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Temperature dependences of the Fe, Co, and Ni heat capacities in the presence of structural and magnetic transitions

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Analytical calculations of heat capacities of iron, cobalt and nickel in the presence of phase transitions of various natures were carried out using relations of the two-phase system model. It has been shown that the used expressions not exhibiting divergences at the absolute-zero temperature adequately describe the experimental data in the range of 0 to 2000 K.

Keywords: thermodynamic model, local equilibrium region, phase transition, heat capacity, transition metal.

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Transition metals Fe, Co and Ni are found in many polycrystalline and amorphous materials. Items made from these materials are expected to be subject to seasonal temperature variations or operated under the conditions of phase (structural, magnetic, aggregate, etc.) transition. The alloy's internal reaction is accompanied by rearrangements of the electronic, atomic, phonon and other subsystems of quasiparticles with possible nucleation of new phases in these subsystems. Those new phases induce, for instance, modifications of thermophysical properties in a local region where the phase transformation takes place (a set of local regions simulates the material in the theoretical construction considered below).

One of the most important thermal characteristics of pure metals sensitive to changes in the system internal state is heat capacity. Evolution of the internal structure can proceed through generation of new phases (first-order phase transitions) or creation of conditions for simultaneous emergence of a new phase throughout the entire volume (second-order phase transitions) in both the system itself and its subsystems. Occurrence of phase transitions (PTs) manifests itself in the temperature dependence of heat capacity as „peaks“ or „wells“ depending on the sign of the transition enthalpy or other physical quantity. The asymmetry of these graphical features can be caused by sequential occurrence of PTs in both the basic atomic system and subsystems of quasiparticles.

Scattering of experimental data on the Fe, Co and Ni heat capacities [1–8] depends on the temperature range they have been obtained in. Preliminary heat treatment of samples with different states also produces a significant impact on the measurements. In addition, scattering of experimental data on heat capacities depends on the choice of the research method, equipment, and atmosphere within the equipment. Among other reasons there are chemical indifference of the crucible and the presence in the samples of volatile components or precedence in them of internal

kinetic processes. Such kinetic phenomena are, e.g. [9] rearrangement of the structure, redistribution of atoms over positions in the unit cell, thermal expansion, release of volatile impurities into the calorimeter atmosphere, etc. Thereat, thermal effects of changes in the sample internal states are summed up by the measuring equipment, which causes a discrepancy between experimental data obtained by different authors.

In the absence of PTs, experimental data on the temperature dependence of the substance heat capacity are often smoothed by approximating functions [10–12]. A significant drawback of this method is unavailability of an only one approximating function able to describe the temperature dependence of the metal heat capacity in the temperature range from absolute zero to melting point. In addition, the applied theoretical constructions also do not use only one continuous function to describe the system heat capacity plot and are still less able to describe temperature dependences of substances' heat capacities in the presence of PTs [10,13]. Hence, it becomes necessary to search for a new theoretical approach to describing the behavior of a solid substance heat capacity in the temperature range from 0 K to melting point.

The goal of this work was to describe temperature dependences of heat capacities of a number of transition metals, which are observed when PTs of various natures occur in the temperature range under study; the description was performed by using relations of the model of a two-phase locally equilibrium region [14]. In describing single-stage [14,15] and multi-stage [16] crystallization of amorphous alloys, heat capacities of complex oxides and other substances [17,18], thermal expansion coefficients of various substances [17], etc., this model demonstrated a fairly good agreement with sets of experimental data on the volume fraction dependence on temperature.

Let us represent the initial metal as a combination of electronic, atomic (marked with subscripts containing

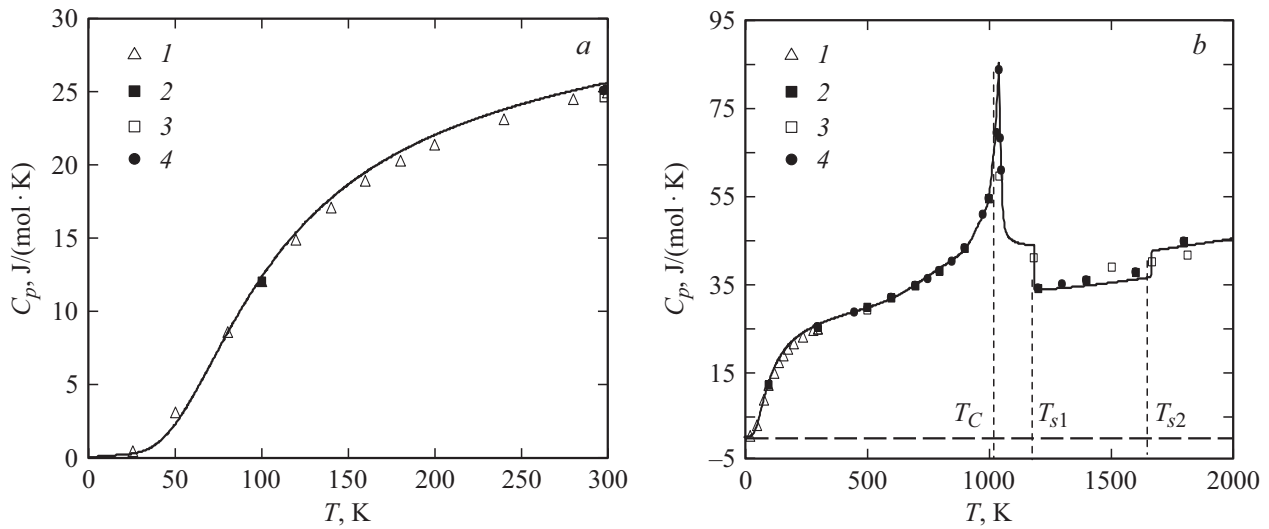


Figure 1. Fe heat capacity in the low-temperature range (a) and in the temperature range of 0 to 2000 K (b). 1 — data from [1], 2 — [2], 3 — [3], 4 — [4]. The solid line represents theoretical data.

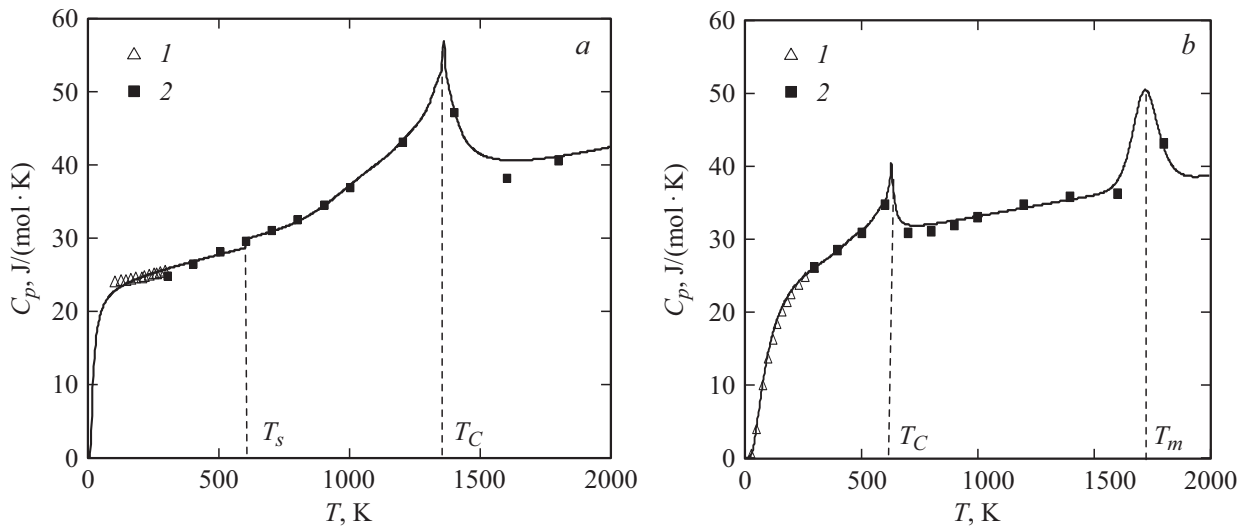


Figure 2. Co (a) and Ni (b) heat capacities in the temperature range of 0 to 2000 K. 1 — data from [1], 2 — data from [2]. The solid line represents theoretical data.

index 0) and quasiparticle (indices $i = 1, 2, \dots$) ensembles. As per [14], volume fraction of the new phase (phase 1) x_{1ij} in subsystem i ($i = 0, 1, 2, \dots$) during phase transition j ($j = 0, 1, 2, \dots$), which gets formed in the parent phase (phase 2), is defined as

$$x_{1ij} = \frac{1}{2} \left[1 - \operatorname{th} \left(a_{ij} \frac{T_{xij} - T}{T} \right) \right], \quad (1)$$

where $a_{ij} > 0$ is the model parameter, T is the temperature [K], T_{xij} is the temperature at which volume fractions of phases coincide.

Define the transition metal heat capacity in the following way [17,18]:

$$C = C_b + C_k. \quad (2)$$

Here local heat capacity

$$C_b = k_1 T + \sum_{i,j} k_{2ij} x_{1ij} \quad (3)$$

(k_1, k_{2ij} are the constant coefficients related to the phase entropies [17,18]) describes the baseline of the heat capacity dependence on temperature: the equation (3) first term accounts for the electronic system contribution to heat capacity, the second term is for that of the atomic ensemble.

The „kinetic“ component of (2), which is responsible for the emergence of peculiarities in the heat capacity curves, is

$$C_k = T \sum_{i,j} k_{3ij} u_{ij}, \quad (4)$$

Theoretical model parameters

Parameter	Metal		
	Fe	Co	Ni
a_{01}	0.79	0.6	0.56
T_{x01}	140	27	156
$k_1 \cdot 10^4$	87	85	50
k_{201}	32.9	31	38.7
a_{02} $\left\{ \begin{array}{l} \beta \rightarrow \gamma(\text{Fe}) \\ \alpha \rightarrow \varepsilon(\text{Co}) \end{array} \right.$	2000	2000	–
	T_{x02}	1188	602
	k_{202}	–10.1	1.2
a_{03} $\left\{ \begin{array}{l} \gamma \rightarrow \delta(\text{Fe}) \end{array} \right.$	2000	–	–
	T_{x03}	1667	–
	k_{203}	6.0	–
a_{11} $\left\{ \begin{array}{l} \text{PT} \\ \text{in subsystems} \end{array} \right.$	3.1	4.0	1.9
	T_{x11}	955	1190
	k_{211}	5.0	–
	k_{311}	3.4	2.7
	a_{121}	15	10
	T_{x21}	997	1314
	k_{321}	1.1	1.1
	a_{13}	58	29
	T_{x31}	1022	1350
	k_{331}	0.4	0.09
	a_{141}	92	28
	T_{x41}	1041	1360
	k_{341}	0.6	0.53
	a_{151}	520	230
	T_{x51}	1043	1361
k_{351}	0.027	0.04	

where $u_{ij} = dx_{ij}/dT$ is the first temperature derivative of the new-phase volume fraction i , k_{3ij} are the constant coefficients.

Parameters and coefficients of the model were assessed by using the curves of temperature dependences of heat capacities and phenomenological relationships. For instance, parameter a for the baseline was determined from the slope ratio of the line tangent to the curve inflection point corresponding to the transition from the high-temperature range to the low-temperature one. Parameter T_x was estimated from the Debye temperature Θ_D through phenomenological relation $T_x = (0.2-0.5)\Theta_D$ obtained in the process of calculating temperature dependences of heat capacities of various metals. To estimate values k_1^0 and k_2^0 of theoretical model coefficients k_1 [mJ/(mol · K²)] and k_2 [J/(mol · K)], it is proposed to use phenomenological relations

$$k_1^0 = \xi^4 \left(\frac{15m_a}{n_a T_m} \right)^2 \frac{H_m}{R}, \quad k_2^0 = \eta^4 \frac{m_a H_m}{n_a T_m}.$$

Here ξ and η are the proportionality parameters taking values from certain intervals (for example, in the case of iron

the ξ value ranges from 2.0 to 2.1, while the η value varies from 1.1 to 1.2), which are necessary to find the optimal values of coefficients k_1 and k_2 ; m_a [g/mol] and n_a are the element atomic mass and number, respectively, T_m [K] and H_m [J/mol] are the melting temperature and specific enthalpy, R is the universal gas constant. To provide optimal values for these parameters, there was used minimization of the sum of standard deviations of theoretical results from experimental data forming the baseline.

Parameters of the considered transition metals (Fe, Co and Ni) are given in the Table, while the calculations are presented in Figs. 1,2. Figs. 1,2 show that the given formulae describe quite well the temperature dependences of heat capacities of the above-mentioned metals in the presence of structural (transition temperature T_x), magnetic (T_C) and aggregate (T_m) transitions. Notice also that the obtained results coincide with the data presented in [5,19] for Fe, in [5,8] for Co, and in [5,7,20,21] for Ni.

Conflict of interests

The author declares that he has no conflict of interests.

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