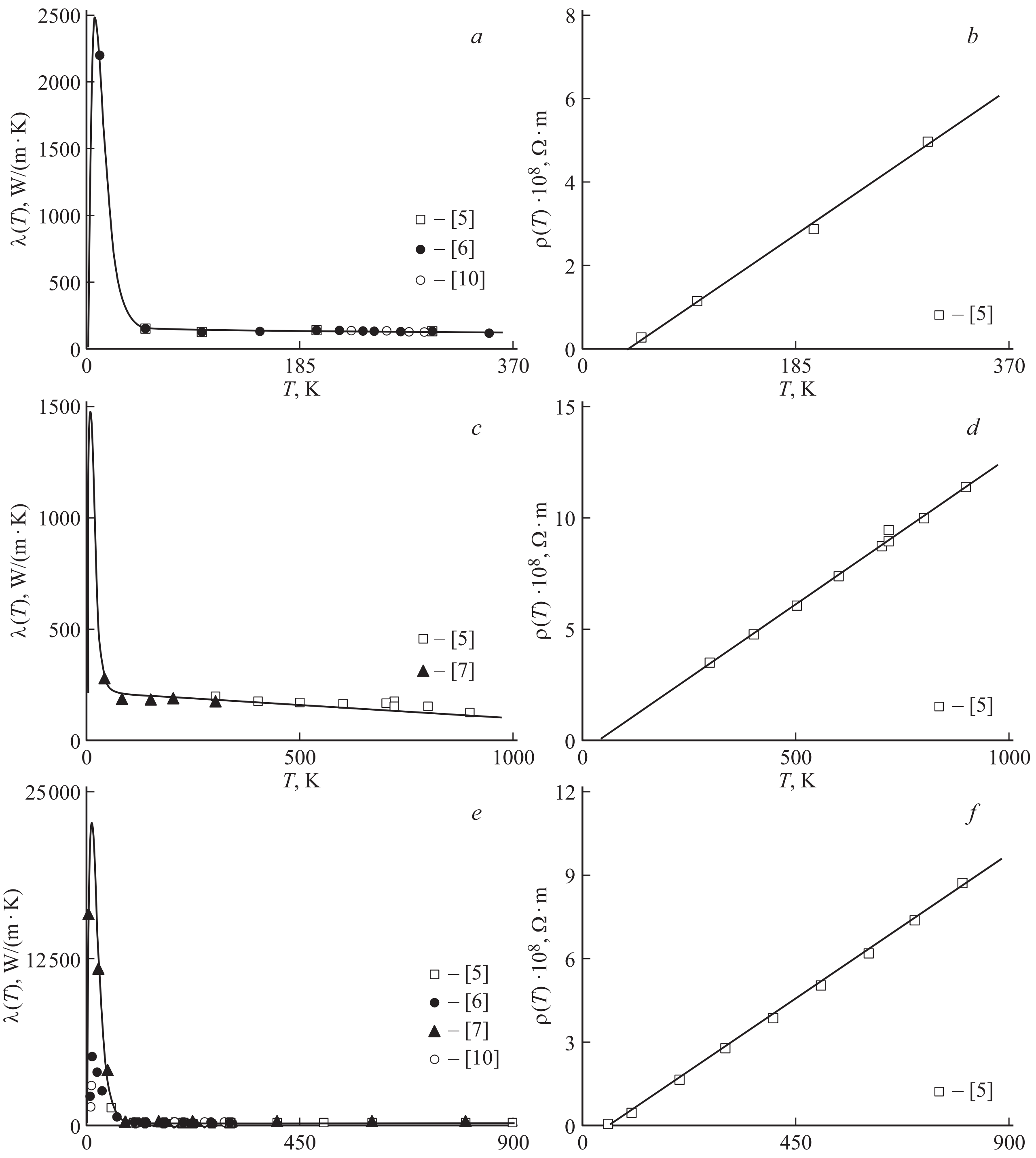

Figure 1. Thermal conductivities (a, c, e) and resistivities (b, d, f) of sodium Na (a, b), calcium Ca (c, d) and aluminium Al (e, f) in solid state.

sium Cs, francium Fr (not presented here due to its radioactivity); IIa — beryllium Be, magnium Mg, calcium Ca, strontium Sr, barium Ba, radium Ra (not presented due to its radioactivity); IIIa — aluminium Al, gallium Ga (not presented due to absence of reliable test data), indium In, thallium Tl; IVa — tin Sn, lead Pb; Va — antimony Sb, bismuth Bi.

During mathematical modeling of temperature behavior of thermal conductivities and resistivities $\rho = 1/\sigma$ $[\Omega \cdot \mathrm{m}]$ of the listed metals we need to consider thermal expansion of samples [18]. Besides, consider the formation of peak of thermal conductivity upon absolute zero approaching by temperature $(T = 0\,\mathrm{K})$. Its occurrence may be associated with scattering of free electrons on defects and impurity

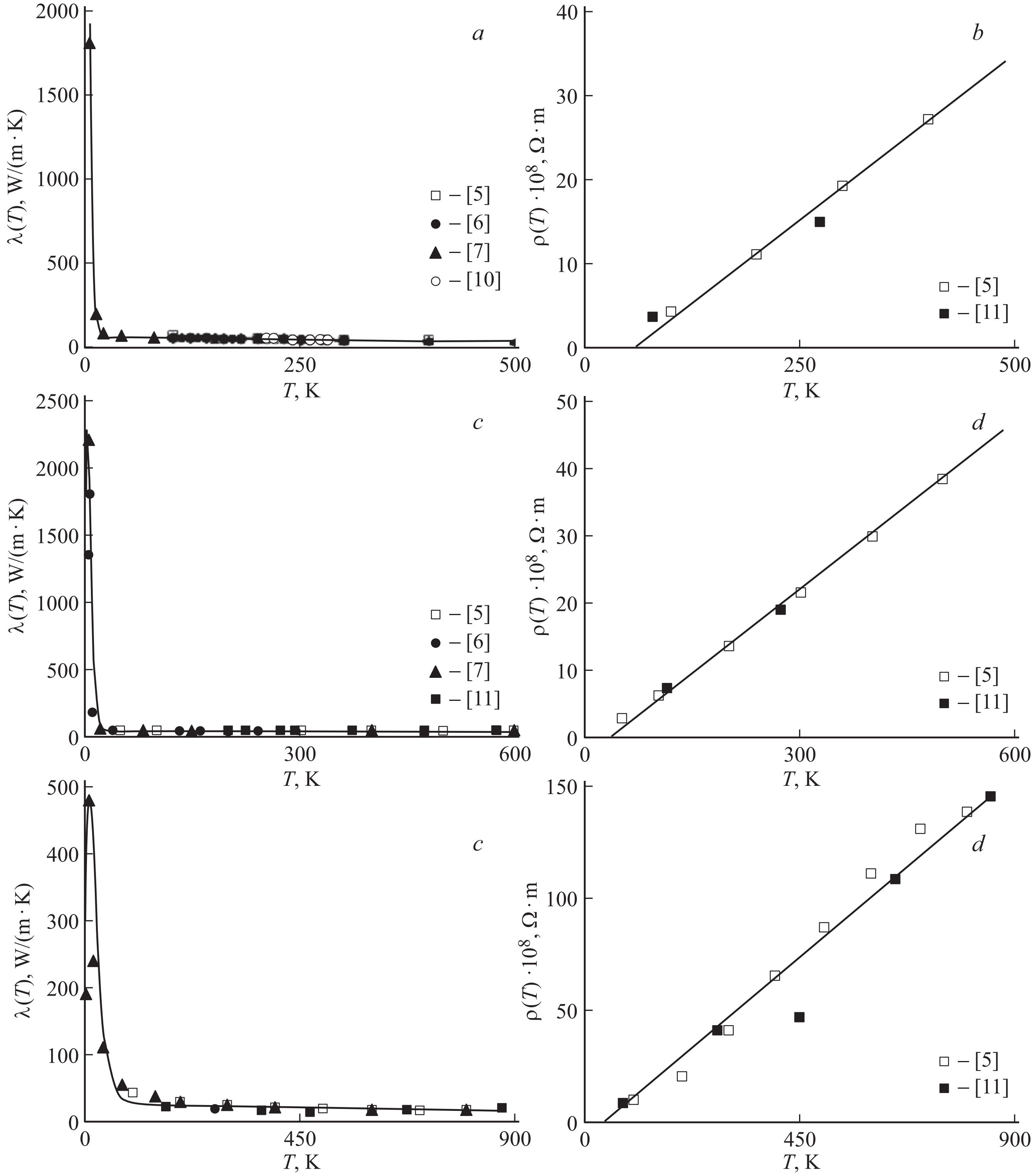

Figure 2. Temperature dependences of thermal conductivity (a, c, e) and resistivity (b, d, f) of thallium Tl (a, b), lead Pb (c, d) and antimony Sb (e, f) in solid state.

centers or with dipole fields of such quasi-particles as exciton, polaron and other objects of similar type [25]. In the latter case, the metal can have dielectric properties at rather low temperatures T [K]. The thermal conductivity peak decreases when doping elements content in metal increases, metal purity decreases, grain size decreases and upon other factors.

To describe said thermal changes in metal itis suggested in temperature range from absolute 0 K to melting point T_{ph} [K] to approximate the experimental data [5–12] by

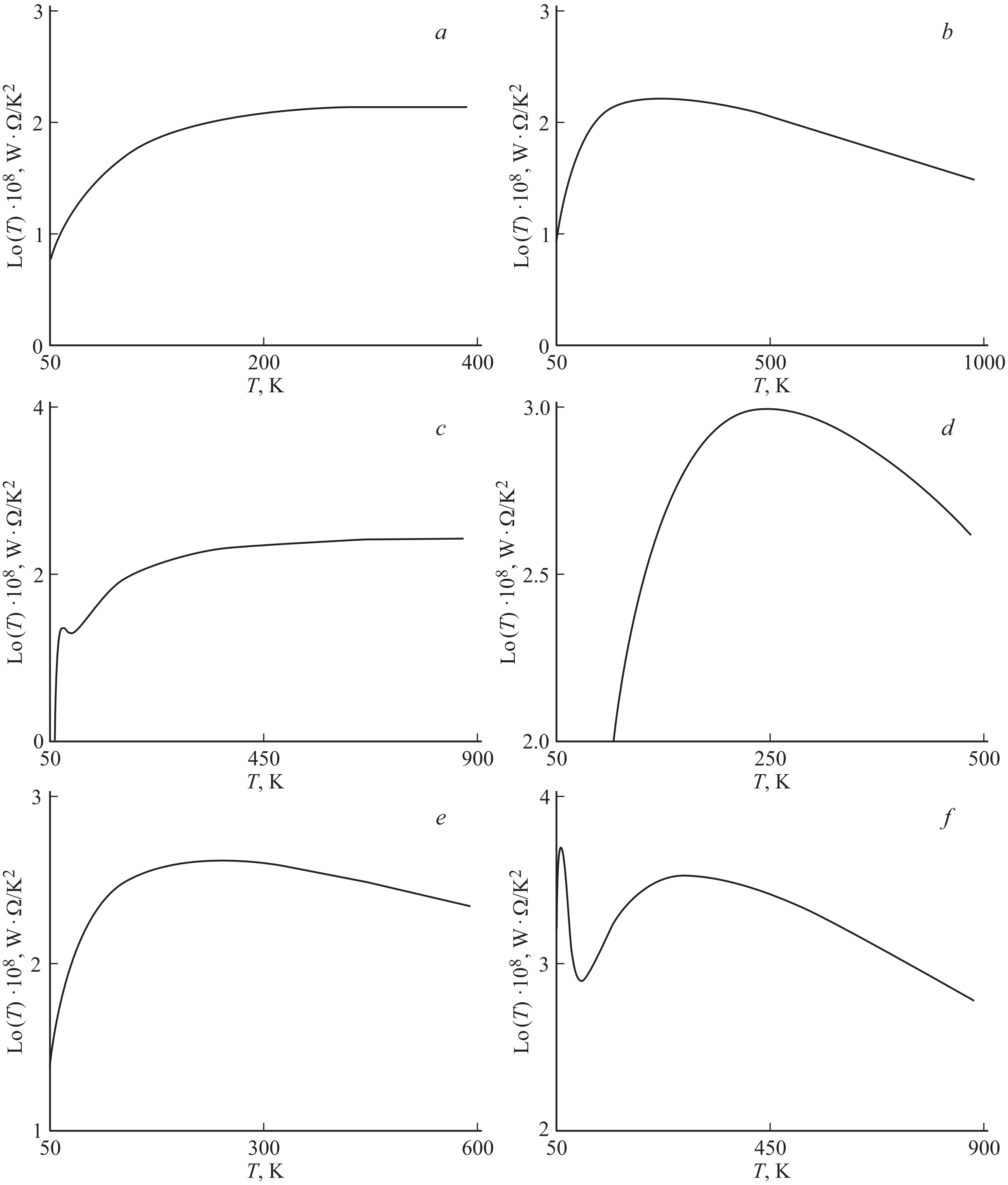

Figure 3. Changes in Lorentz number Lo with temperature for metals of main subgroups Ia–Va in solid state: sodium Na (*a*), calcium Ca (*b*), aluminium Al (*c*), thallium Tl (*d*), lead Pb (*e*), antimony Sb (*f*).

formulas

$$\begin{cases} \lambda(T) = aT\exp(-bT) + \lambda_{0s}[1 + \alpha_{1s}(T - T_{\mathrm{ph}})], \\ \rho(T) = \rho_{0s}[1 + \alpha_{2s}(T - T_{\mathrm{ph}})], \end{cases} \tag{1}$$

where $a, b, \lambda_{0s}, \alpha_{1s}, \rho_{0s}, \alpha_{2s}$ — constant coefficients. The first term in the first equation (1) describes contribution to thermal conductivity of electron-like subsystems (electrons, singly negatively charged impurity centers etc.). In vicinity of absolute zero we can decompose the exponent into Maclaurin row, and then the first term is presented as $aT\exp(-bT) \approx aT - abT^2$. Therefore, parameter a determines electron thermal conductivity coefficient, and parameter b (in product with a) — thermal conductivity coefficient of electron-like subsystem. The second term in the first equation (1) is associated with thermal expansion of sample. Parameter λ_{0s} sets value of thermal conductivity of atomic-like subsystem T_{ph}, and parameter α_{1s} — thermal expansion of metal. Parameters ρ_{0s} and α_{2s} in second equation of system (1) for resistivity have same physical meaning. From system (1) it is obvious that when temperature reaches $T = 0\,\text{K}$ the thermal conductivity and resistivity of metal reach residual values $\lambda(0) = \lambda_{0s}[1 - \alpha_{1s}T_{\text{ph}}]$ and $\rho(0) = \rho_{0s}[1 - \alpha_{2s}T_{\text{ph}}]$ respectively. On second boundary of the temperature range at $T = T_{\text{ph}}$ they are equal to $\lambda(T_{\text{ph}}) = aT_{\text{ph}}\exp(-bT_{\text{ph}}) + \lambda_{0s}$ and $\rho(T_{\text{ph}}) = \rho_{0s}$.

Tables 1 and 2 show the values of constant coefficients for calculating the values of the approximating functions of system (1). Table 1 does not show parameters to calculate the resistivity of barium, as the experimental data are described by nonlinear dependence

$$\rho(T) = 0.08T\exp(-0.00123T). \quad (2)$$

Table 1. Parameters of temperature dependence of thermal conductivity and resistivity of solid metals from the main subgroups Ia–IIa of Periodic System

№	Metal	Parameters of approximating functions				
		a	$b\cdot10^3$	λ_{0s} $\rho_{0s}\cdot10^8$	$\alpha_{1s}\cdot10^3$ $\alpha_{2s}\cdot10^3$	T_{ph}
Subgroup Ia						
1.	Li	139.8164	76	64.0	−1.6	453.69
				15.55	2.53	
2.	Na	1015.994	160	126.0	−0.5	371.01
				6.37	2.9	
3.	K	2492.357	430	105.4	1.0	336.86
				6.37	2.9	
4.	Rb	136.0975	340	55.2	−0.5	312.47
				12.0	3.3	
5.	Cs	756.14	152	136.0	−0.09	301.59
				4.8	3.8	
Subgroup IIa						
6.	Be	466.0197	36	33	−3	1558
				44.9	0.73	
7.	Mg	1877.93103	124	140	−0.2	923
				14.9	1.12	
8.	Ca	500.3643	146	97	−1.2	1112
				14.2	0.93	
9.	Sr	48.4127	46	22	−0.8	1041
				45.9	0.95	
10.	Ba	3.53597	60	7	−3	998
				–	–	

Table 2. Parameters of temperature dependence of thermal conductivity and resistivity of solid metals from the main subgroups IIIa–Va of Periodic System

№	Metal	Parameters of approximating functions				
		a	$b\cdot10^3$	λ_{0s} $\rho_{0s}\cdot10^8$	$\alpha_{1s}\cdot10^3$ $\alpha_{2s}\cdot10^3$	T_{ph}
Subgroup IIIa						
1.	Al	6445.05435	102	214.0	−0.23	933.61
				10.2	1.14	
2.	In	6109.0033	402	71	−1.15	429.78
				13.4	2.39	
3.	Tl	2732.175	460	30	−2	576.2
				40.8	1.93	
Subgroup IVa						
4.	Sn	27875.1622	303	54	−1.2	505.12
				21.5	2.1	
5.	Pb	1910.3738	316	29	−0.7	600.65
				46.8	1.75	
Subgroup Va						
6.	Sb	105.06092	84	15.5	−0.79	903.5
				154.1	1.16	
7.	Bi	379.83015	157	6.9	−1.25	544.59
				210.7	1.77	

The rest characteristics of metals of main subgroups Ia–Va are rather well approximated by functions of system (1), which is represented by solid lines in Figures 1 and 2 (sources of experimental data and their notations are shown in right bottom corner of Figures). Besides, from Figure 1, *e* it is evident that the proposed functions allow us to predict the behavior of the thermal conductivity of calcium in the vicinity of absolute zero.

3. Check of fulfillment of relation in form of Wiedemann–Franz–Lorentz law

If there are analytical expressions for electronic component of thermal conductivities λ_e and resistivities ρ of metals it is easy to check the approximated Wiedemann–Franz–Lorentz law written as

$$\lambda_e/(\sigma T) = \lambda_e\rho/T \approx \text{Lo}, \quad (3)$$

where Lo — Lorentz number, equal as per Sommerfeld to $2.47\cdot10^{-8}\,\text{W}\cdot\Omega/\text{K}^2$.

Law (3) determines relation of metal thermal conductivity to its electrical conductivity in form of linear function of temperature. However, the constancy of the angular coefficient Lo is observed only in certain temperature range ([8], p. 68–69 and [9] p. 208). Beyond this range the Lorentz number depends on temperature, this is associated with increase of contributions to thermal conductivity of electrons scattering in impurity centers at low temperatures, and increase in role of lattice component at high temperatures. So, definite interest is linked with check of relation of form (3) for relation of thermal conductivity λ of sample to its electrical conductivity. Figure 3 shows design temperature dependences of Lorentz functions for metals from different main subgroups. Figure 3, *a–f* shows that relation (3) is not met even approximately in region below Debye temperature T_{D} (for example, for sodium $T_{\mathrm{D}} = 155\,\mathrm{K}$ [26]) due to nonlinear temperature dependences of Lorentz functions, this is confirmed by the experimental data, e.g. for alkali metals ([8], p. 68, Figure 23). For calcium Ca (Figure 3, *b*), thallium Tl (Figure 3, *d*), lead Pb (Figure 3, *e*) and antimony Sb (Figure 3, *f*) relation in form of Wiedemann–Franz–Lorentz law is not met in all temperature range of solid state existance. Calculations show that the closer the dimensionless number $L(T) = \mathrm{Lo}(T)/\mathrm{Lo}(T_{\mathrm{ph}})$ is to 1 in range from Debye temperature T_{D} to melting point T_{ph}, the more accurate the relation in form of Wiedemann–Franz–Lorentz law is met.

4. Conclusion

When developing new technologies for extracting metals from ores, treating metals, creating new alloys and solving other problems, it is important to know such characteristics of metals as thermal conductivity and electrical resistivity. Used theoretical models, unfortunately, do not result in analytical expressions that adequately describe the experimental data. As result the mathematical approximation is applied. Functions suggested in the paper not only rather well describe the arrays of test data, but also ensure prediction of behavior of said characteristics in temperature ranges where experiments are not executed. Besides, they give possibility to check fulfillment of Wiedemann–Franz–Lorentz law for the relation of sample thermal conductivity to its electrical conductivity. Note also the universalism of the suggested temperature dependences, as they ensure description f behavior of thermal conductivities and resistivities of metals from different main subgroups from different main subgroups of Mendeleev Periodic System (excluding resistivity of barium).

Conflict of interest

The author declares that he has no conflict of interest.

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