

Features on the graphs of thermal characteristics of metals in the absence and presence of phase transitions

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It is shown that the model of a two-phase system for the first time made it possible not only to calculate the temperature dependences of the heat capacities and thermal expansion coefficients of a number of metals in the ranges of the studied temperatures, but also to calculate their values outside these intervals. The relationship between the appearance of features in the form of „peaks“ and „pits“ on the graphs with the course of phase transitions and processes in phase subsystems has been established. It has been demonstrated that in the region close to absolute zero, compression of crystals of metals of hexagonal and cubic syngonies is possible with an increase in temperature in the direction perpendicular to the axis of the applicate.

Keywords: phase transition, thermodynamic model, heat capacity, syngony, linear thermal expansion coefficient.

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1. Introduction

Experimental studies of thermal expansion and heat capacity of metals in wide temperature range are accompanied by monitoring of features of their behaviour [1–5]. They manifest in form of „peaks“ and „pits“, occurred in region of implementation of one or another phase (polymorphous, magnetic, aggregate transition. „Approximation of experimental data is performed by different methods: using combination of Debye and Einstein functions, using spline functions, polynomial dependencies etc.“ [6, p.8]. But no one of the proposed theoretical constructions describes the heat capacity graphs in the presence of phase transition [6; 7, p.183].

In paper [8] a simple thermodynamic model of two-phase system is presented, using it thermo- and chronochanges of amorphous alloys [9–13] were adequately described, as well as base lines of temperature dependences of heat capacities and thermal expansion coefficients of different substances [14].

This paper objective is description based on ratio [14] of graphs of heat capacity of metals upon presence in region of experimental study of phase transition and behaviour of main components of tensor of coefficients of linear thermal expansion of anisotropic crystals of hexagonal and cubic crystal systems near absolute zero, as well as changes in the indicated thermal characteristics in wide temperature ranges.

2. Features on graph of heat capacity of metals

Substantial heat capacity of a substance taking into account „kinetic“ contribution is calculated as per [14] by

formula

$$C(T, x, u) = k_1T + k_2x + k_3Tu, \quad (1)$$

where T — temperature, x — bulk proportion of formed phase, $u = dx/dT$ — its first derivative with respect to temperature, k_i ($i = 1, 2, 3$) — coefficients. Constancy of function $f(x, u)$ in formula (19) of paper [14] is associated with the supposition that main contribution to its value is provided by point of phase transition determining height (depth) of extremum. This is associated with limitation of function $f(x, u)$ in temperature range of implementation of kinetic formation of „peak“ („pit“). The bulk proportion x is calculated from ratio [8]:

$$x(T) = 0.5[1 - \text{th } \varphi(T)], \quad (2)$$

where argument $\varphi(T) = a((T_x/T) - 1)$, $a = 2T_xu_x$ — model parameter, $u_x = u(T_x)$ — extreme value of derivative dx/dT , calculated at temperature T_x of maximum heat release.

During experimental study of substance the total manifestation is considered: redistribution of atoms in space, presence of volatile components and phase transitions, progress of chemical reactions etc. These kinetic processes can change the temperature dependence of substance heat capacity. Figure 1 demonstrated curves of heat capacity (1) of model substance at values of parameters $a = 10$, $T_x = 125$ K, $k_1 = 0.05$, $k_2 = 40$ and k_3 : 1 — (–6), 2 — 0, 3 — 6.

Said processes occur not only in basic phase, but in its subsystems of quasiparticles (phonons, magnons etc.). Their effect on the experimental curves is manifested as „peaks“ and „pits“, which extremums are located near temperature of phase transitions. If in the new phase the effect of its own kinetic processes is insignificant, and the subsystem of

Table 1. Parameters of theoretical model to calculate temperature dependences of metal heat capacity

Metal	a	$a_{(1/2)}$	T_x , K	$T_{x(1/2)}$, K	T_{pl} , °C	$k_{1/(1/2)} \cdot 10^4$	$k_{2/(1/2)}$	$k_{3/(1/2)}$
Ag	0.65	10.0	73	1293	1274	49.5/0	32.0/0	0/0.52
Ni	0.56	13.8	156	562 (631*)	1455	50/0	38.7/0	0/1.4
Rh	0.85	—	115	—	1963	62	31.54	—
Ti***	0.53	6.0/10.0	153	1288/1844 (1156**)	1941	46/0/0	37.9/0/0	0/−0.9/0.6

Note. * — Curie temperature [15, p.192]

** — polymorphic transformation temperature $\alpha \rightarrow \beta$ [16, p.242]

*** — heat capacity of Ti was calculated considering polymorphic transformation sequence as per formula (4).

the type i contributes only to „kinetic“ (k) component of formula (1), i. e.

$$C_{k(i)} = k_{3(i)} Tu_{(i)}, \quad (3)$$

then graphs of temperature dependence of heat capacity at values of model parameters $a = 2.5$, $T_x = 100$ K, $k_1 = 0.05$, $k_2 = 40$, $a_{(i)} = 20$, $T_{x(i)} = 250$ K, $k_{1(i)} = 0.05$, $k_{2(i)} = 30$ and $k_{3(i)}$: 1 — (−1.5), 2 — 0, 3 — 2.5 are shown in Figure 2.

Most often, this type of dependence of heat capacity on temperature is observed in pure metals. Table 1 presents the parameters of the model of four metals for which in the experimental study interval (Figure 3): a — there are no phase transitions (black circles — data [1], black squares — [3], white triangles — [4]); b — change in the aggregate state is observed (squares — data [1], circles — [3], triangles — [4]); c — polymorphic transformations occur (squares — data [1], circles — [3]); d — a magnetic phase transition occurs (squares — data [1], circles — [3]).

Figure 3 shows experimental data and calculations of theoretical temperature dependences of heat capacities of metals (lines of dots in graphs indicate path of base curve of heat capacity upon feature absence). Note that graph of

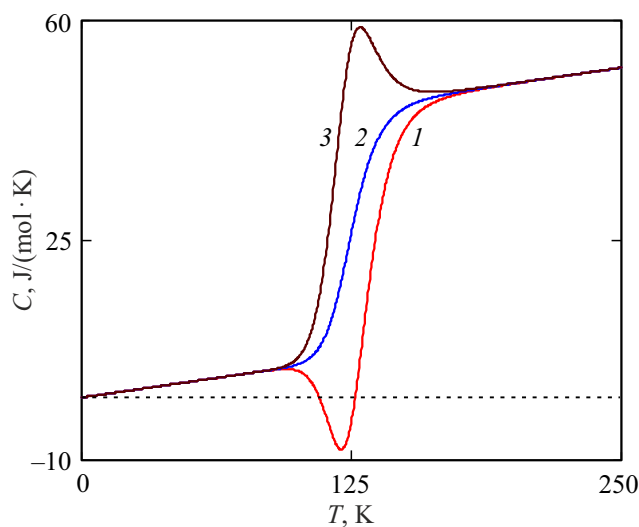


Figure 1. Heat capacity of model substance vs. temperature upon presence of kinetic processes.

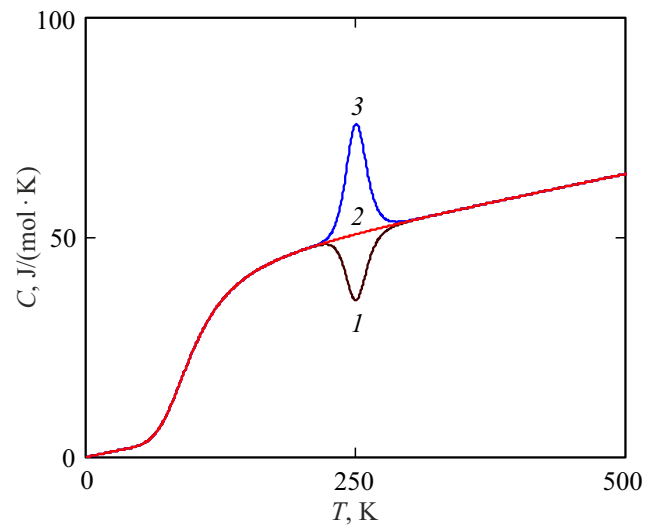


Figure 2. Graph of heat capacity of model substance upon implementation of phase transition in subsystem i at temperature $T = 250$ K.

heat capacity for titanium Ti (Figure 3, c) was plotted as per formula

$$C = k_1 T + k_2 x + k_{3(1)} Tu_{(1)} + k_{3(2)} Tu_{(2)}, \quad (4)$$

where values in equation (4) are set by ratio

$$u_{(1)} = dx_{(1)}/dT, \quad x_{(1)} T = 0.5[1 - \text{th} \varphi_1(T)],$$

$$\varphi_1(T) = a_{(1)}((T_{x(1)}/T) - 1), \quad u_{(2)} = dx_{(2)}/dT,$$

$$x_{(2)} T = 0.5[1 - \text{th} \varphi_2(T)], \quad \varphi_2(T) = a_{(2)}((T_{x(2)}/T) - 1),$$

$$k_{3(2)} = 0.6, \quad a_{(2)} = 10.0, \quad T_{x(2)} = 1844 \text{ K.}$$

Thus, Figure 3 demonstrates applicability of theoretical model to describe experimental data in wide range of temperatures. Features in the temperature dependences of the heat capacity and the thermal expansion coefficient (TEC) can manifest themselves not only in the form of „peaks“ and „pits“. Their appearance is determined by the phenomena and processes occurring in the phase subsystems: changes in their compositions; removal of internal stresses; subsystems transition to metastable state;

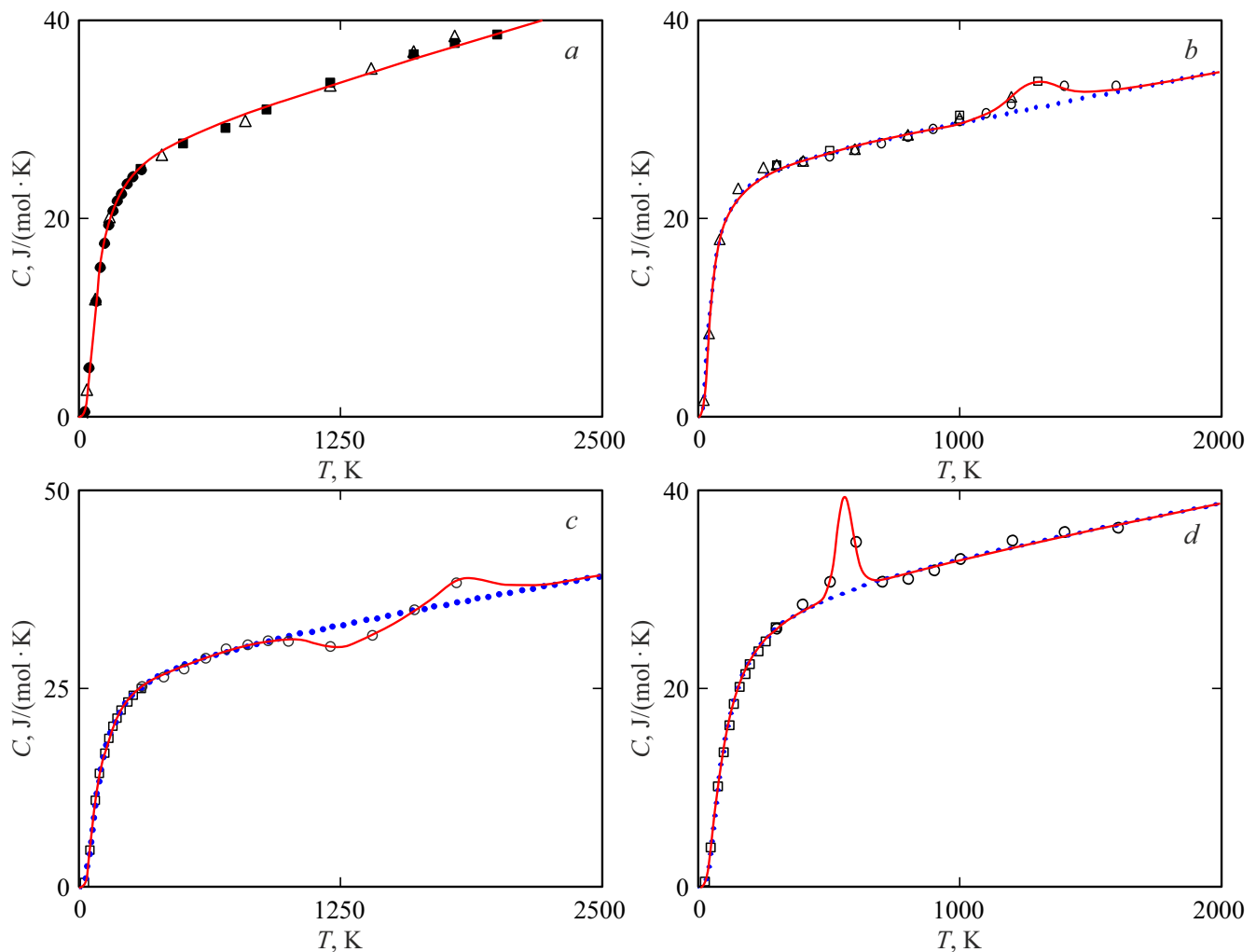


Figure 3. Temperature dependence of heat capacity: *a* — rhodium Rh in the absence of phase transitions; *b* — silver Ag in the presence of transition to new aggregate state; *c* — titanium Ti taking into account the sequence of polymorphic transformations; *d* — nickel Ni during magnetic phase transition.

rearrangement of components, defects and quasiparticles in space; occurrence of vector fields, etc. From the mathematical point of view, they influence the shape of the temperature curves through expressions such as the second and third terms in the calculation formula (1). Hence, the experimental data on the temperature dependences of the TEC are influenced by: elastic stresses, if the sample was not pre-annealed; defects (e.g. vacancies), which at room temperature are in „frozen“ state; impurities and quasiparticles that can contribute to the occurrence of „static“ and/or „kinetic“ effects. In this relation let's consider TEC calculation for some metals.

3. Effect of subsystems on thermal expansion of anisotropic crystals

Isotropic solid bodies are characterized by same value of TEC in all directions. Major of crystals are anisotropic and upon heating demonstrate uniform deformation ε_{ij} [17,18].

Upon change in sample temperature by value ΔT tensor of deformations is

$$\varepsilon_{ij} = \alpha_{ij}\Delta T, \quad (5)$$

where α_{ij} — symmetric tensor of second rank of linear TEC. If we select main directions of tensor of deformations ε_{ij} as coordinate axes then tensor (5) accepts the diagonal appearance. The main diagonal contains the components

$$\varepsilon_1 = \alpha_{11}\Delta T, \quad \varepsilon_2 = \alpha_{22}\Delta T, \quad \varepsilon_3 = \alpha_{33}\Delta T, \quad (6)$$

here α_{ii} ($i = 1, 2, 3$) — own values of tensor of linear TEC. „For crystals of hexagonal and trigonal crystal systems, the expansion coefficient is determined in two directions — parallel and perpendicular to the axis of the sixth (third) order. At that $\alpha_{11} = \alpha_{22} = \alpha_{\perp}$, $\alpha_{33} = \alpha_{\parallel}$ “ [18, c.32], $\alpha_{cp} = (2\alpha_{\perp} + \alpha_{\parallel})/3$.

According to Neumann principle [17,18] upon absence of phase transformations the thermal expansion (compression) has crystal symmetry both during heating, and during

Table 2. Parameters of theoretical model to calculate temperature dependences of metal LTEC

Metal		$a_{1/(2)}$	$a(1)$	$T_{x1/(2)}, K$	$T_{x(1)}, K$	$T_{pl}, ^\circ C$	$q_{1/(1/2)} \cdot 10^4$	$q_{2/(1/2)}$	$q_{3/(1/2)}$
Cd	α_{\parallel}	0.750	0	52	0	321	17	39	0
	α_{\perp}	0.490	0	60	0	321	600	12	-20.6
Zn	α_{\parallel}	0.729	6.30	59	693	419.5	0/37/0	0/37.4/0	0/1.2/0
	α_{\perp}	0.900	0	61	0	419.5	0/0/240	0/0/8.1	0/0/ (-14.2)
Cr		0.800	0.44	180	43	1890	28/0	9.8/0	0/(-1.44)
α -Mn	[5]	0.940	0.98	106	16	1245	209	25	0/(-12.0)/(-1.7)
	[20]	0.790	0	120	0	1245	220.8	23	0

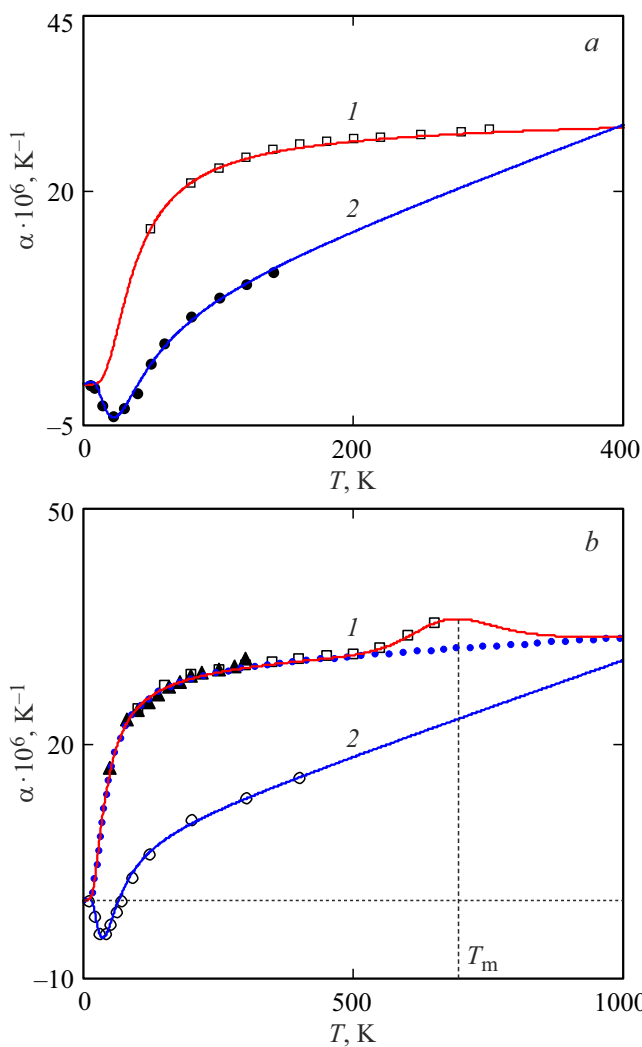


Figure 4. LTEC of cadmium Cd (a) and zinc Zn (b) vs. temperature: 1 – α_{\parallel} ; 2 – α_{\perp} .

cooling. In other words, regardless of temperature the crystal relates to one or another crystallographic class. The eigenvalues of the tensor of linear TEC are generally determined by different temperature dependences. Note that

in the vicinity of absolute zero, where even thermal fluctuations „freeze out“ the graphs of the principal components of the TEC tensor may have features due to „static“ and/or „kinetic“ effects.

Considering Gruneisen second ratio (see, for example, [18, p.13; 19, p. 26]) and formula (1) the linear thermal expansion coefficient (LTEC) in any direction can be

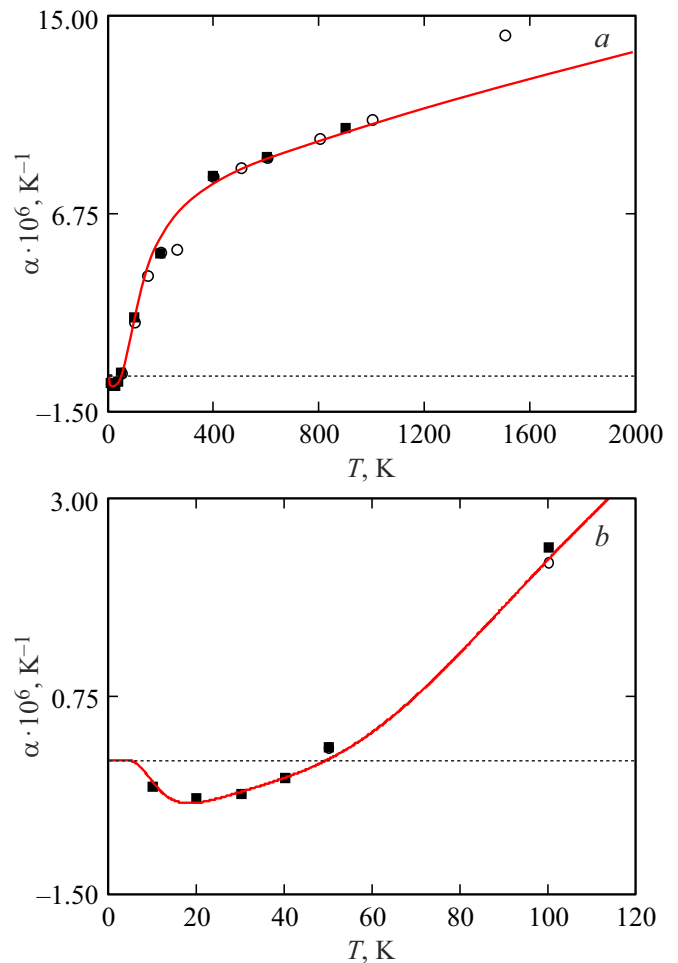


Figure 5. Temperature dependence of LTEC of chromium Cr (a) and region increasing in vicinity of absolute zero (b).

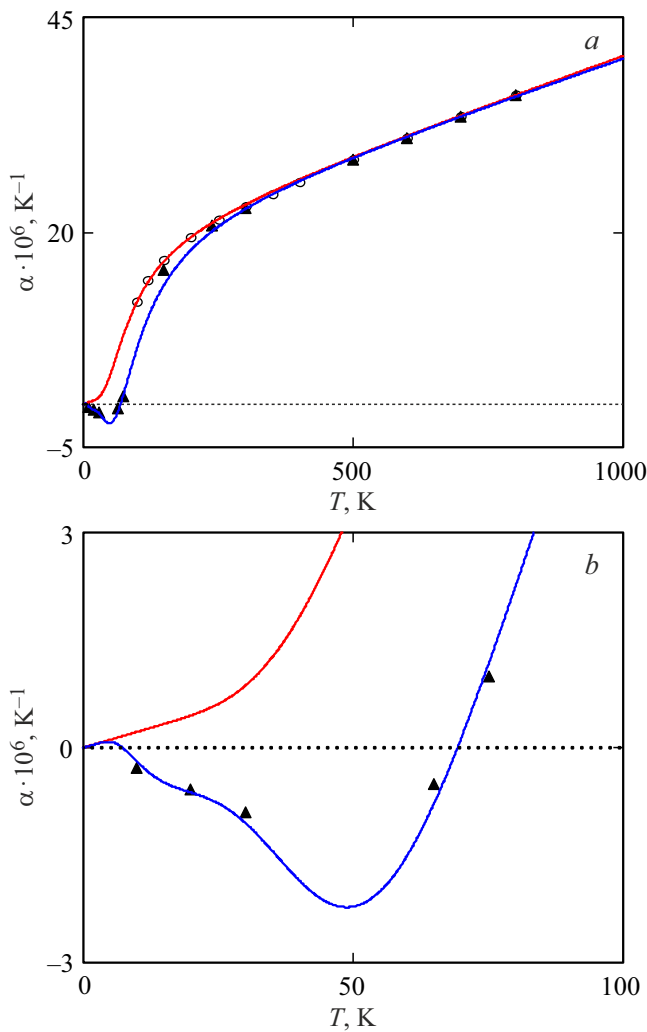


Figure 6. LTEC of magnesium α -Mn vs. temperature (a) and region increasing in vicinity of absolute zero (b).

calculated by formula

$$\alpha(T, x, u) = q_1T + q_2x + q_3Tu, \quad (7)$$

where q_i ($i = 1, 2, 3$) — model coefficients. In formula (7) first term describes effect on thermal expansion of body of electronic subsystem; second — change in composition of phase i.e. is responsible for „static“ effects; third — describes contribution to LTEC of „kinetic“ processes associated with „rate“ (first derivative of phase composition with respect to temperature) change of bulk proportion of phase.

As examples Table 2 shows model parameters of four metals to calculate their LTEC by formula (7). Crystals of cadmium Cd and zinc Zn relate to hexagonal crystal system. Their temperature dependences of LTEC are shown in Figure 4. For cadmium Cd: α_{\parallel} (1) (white squares — data [1]) and α_{\perp} (2) (black circles — data [18]) — in Figure 4, a; for zinc Zn: α_{\parallel} (1) (white squares — data [20], black triangles — [1]) and α_{\perp} (2) (white circles —

data [18]) — in Figure 4, b respectively. Figure 4, a, b shows effect of „kinetic“ process of phase composition change on temperature course α_{\perp} . Figure 4, b shows feature as „peak“, its occurrence is associated with zinc Zn transition to new aggregate state at temperature 693 K ($T_{pl.} = 419.5^{\circ}\text{C}$).

Crystals of chromium Cr and manganese α -Mn have body-centered cubic lattice (cubic crystal system). Figure 5 shows the temperature dependence of LTEC of chromium Cr (Figure 5, a: black squares — data [5], white circles — [18]), while the enlarged region in the vicinity of absolute zero (Figure 5, b) demonstrates the influence of „kinetic“ rearrangement of the subsystem, the heat release extremum of which is at temperature $T = 43$ K. Figure 6 shows course of temperature curves of LTEC of manganese α -Mn (Figure 6, a: black triangles — data [5]; white circles — [20]) and region increasing in vicinity of absolute zero (Figure 6, b). For theoretical description of data [20] it was necessary to consider both own „kinetic“, and „static“ effects, i.e. calculate as per formula

$$\alpha = q_1T + q_2x + q_3Tu + q_{2(1)}x_{(1)}, \quad (8)$$

where $x_{(1)}(T) = 0.5[1 - \text{th}(\phi_{(1)}(T))]$, $\phi_{(1)}(T) = a_{(1)}((T_{x(1)}/T) - 1)$, $q_{2(1)} = -1.7$, $a_{(1)} = 0.98$, $T_{x(1)} = 16$ K. The appearance of the „static“ effect is apparently associated with the „freezing“ of thermal fluctuations or the displacement of defects and other nonequilibrium states to the crystal boundaries.

4. Conclusion

One of the unsolved problems of solid body physics is the theoretical description of the thermal characteristics of matter not only in the intervals of experimental study, but also outside this area. Besides, the appearance of „peaks“ and „pits“ on the temperature dependences of heat capacities and thermal expansion coefficients of various substances, the occurrence of negative values of the relative elongation of samples in any direction in the vicinity of absolute zero significantly complicate the formulated problem. So, in present paper we first suggests the approach to calculation of thermal heat capacities and thermal expansion coefficients based on ratios of thermodynamic model of two-phase system. Good agreement between theoretically calculated curves and experimental data indicates the reliability of the initial assumptions of the model and the wide range of its applicability.

Conflict of interest

The author declares that he has no conflict of interest.

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