SECOND-ORDER PHASE TRANSITIONS IN CRYSTALLINE MEDIA UNDER THE TEMPERATURE EFFECTS

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Various approaches to describe phase transitions in crystalline media are considered: Landau phenomenological approach of second-order phase transitions as well as Kolmogorov's, Avrami's and Christian's theories of crystallization. An analysis of the existing approaches indicates that they do not always adequately describe the experimental results. A qualitative model for describing the dependence of a crystalline substance heat capacity on temperature at a constant volume is proposed in this paper. The model describes the change in the number of particles of a new phase of a crystalline substance at a constant volume and is based on Einstein principle of detailed balance. An expression for metal heat capacity adequately corresponded to Dulong-Petit heat capacity is obtained. A model for describing the dependence of heat capacity on temperature in case of phase transitions is proposed.

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INTRODUCTION

A change in the state of a system during second-order phase transitions (PT) can be described as a change in its symmetry (for example, a crystal transition from a phase with cubic symmetry to a tetragonal one or vice versa). A the heart of Landau's phenomenological theory of second-order PT is PT understanding as a change in the symmetry of a system, for example, a crystal [1]. To describe the change in symmetry the concept of an order parameter is introduced in this theory and a certain parameter that is linearly transformed under the action of the symmetry group of the system is chosen. This can be, for example, shear strain, atom displacement amplitude and charge density wave amplitude, striction amplitude, [2], the magnetic moment in a ferromagnetic, the wave function of a Bose-condensate in $^4He_2$.

The approach proposed by Landau is to represent the thermodynamic potential in the form of the function $\Phi(P,T,\eta)$:

$$\Phi(P,T,\eta) = \Phi_0(P,T,0) + A\eta^2 + B\eta^4 + ..., \quad (1)$$

where η – the order parameter characterized the phase symmetry, $\quad A(P,T) = \dfrac{1}{2}\dfrac{\partial^2\Phi(P,T,0)}{\partial\eta^2}$,

$$B(P,T) = \dfrac{1}{4!}\dfrac{\partial^4\Phi(P,T,0)}{\partial\eta^4} > 0.$$

In expansion (1) the coefficients at uneven degrees η are equal to zero due to the crystal symmetry [1]. The order parameter in expression (1) is equal to zero for an unperturbed crystal with the highest degree of symmetry. When symmetry is broken as a result of external factors, it becomes nonzero.

The body heat capacity at the Curie point is determined by the expression:

$$c_p = c_{p0} + \dfrac{T}{2B}\left(\dfrac{\partial A}{\partial T}\right)^2, \quad (2)$$

where c_{p0} – body heat capacity with the greatest symmetry.

Thus, heat capacity at the Curie point ($A = 0$) changes abruptly, besides it increases when passing from a more symmetric c_{p0} to a less symmetric crystal.

However, it is not always possible to describe PT by introducing the order parameter, for example, martensitic transformations (MT) of steels [2]. Therefore, it is proposed in the scientific literature to use other types of the order parameter for describing MT. The order parameter can be the atoms displacement amplitude [3], the amplitude of electrostriction and ferroelectricity [4, 5], or the amplitude of charge density waves [6].

Further development of Landau [1] and Devonshire [4] theories was carried out by F. Falk in [7] based on using shear strain as an order parameter. In this work, based on the Landau theory, a phenomenological model of the Gibbs free energy function $G = U - TS + PV$ is presented, which considers the PT and is presented as a series in order parameter degrees (shear strain) ε:

$$G(\varepsilon,T,\sigma) = G_0 + a(T-M)\varepsilon^2 - b\varepsilon^4 + c\varepsilon^6 - \sigma\varepsilon, \quad (3)$$

where T, M – absolute temperature and temperature of the beginning of the phase transformation, respectively; σ – external stress; a, b, c – positive constants.

The dependence of Gibbs free energy (3) on strain, temperature and external stress follows from the condition of the minimum free energy $dG(\varepsilon,T,\sigma)/d\varepsilon = 0$, and from the condition $d^2G(\varepsilon,T,\sigma)/d\varepsilon^2 > 0$ [2].

However, the representation of free energy in the form (3) does not correspond to the experimental data [8]. Although the dependence $\sigma(\varepsilon) = const$ at constant temperature is in qualitative agreement with the experimental data for certain values of the order parameter, the description of martensitic transformations using model (3) near the onset temperature of martensitic transformation contradicts the results of experiments [2].

Such a contradiction requires searching for another order parameter related to MT.

As noted above, the set of possible order parameters responsible for PT or MT is large enough. However, despite this, the main features of MT described by order parameters differ in physical meaning have one common feature: the existence of a nonzero value of the order parameter in the low-temperature phase should be accompanied by a deformation. The physical reason for strain occurrence lies in the fact that those changes in the lattice, which are described by the order parameter, cause certain internal stresses and deform the unit cell of the formed phase. This mechanism of deformation occurrence in the process of MT is called strictional. Internal stress $\sigma_{in}(\varphi)$ can be considered as a function of the order parameter φ, which allows the possibility of its expansion in a series in this parameter [9].

Thus, the free energy becomes a function of two variables (order parameter, and deformation (striction), in which it can be expanded in a series and presented in the form of a scalar model. It should be noted that such a representation of a free energy is only the simplest possible version of the theory describing second-order PT in bodies with striction. Therefore, in the general case, the deformation is a symmetric tensor of second rank.

Moreover, as practice shows, even a simple scalar model describes MT and thermodynamic parameters of a solid with sufficient accuracy.

However, the theoretical studies of MT thermodynamic features within the framework of a model that considers striction and a comparison of their conclusions with experiments, as well as models that use the deformation as an order parameter indicate a qualitative, but not quantitative agreement between the model under consideration and the experiment [2].

Therefore, in order to achieve a quantitative agreement between the theory and the experiment on PT including MT in solids it is necessary to continue searching for and developing new models of PT in crystalline media.

Other processes that are closely related to second-order PTs are crystallization processes that occur during cooling of solids from a high-temperature phase state. Any transition of a crystal to a liquid, or vice versa, or to crystals of a different symmetry is associated with disappearance or appearance of some symmetry elements [1]. Therefore, we can assume, that the processes similar to the processes of the second-order PT, in which the symmetry of the system changes, are observed during substance crystallization.

Crystallization of a substance under certain schematic and general enough assumptions was first described in [10]. Later M. Avrami [11], J. Christian [12] and also [13, 14] devoted their studies to this topic in more complex formulations of this problem.

The kinetics of isothermal PT in solid condition is usually described by the Avrami equation:

$$f(t,K,n) = 1 - exp\left(-Kt^n\right), \qquad (4)$$

where $f(t,K,n)$ – part of the transformed value; t – reaction time and K and n – constant coefficients. The coefficient K in equation (4) is a certain combination of the velocities of nucleation and growth of particles of the new phase and the coefficient n describes the "spatial dimension" of growth, as well as the possible time dependence of the above velocities.

The theory of phase change kinetics is presented in [11]. This theory is based on experimentally proved assumptions that the new phase is generated from the germ nuclei that already exist in the old phase and the number of which can be changed by preliminary treatment. The density of the germ nuclei decreases due to the activation of some of them in order to become nuclei of grain growth of a new phase and the absorption of other grains by their growing analogs. Here, quantitative relationships between the density of germ nuclei, growth nuclei, and transformed volume were obtained. These relationships are reflected in a characteristic time scale for any substance and process. It is shown that the kinetics of a phase reaction depends on solution of a functional equation of a certain type. Some general properties of temperature-time and transformed phase-time curves are described and explained.

In the simplest case of formula (4), when nucleation of particles of a new phase occurs uniformly over the volume of the sample and the velocities of their nucleation and growth are constant, then the increase in the fraction of the transformed volume occurs isotropically, according to A.M. Kolmogorov's expression:

$$f_K(t,K,n) = 1 - exp\left(-\frac{\pi}{3} I \omega^3 t^4\right). \qquad (5)$$

The exponent in (4) and (5) appears as a result of considering collisions of growing particles. The coefficients K and n can be evaluated by plotting the experimental data in double logarithmic coordinates $y = \ln\left(-\ln(1-f)\right)$ and $x = \ln t$ obtaining a straight line of the form: $y = \ln K + nx$.

However, the calculations of PT kinetics during crystallization do not always lead to a correct description of the experimental results, since the value of the fraction of the transformed volume depends on the coefficient n that can change during the PT [15]. This fact is confirmed by an analysis of diagrams of isothermal transformation in alloys obtained by magnetometric [16–18] and dilatometric [19] methods.

Therefore, the above-considered discrepancies between the theoretical description and experimental data on PT in metals and alloys require searching for new physical models that more adequately correspond to experiment.

One of such qualitative models described the second-order PT in crystal lattices under the effect of temperature can be a model based on the Einstein's principle of detailed balance. Let's consider the conditions for applying this model in more detail.

QUALITATIVE MODEL FOR DESCRIBING THE DEPENDENCE OF THE HEAT CAPACITY OF A CRYSTALLINE SUBSTANCE ON THE TEMPERATURE AT A CONSTANT VOLUME

To describe phase changes (PT or MT) let us consider a qualitative model based on a change in the number of particles of a new phase of a crystalline substance at a constant volume. By the fraction of a new phase according to the accepted assumption of the Dulong and Petit law [20] we mean an atom of the solid crystal lattice that performs harmonic vibrations in three directions determined by the geometry of the lattice. Moreover, the vibrations in different directions are absolutely independent of each other. We denote the atom energy as $\varepsilon_2 = NkT$, where N – the number of degrees of freedom, which is 3 for simple solids; T – the temperature of the solid, and k – the Boltzmann constant.

A particle of the original (old) phase is an atom of the crystal lattice of a solid, which is characterized by energy $\varepsilon_1 < \varepsilon_2$.

The number of particles of a new phase is determined from Einstein principle of detailed balance:

$$n(t) = \sum_{i=1}^{M} \frac{N_0}{2^i}\left(1 - \exp(-\mu \cdot t)\right) = n_0\left(1 - \exp(-\mu \cdot t)\right)$$ [21, 22], where $n(t)$ – the number of particles of a new phase; n_0 –he number of particles of the original (old) phase equal to Avogadro number $N_A = 6.0221 \cdot 10^{23}$ mol^{-1}; t – time; μ – probability of induced transitions of particles between energy levels ε_1 and ε_2 [23]. The expression for $n(t)$ was obtained under the condition of a significant excess of the characteristic time of balance establishing in the system over the time of induced transitions of particles between energy levels ε_1 and ε_2.

The probability of induced transitions μ is proportional to the number of phonons n_{ph} that promote transitions between energy levels [24]. In turn, the number of phonons is proportional to the equilibrium statistical Gibbs distribution [25] $n_{ph} = n_{ph,0}\exp\left(-a(T_D/T)\right)$, where a – dimensionless constant characterized the average phonon energy, T_D - Debye temperature, which is related to the solid melting point T^* (Lindemann criterion) [26]. Under these assumptions the probability of induced transitions can be represented as $\mu(T) = \mu_0\left(T/T_D\right)\exp\left(-a(T_D/T)\right)$.

Further, we assume that $\mu_0\left(T/T_D\right)$ is a power function of temperature $T: \mu_0\left(T/T_D\right) = \mu_0' \cdot \left(T/T_D\right)^{\gamma}$, where γ – a constant.

The time t in the expression for the number of particles of a new phase $n(t)$ can be considered proportional to the temperature $t = \alpha T$, because we consider the process of time – temperature transformation to be linear.

Based on the foregoing, the heat capacity of the metal c_V can be estimated by the value proportional to the number of particles of a new phase of solid [27, 28]:

$$c_V = A\nu n(T) = A\nu n_0\left(1 - e^{-(T/T_D)^{1+\gamma}}\, b \cdot e^{-a(T_D/T)}\right),$$ where A – proportionality factor, ν - number of atoms in a crystal cell, $b = \alpha\mu_0' T_D$ – constant number.

The constant A is defined as follows. According to the empirical Dulong and Petit law the heat capacity of simple solids c_V at temperatures above the Debye temperature is close to $c_V \approx 3\nu R$, where $R \approx 8.31$ J/(mol K) is an universal gas constant. Since $c_P > c_V$ [29] and the difference $c_P - c_V$ is relatively small in solid bodies [27], then we can assume that $c_P \simeq c_V$. Therefore, the proportionality factor in the expression for heat capacity is equal $A = 3\nu R$. The expression for heat capacity at a constant pressure takes the form:

$$c_P \simeq c_V = 3\nu R\big[1 - \exp\left(-(T/T_D)^{1+\gamma}\right) \times$$
$$\times b \cdot \exp\left(-a(T_D/T)\right)\big]. \qquad (6)$$

In Fig. 1 markers "×" depicts a curve that describes the dependence of heat capacity (6) on dimensionless temperature T/T_D. This curve was obtained by selecting constants a, b, γ using the ORIGIN software package in such a way that its deviation from the Debye curve was minimal. Indicators of statistical processing of the curve deviation (6) from the Debye curve are presented in Table.
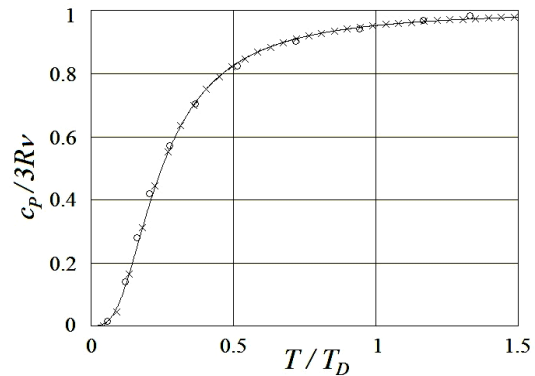

Fig. 1. Dependence of heat capacity $c_P/3R\nu$ on temperature T/T_D for a crystalline solid.

Solid line "–" Debye theory, markers "○" – solid silver with melting point 962 K and Debye temperature 225 K [30], markers "×" – formula (6)

Statistical processing shows a sufficiently small average deviation of the curve (6) from the Debye curve at the level of $4.8509 \cdot 10^{-6}$. Its deviation in the high-temperature area is a value within a range of 0.5...1.5%, which is significantly less, for example, the value of the standard deviation for measurement of the relative heat capacity of ARMCO iron, which is about 4% [31].

Thus, the qualitative model (6) based on induced transitions gives a quantitatively true description of the

dependence of heat capacity of crystalline mediums on temperature.

Result of statistical processing of the curve deviation (6) from the Debye curve

b		γ	
Value	Standard Error	Value	Standard Error
4.27803	0.00405	−0.69449	0.00191
a		Statistics	
Value	Standard Error	Red. Chi-Sqr.	Adj. R-Sqr.
0.34485	$8.1375 \cdot 10^{-4}$	$4.8509 \cdot 10^{-6}$	0.99992

HEAT CAPACITY JUMPS OF A CRYSTALLINE SUBSTANCE BY THE EXAMPLE OF IRON (EXPERIMENT)

Appearance of a new phase of the crystal lattice, when quenching low carbon steels, for example, is accompanied by austenite $\rightarrow$ martensite PT, change in the crystal symmetry and heat capacity jump [2].

An example of a heat capacity jump is also given in [31], where the jump of the second-order of ARMCO iron heat capacity has been investigated near the temperature of 1180 K (BCC-FCC PT) and near the temperature of 1665 K (PT FCC-BCC).

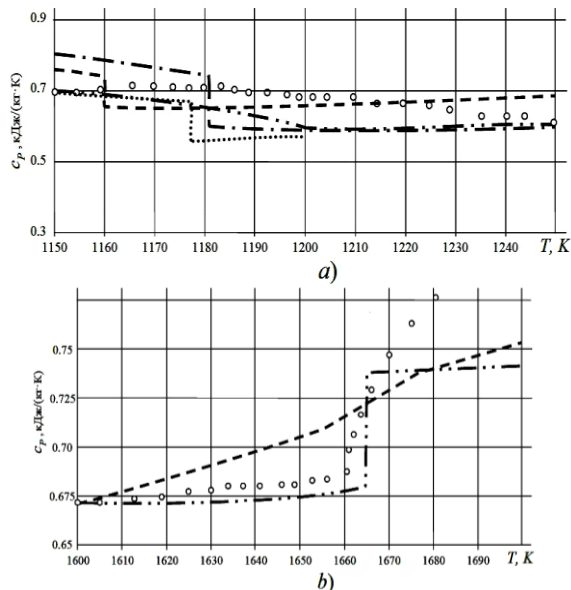A sample of such jump for ARMCO iron is given in Fig. 2.

Fig. 2. Dependence of ARMCO iron heat capacity on temperature at PT: a – BCC- FCC; b – FCC-BCC

Curves in Fig. 2 noted by barcode - dotted line and markers indicate a jump down of heat capacity within the temperature of 1180 K as a result of changing the symmetry of crystal BCC to FCC – Fig. 2,a and within the temperature of 1670 K – the jump up as a result of changing the crystal symmetry FCC to BCC – Fig. 2,b.

As we see, the heat capacity jump (heat capacity jump – the difference in the heat capacity of the substance in the final and initial PT) within temperature of 1180 K is the amount of order $\Delta c_{P1} \approx -(0.1...0.12); -0.1$ [32] kJ/(kg·K) and within

the temperature of 1670 K – $\Delta c_{P2} \approx 0.05...0.07;\ 0.04$ [32] kJ/(kg·K).

Thus, change in the crystal symmetry $Fe_\alpha \rightarrow Fe_\gamma$ at a temperature of 1180 K and vice versa at a temperature of 1670 K, as noted in [1], leads to marked in Fig. 2 jumps of heat capacity. However, as noted in [31], the amplitude of such jumps is small.

HEAT CAPACITY JUMPS OF A CRYSTALLINE SUBSTANCE BY THE EXAMPLE OF IRON (MODEL)

The jumps in the heat capacity can be associated with a change in the probability of induced transitions of atoms in the crystal cell as a result of the crystal symmetry change. But the probability of induced transitions in expression (6) depends on four parameters: a, b, γ, T_D. To describe jumps in heat capacity it is necessary to choose jumps of only one of them according to the Occam's razor methodological principle.

We assume that the Debye temperature changes in jumps with a change in the crystal symmetry. Leave the rest of the parameters unchanged. For the model calculation of jumps in the iron heat capacity we assume that the parameter T_D in (6) changes abruptly as follows:

– at temperatures $T < 1180\,\text{K}$ the parameter $T_D = 420$ K [20, 33];

– at temperature $T = 1180\,\text{K}$ the Debye temperature increases abruptly from $T_D = 420$ K to $T_D = 420 \cdot 0.9 = 378$ K and remains the same until the temperature is reached $T = 1670$ K;

– at temperature $T = 1670\,\text{K}$ the Debye temperature increases abruptly from $T_D = 420 \cdot 0.9 = 378$ K to $T_D = 420 \cdot 1.2 = 504$ K and remains the same until the temperature is reached the iron melting point.

Heat capacity $c_P/3R\nu$ vs. temperature T/T_D graph for iron with PT, which occur near temperatures of 1180 and 1670 K is presented in Fig. 3.

It follows from Fig. 3 that the proposed qualitative model for describing the heat capacity based on the model of induced transitions between the energy levels of particles of new and old phases can be used to calculate heat capacity jumps in the presence of phase transitions in crystalline media. The given example of calculating the behavior of iron heat capacity during phase transitions are in qualitative agreement with the experimental results given in [31]. The proposed model for describing dependence of temperature on heat capacity in the presence of a PT has a physical explanation, which is based on considering the change in the probability of induced transitions of atoms in the crystal cell due to a change in the crystal symmetry. Such a change in the probability of induced transitions is due to the fact that with increasing temperature the linear dimensions of the crystal lattice increase [34], and this, in turn, leads to increasing the energy of the energy level ε_2. Therefore, the probability of induced transition of the old phase into a new one decreases.
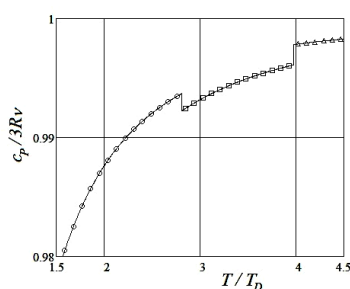
Fig. 3. Dependence of heat capacity $c_P/3R\nu$ on temperature T/T_D for iron with PT $Fe_\alpha \rightleftarrows Fe_\gamma$.

Debye temperatures are marked as:

$\circ - T_D = 420\,K;\ \square - T_D = 378\,K;\ \Delta - T_D = 504\ K$

Thus, the model of a second-order PT in crystal lattices under the effect of external factors, based on the principle of detailed balance, can be used to describe their heat capacity and other thermodynamic parameters at temperature change.

CONCLUSIONS

Various approaches describing phase transformations in crystalline media are analyzed in the paper: Landau's phenomenological approach to describe second-order phase transitions and Kolmogorov's, Avrami's, Christians' theories of crystallization obtained under certain schematic and general enough assumptions. The analysis of existing theories points to not always adequate description of the processes of experimental results. And first of all, due to the uncertainty of the order parameter choice in Landau theory, or the inconstancy of the transformed volume fraction in the PT process. Therefore, a qualitative model for describing the dependence of heat capacity of a crystalline substance on temperature at a constant volume is proposed in the paper. The model allows considering the change in the number of particles of a new phase of a crystalline substance at a constant volume and is based on Einstein's principle of detailed balance. It is shown that a metal heat capacity can be estimated by a value proportional to the number of particles of a new phase of a solid. Comparison of the obtained expression for the heat capacity of a metal with the Dulong-Petit formula, for example, for solid silver gives a small difference. Statistical processing shows a fairly small average deviation of curves at the level of $4.8509 \cdot 10^{-6}$. The resulting expression for the heat capacity is applied to describe the jumps in the heat capacity for iron near PT temperatures $Fe_\alpha \rightleftarrows Fe_\gamma$. An example of calculating the behavior of the iron heat capacity during PTs, which qualitatively agrees with the experimental results, is given. The proposed model for describing temperature dependence on heat capacity during PT has a physical explanation, which is based on considering the change in the probability of induced transitions of crystal cell atoms as a result of a change in the crystal symmetry. Such a change in the probability of induced transitions is due to the fact that with increasing temperature the linear dimensions of the crystal lattice increase, which, in turn, leads to increasing energy of the upper energy level and

decreasing the probability of induced transition of the old phase to a new one.

The proposed model for describing the heat capacity of crystalline media is based on the Einstein's principle of detailed balance and can be used to describe the heat capacity and other thermodynamic parameters of such media.

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ФАЗОВІ ПЕРЕХОДИ ДРУГОГО РОДУ В КРИСТАЛІЧНИХ СЕРЕДОВИЩАХ ПІД ДІЄЮ ТЕМПЕРАТУРИ

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Розглянуто різні підходи до опису фазових переходів у кристалічних середовищах: феноменологічний підхід Ландау до опису фазових переходів другого роду, а також теорії кристалізації Колмогорова, Аврамі та Крістіана. Аналіз існуючих підходів показує, що вони не завжди адекватно описують експериментальні результати. У роботі запропонована якісна модель для опису залежності теплоємності кристалічної речовини від температури. Модель описує зміну кількості частинок нової фази кристалічної речовини при постійному об'ємі та заснована на принципі детальної рівноваги Ейнштейна. Отримано вираз для теплоємності металу, що адекватно відповідає теплоємності Дюлонга-Пті. Запропоновано модель для опису залежності теплоємності від температури в кристалічних середовищах.

ФАЗОВЫЕ ПЕРЕХОДЫ ВТОРОГО РОДА В КРИСТАЛЛИЧЕСКИХ СРЕДАХ ПОД ДЕЙСТВИЕМ ТЕМПЕРАТУРЫ

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Рассмотрены различные подходы к описанию фазовых превращений в кристаллических средах: феноменологический подход Ландау к описанию фазовых переходов второго рода, а также теории кристаллизации Колмогорова, Аврами и Кристиана. Анализ существующих данных показывает, что они не всегда адекватно описывают экспериментальные результаты. В работе предложена качественная модель для описания зависимости теплоемкости кристаллической среды от температуры. Модель описывает изменение количества частиц новой фазы кристаллической среды при постоянном объеме и основана на принципе детального равновесия Эйнштейна. Получено выражение для теплоемкости металла, которое адекватно соответствует теплоемкости Дюлонга-Пти. Предложена модель для описания зависимости теплоемкости от температуры.