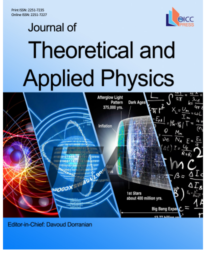

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Determination of entropy and Debye temperature of the phases of Al-Cu-Co and Al-Ni-Co decagonal quasicrystals at the normal and high temperatures

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Original Research

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Abstract:

This paper deals with determination of the entropy of quasicrystalline phases of Al-Cu-Co and Al-Ni-Co alloys by the information-and-statistical method at the temperature of 300 K. Scanned digital images of quasicrystals were processed with the use of this method. Statistical data of the multicomponent structure were divided into separate components of the normal distribution of parameters corresponding to certain phases. We calculated the Gaussian parameters on the basis that dependence of the logarithmic representation of the normal distribution function took the form of a quadratic function. It allowed us to find the mean-square deviation and to calculate the entropy of quasicrystalline phases at 300 K. The resulting values were further used to calculate the Debye temperature of the phases. Decagonal quasicrystals have anisotropic structure. It is assumed that anisotropy manifests itself in the difference of the dispersion laws in the xy plane and in the direction of the z axis, which is described by the model of anisotropic crystals. Using this model, we have found an expression describing the dependence of the entropy on the temperature and Debye temperature of the phases. From here, we calculated the Debye temperature of the phases. Next, using the Debye temperature values, we calculated the entropy of phases at higher temperatures. Therefore, with the use of the presented calculation methods, it is possible to determine the Debye temperature and the entropy of quasicrystalline phases that was done in our study for Al–Cu–Co and Al–Ni–Co quasicrystals.

Keywords: Quasicrystals; Entropy; Debye temperature; Dispersive law; Anisotropy; Probability density distribution

1. Introduction

The unique structure of quasicrystals determines their unusual physico-chemical properties. Quasicrystals have low friction and surface tension coefficients, as well as high values of hardness, wear resistance and corrosion stability. Owing to these properties, quasicrystals are applied in practice as the films, coatings and components of the composite materials [1, 2]. In the process of manufacturing of the composite materials with quasicrystalline filler alloys, as well as in the development of process diagrams for the film coatings, there is a question of stability of quasicrystalline phases in the conditions of high-temperature exposure [3, 4]. The determined value of the entropy of quasicrystalline structures can be an informative indicator of their stability [5].

From the statistical physics standpoint, entropy is the realization of statistical weight of a system [6, 7], or it determines the density of levels of the energy spectrum in the macroscopic system. This density, because of the additivity of the entropy, becomes higher with the growing number of components of the structure and with the increase in energy, that is, $S = S(E)$. Considering the additivity of the entropy, which is an expression of the multiplicativity of the composite index of statistical weight $\Delta\Gamma = \Pi_a \Delta\Gamma_a$, it is customary to distinguish [8–10] the configurational $\Delta S_{conf} = -R\sum_i x_a \ln x_a$ and thermal components. The configuration entropy is a direct consequence of statistical interpretation of the concept of entropy itself.

Configuration entropy is determined by calculation [8, 9, 11]. A number of authors simulate the interaction of lattice atoms in crystalline and quasicrystalline structures excluding temperature impact, i.e. at the temperature close to absolute zero [12, 13]. At the same time, the authors, when forming the integral distribution of frequencies, also include anharmonic oscillations in their calculations, i.e. the interacting phonons. Configuration entropy plays an important role in the stability of quasicrystals [14–16]. Using the computer modeling and free energy calculations, the paper [17] shows that a dodecagonal quasicrystal is stabilized by configuration entropy.

The most common method for the thermal entropy determination is the method of differential scanning calorimetry (DSC). This method consists in the determination of the heat capacity and further calculations of the entropy [8, 18], based on the formation of an exact differential being the entropy according to the expression $dS = dQ/T$ [8, 19], where $1/T$ – correction factor, allowing to transform inexact differential dQ into exact one. The authors of [20] determine the entropy of melting of aluminium-based quasicrystals by the method of the differential thermal analysis. However, measurement of the entropy by the DSC method does not take into account the configuration entropy. In this context, difference between the measured and actual values of the entropy can be significant. Therefore, the development of new methods to determine the entropy of quasicrystals, including configurational and thermal components, is an urgent issue.

This paper proposes an original method for determination of the entropy at the normal temperature, which allows further determining the entropy of quasicrystals at higher temperatures with the use of model representations of anisotropic crystals and the Debye formalism. The main concepts of the proposed method are detailed below. By expanding the interpretation of the statistical distribution proposed by Einstein and using its direct relationship with the dispersion in the Gaussian distribution, it is possible to indirectly assess and calculate the entropy of the system under consideration. To do this, it is necessary to determine a number of variable indicators of the system under study, which are in satisfactory agreement with the normal Gaussian distribution. We choose as the above indicators the coefficients of absorption (reflection) of the light flux from the surface of the processed quasicrystal alloy section. Ultimately, the absorption of light or its reflection from the material surface depends on many factors and states, which in their turn determine and form the system's statistical weight and the entropy in its complex expression. In this interpretation of the statistical weight, it is necessary to note the fact that its main component will be formed by the oscillating frequencies determined by the temperature factor [21]. In this case, the proposed method determines the total entropy including both the configurational and thermal components. This assertion is based on the assumption that the coefficient of absorption or reflection of the light flux is an integral indicator of the specific configuration of the structure and mainly the thermal fluctuations of the oscillators distributed in it.

After formation of sufficiently large statistical series, it is possible to obtain significant statistical parameters, and above all the dispersion, which can be correlated with specific quasicrystal phases. Therefore, the entropy, including the configuration one, can be estimated with sufficient accuracy. This direction in the study was proposed by the authors of [22]. Using the proposed statistical method, the authors of the paper [22] study WC and W_2C crystalline phases of the W-C alloy and determine their entropy. The obtained results agree satisfactorily with the reference experimental data at the room temperature. However, since this method was successfully used earlier to determine the entropy of crystalline phases of tungsten carbides, it can be said that the calculated data for the entropy of quasicrystalline and crystalline phases obtained in this paper can be close to real values.

Using the method proposed in the paper, the entropies of phases of Al-Cu-Co and Al-Ni-Co decagonal quasicrystals are determined in a wide range of temperatures.

Calculation of the entropy of alloy phases by statistical processing of photo images

Digital micrographs of sections of quasicrystalline alloys of $Al_{65}Co_{20}Cu_{15}$ and $Al_{72}Co_{18}Ni_{10}$ composition were obtained using the Neophot optical metallographic microscope. The microstructure of samples was also investigated with the use of GX-51 metallographic microscope. The local chemical composition of phases was determined using JSM-6491LV scanning electron microscope and energy-dispersive analyzer. X-ray powder diffraction was carried out on the APOH-ym-1 diffractometer in the CuKα characteristic radiation.

In the structure of the $Al_{65}Co_{20}Cu_{15}$ alloy, decagonal quasicrystalline D-phase is formed (Fig. 1 (a)) with the chemical composition corresponding to $Al_{63}Co_{24}Cu_{13}$ (Table 1),

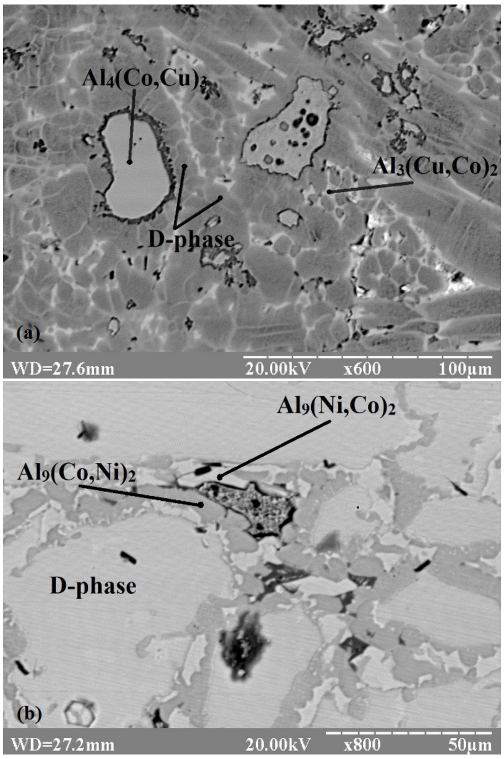

Figure 1. Back-scattered SEM image: (a) - $Al_{65}Co_{20}Cu_{15}$ alloy; (b) - $Al_{72}Co_{18}Ni_{10}$ alloy.

Table 1. Chemical composition of the phases of the $Al_{65}Co_{20}Cu_{15}$ alloy determined by energy dispersive X-ray spectrometer, at.%.

Phase Component	$Al_{63}Cu_{13}Co_{24}$	Al_4(Co, Cu)$_3$	Al_3(Cu, Co)$_2$
Al	62.99	56.39	59.48
Cu	12.99	9.75	30.91
Co	24.02	33.86	9.61

according to data of energy dispersive X-ray spectrometer. In the center of crystals of *D*-phase, rounded inclusions of the Al_4(Co, Cu)$_3$ crystalline phase are visible, and the Al_3(Cu, Co)$_2$ crystalline phase is present along the boundaries of the quasicrystalline phase. The described phase composition of the $Al_{65}Co_{20}Cu_{15}$ alloy is also confirmed by the results of X-ray powder diffraction (Fig. 2 (a)).

Three phases are formed in the structure of the $Al_{72}Co_{18}Ni_{10}$ alloy. Crystals of the decagonal quasicrystalline *D*-phase, the stoichiometric composition of which, according to data of energy dispersive X-ray spectrometer, is described by the formula of $Al_{69}Co_{21}Ni_{10}$ (Fig. 1 (b), Table 2). *D*-phase crystals have the rims of the Al_9(Co,Ni)$_2$ crystalline phase. The Al_9(Ni,Co)$_2$ crystalline phase is formed in the structure as well. Using X-ray powder diffraction, it is difficult to separate the lines of Al_9(Co, Ni)$_2$ and Al_9(Ni, Co)$_2$ crystalline phases, since they have the same monoclinic lattice with similar parameters (Fig. 2 (b)).

The digitized images of the phases were scanned using the special original TLC_Manager_4_0_15 software [22, 23], where the relevant matrices, expressed through the coefficient of light absorption by the sample surface, were generated. After normalization of the matrix values to the maximum ones and smoothing over the entire plane [22, 23], the probability density distribution of the light absorption coefficients was constructed. Further, the distribution was broken down into Gaussian components, and each of them corresponded to a specific phase. For this purpose, the logarithm of values of the chosen undeformed section on the edge of the distribution curve was found, and they were approximated by a quadratic function. The dependence of the logarithmic representation of the normal distribution function has the form of a quadratic function [22]

$$\ln f(\kappa_i) = \ln A - \frac{1}{2\sigma^2}(K_i - \bar{K})^2 = -\frac{1}{2\sigma^2}K_i^2 + \frac{\bar{K}K_i}{\sigma^2} + (\ln A - \frac{1}{2\sigma^2}\bar{K}^2), \tag{1}$$

Table 2. Chemical composition of the phases of the $Al_{72}Co_{18}Ni_{10}$ alloy determined by energy dispersive X-ray spectrometer, at.%.

Phase Component	$Al_{69}Cu_{21}Ni_{10}$	Al_9(Co, Ni)$_2$	Al_9(Ni, Co)$_2$
Al	68.75	81.81	72.04
Ni	9.93	5.10	18.64
Co	21.32	13.09	9.32

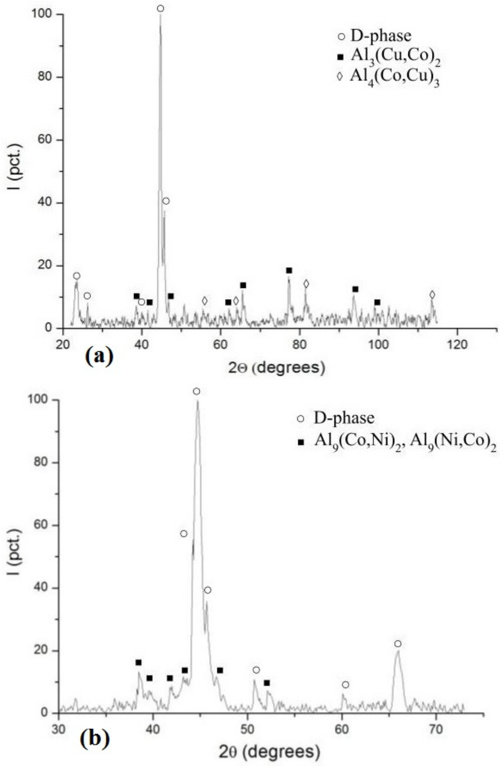

Figure 2. X-ray powder diffraction pattern: (a) - $Al_{65}Co_{20}Cu_{15}$ alloy; (b) - $Al_{72}Co_{18}Ni_{10}$ alloy.

where κ_i – current value of the light absorption coefficient, $\bar{K}$ – arithmetic mean, σ – mean-square deviation, A - amplitude. The regression coefficient during approximation of the designated values is close to one, which indicates that the selected section of the combined distribution is the Gaussian function. It was further taken into account that

$$\ln f(K_i) = a_2 K_i^2 + a_1 K_i + a_0, \tag{2}$$

$$a_2 = -\frac{1}{2\sigma^2}, \; a_1 = \frac{\bar{K}}{\sigma^2}, \; a_0 = (\ln A - \frac{1}{2\sigma^2}\bar{K}^2), \tag{3}$$

where a_2, a_1, a_0 - coefficients of the quadratic dependence. Next, using the obtained approximation coefficients, A, σ, $\bar{K}$ parameters were found, and the first Gaussian was constructed. After subtracting the values of the first Gaussian from the combined distribution curve, we isolated the next undeformed section, and the procedure was repeated again until the total curve was completely decomposed. Fig. 3 shows the isolated Gaussians, comprising the combined distribution for the phases of quasicrystalline alloys. To identify the attribution of the resulting Gaussians to the alloy phases, the mean values of the obtained Gaussians were compared to the mean values of the reference distribution constructed after analysis of photo images of the structure with the use of X-ray microanalysis.

It should be noted that the method of total decomposition into components can be used in the case if the Gaussians have clearly expressed separating maximums. It is possible, when the phases of interest are clearly distinguishable in the photo image.

According to [7, 22], the function e^S can give the probability distribution for the coefficients of intensity of light

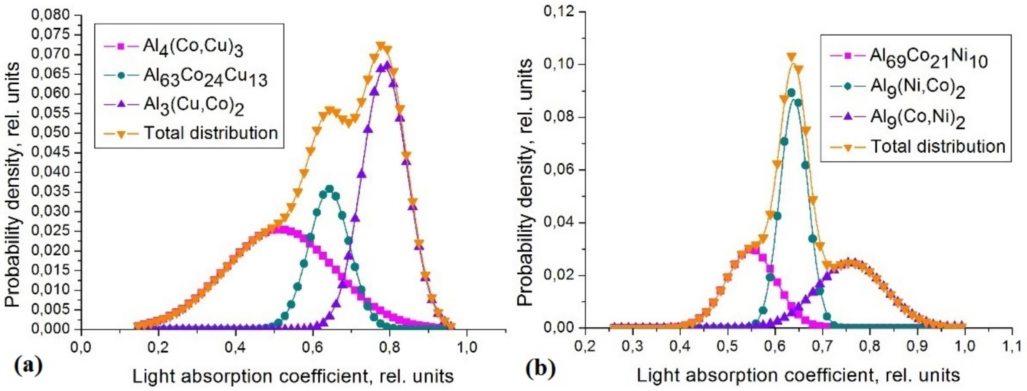

Figure 3. Light absorption coefficients' distribution curves: (a)- $Al_{65}Co_{20}Cu_{15}$ alloy; (b) - $Al_{72}Co_{18}Ni_{10}$ alloy.

absorption. The density of probability distribution is written as

$$f(K) = const \cdot e^{S'(K)}, \tag{4}$$

where $S'(K)$ - entropy as a function of realization of the statistical states of phases in the alloy structure. Since the entropy reaches its maximum for the mean values of $\bar{K}$, then $(dS'/dK)|_{K=\bar{K}} = 0$, $(d^2S'/dK^2)|_{K=\bar{K}} < 0$. Expanding $S'(K)$ in a power series of κ, limited to a second-order term, we obtain

$$S'(K) = S'(\bar{K}) - \frac{\beta}{2}K^2, \tag{5}$$

where $\beta = (d^2S'/dK^2)|_{K=\bar{K}}$. Substituting in (4), we obtain for the density of probability distribution

$$f(K) = const \cdot e^{S'(\bar{K})} e^{-\frac{\beta}{2}(K-\bar{K})^2}. \tag{6}$$

Comparing the expression for the Gaussian distribution with (6), we get

$$f(K) = const \cdot e^{S'(\bar{K})} e^{-\frac{\beta}{2}(K-\bar{K})^2} \approx \frac{C}{\sqrt{2\pi\sigma^2}} \cdot e^{-\frac{(K-\bar{K})^2}{2\sigma^2}}, \tag{7}$$

where σ - mean-square deviation, C – constant determining the percentage ratio of the area of the given Gaussian to the combined distribution area. Since const is equal to the constant C, the entropy of each phase upon reaching the equilibrium is given by the expression

$$S'(\bar{K}) = -\ln\sqrt{2\pi\sigma^2}. \tag{8}$$

When we compare the expression (1) with the Gaussian distribution, we find that the identity below should be satisfied

$$\ln A = \ln\left(\frac{C}{\sqrt{2\pi\sigma^2}}\right). \tag{9}$$

However, the calculations show that with the use of Gaussian parameters taken from (3) the equation (9) will be satisfied within the accuracy of the $\ln B$ constant value

$$\ln A = \ln\left(\frac{C}{\sqrt{2\pi\sigma^2}}\right) - \ln B. \tag{10}$$

For each phase of the definite distribution, the value of $\ln B$ will be constant. Consequently, the $\ln B$ value represents some kind of an additive constant determined by the specific procedure of the image scanning.

Taking this constant into account, the equality (8) can be rewritten as

$$S(\bar{K}) = \frac{-\ln(\sqrt{2\pi\sigma^2}) + \ln B}{2C}. \tag{11}$$

Since in the area of the photo image scanned there was a percentage distribution between the indicated phases, it was necessary to divide the obtained values by C in order to bring the obtained entropy values to 100%. For reasons of convenience of the further calculations, due to the presence of an indefinite coefficient $\ln B$, the calibration coefficient of $1/2$ was introduced in (11).

After calculations, the entropy (11) was multiplied by $R = 8.31$ J/(mol K) to obtain the required dimension. The resulting values of the entropies of alloy phases at the temperature of 300 K for $Al_{65}Co_{20}Cu_{15}$ and $Al_{72}Co_{18}Ni_{10}$ are given in Table 3.

Modeling of the temperature dependence of the entropy of crystalline phases

The proposed approach to determining entropy, based on a statistical analysis of the distribution of light absorption

Table 3. Calculated values of the entropy and the Debye temperature phases of the $Al_{65}Co_{20}Cu_{15}$ and $Al_{72}Co_{18}Ni_{10}$ alloys.

Alloy	Phase	Entropy (300 K), J/(mol· K)	Debye temperature K	Dispersion	Amplitude
$Al_{65}Co_{20}Cu_{15}$	$Al_{63}Co_{24}Cu_{13}$	125.34	170	0.002786	0.035809
	$Al_4(Co,Cu)_3$	33.53	300	0.0044205	0.02545
	$Al_3(Cu,Co)_2$	84.52	40	0.003381	0.047385
$Al_{72}Co_{18}Ni_{10}$	$Al_{69}Co_{21}Ni_{10}$	97.63	600	0.0028015	0.0298
	$Al_9(Co,Ni)_2$	80.91	45	0.0053015	0.0248
	$Al_9(Ni,Co)_2$	65.92	85	0.0008015	0.0908

coefficients from the surface, makes it possible to estimate this indicator at a fixed temperature of taking images of 300 K. To calculate the possible temperature dependence of the entropy of the studied structures, a model representation was proposed using a modified Debye interpolation formula [26]. The entropy values of structures obtained at 300 K using the information-and-statistical method made it possible to estimate the corresponding coefficients of the model structure. This approach made it possible to obtain a fairly adequate understanding of the temperature dependence of the entropy of crystalline and quasicrystalline structures. Next, we consider this model representation for crystal structures.

Free energy of a body F according to [7, 26]

$$F = \frac{VT}{2\pi^2 u^3} \int_0^\infty \omega^2 \ln(1 - e^{-\frac{\hbar\omega}{T}}) d\omega, \tag{12}$$

where V - volume of a body, T - temperature, u - group velocity, $\hbar$ – the Planck's constant.

Because of isotropic structure of the crystalline phase, only one direction of polarization is considered in (12). The dispersion law has a linear dependence

$$\omega = uk, \tag{13}$$

where k – wave vector. Using the Debye formalism [7], we replace the upper integration boundary in (12) by $y = \hbar\omega_D/T$, where ω_D – the Debye frequency, and substitute (13) in (12); after that, we obtain

$$F = \frac{VTT^3}{2\pi^2 u^3 \hbar^3} \int_0^y \ln(1 - \exp(-x)) x^2 dx, \tag{14}$$

where $x = \hbar uk/T$. Then we integrate by parts and get

$$F = \ln(1 - \exp(-x)) \frac{x^3}{3} \Big|_0^y - \int_0^y \frac{x^3}{3} \frac{1}{1 - \exp(-x)} dx. \tag{15}$$

Expanding of the function $\exp(-x)$ in (15) to the second term and further integration give us the expression

$$F = \frac{Vk_D^3}{2\pi^2 3} (T \ln(\hbar uk) - T \ln T - \frac{T}{3}), \tag{16}$$

where k_D – the Debye wave vector. From here, the body entropy

$$S = -\frac{\partial F}{\partial T} = \frac{Vk_D^3}{2\pi^2 3} (-\ln(\hbar uk) + \ln T + \frac{4}{3}). \tag{17}$$

The factor in front of the bracket in (17) is similar to the Debye sphere $3R = Vk_D^3/2\pi^2 3$, and the expression under the logarithm is similar to the Debye temperature $\hbar uk = \theta$. Accordingly, the entropy of the crystalline phase can be expressed as follows

$$S = 3R(-\ln\theta + \ln T + \frac{4}{3}). \tag{18}$$

For the crystalline structures of Ni, Fe, Zn, Al, Cu, Ag, Au, using the known values of the Debye temperatures [24] and the expression (18), the entropy values at 298 K were found. The obtained entropy values agree satisfactorily with the reference values [25] (Table 4). Therefore, using (18) it is possible to find the entropy of crystalline structures of substances at high temperatures.

Modeling of the temperature dependence of the entropy of decagonal quasicrystalline phases

To obtain the temperature dependences of quasicrystalline decagonal phases, the model of anisotropic crystals was used [26]. Anisotropic structure of the quasicrystalline decagonal phase has a quasicrystalline pattern in the xy plane and crystalline pattern in the direction of the z axis [27]. Now we shall describe the structure of the quasicrystalline decagonal phase using the model of strongly anisotropic crystals [7]. The decagonal phase can be considered as a multilayer structure with an interaction between the layers. Oscillations are present in the structure in the layers themselves, and there are oscillations of the layers relative to each other and of the bends of the layers. We assume that the anisotropy of the quasicrystalline decagonal phase is manifested in the difference of the dispersion laws in the xy plane and in the direction of the z axis. In the xy plane for the quasicrystalline structure, the dispersion law is represented by a quadratic dependence $\gamma\chi^2$ ($\chi^2 = k_x^2 + k_y^2$) [7], where γ - group velocity in the plane, and in the direction of the z axis for the crystalline structure the dispersion law takes the form of a linear dependence $\approx uk_z$. The total frequency of sound waves can be expressed as follows, according to [7]

$$\omega^2 = u^2 k_z^2 + \gamma^2 \chi^4 \tag{19}$$

Taking into account the contribution from sound vibrations, free energy of the quasicrystalline decagonal phase is deter-

Table 4. Calculated values of the entropy of substances at 298 K.

Substance	Debye temperature, K [24]	Reference entropy (298 K), J/(mol· K) [25]	Calculated entropy (298 K), J/(mol· K)
Ni	375	29.87	27.51
Fe	460	27.15	22.42
Zn	234	41.63	39.27
Al	394	28.35	26.28
Cu	315	33.15	31.85
Ag	215	42.55	41.38
Au	170	47.40	47.23

mined by the formula [7]

$$F = \frac{8VT}{(2\pi)^3}\int_0^{\hbar u k_{\max}/T} dk_z \int_0^{\hbar\gamma\chi^2_{\max}/T} \ln\left(1-\exp\left(-\frac{\hbar}{T}\sqrt{u^2k_z^2+\gamma^2\chi^4}\right)\right)2\pi\chi d\chi. \tag{20}$$

Using the Debye formalism for the model of anisotropic crystals, the upper integration boundaries in (20) were replaced. Then the formula (20) will also be true for the case of high temperatures, similar to the Debye model [7]. For the inner integral, we obtain the following expression

$$\frac{\pi T}{\gamma\hbar}\int_0^x \ln(1-e^{-z})dz = \frac{\pi T}{\gamma\hbar}\left[x\ln(1-e^{-x}) - 3\int_0^x \frac{zdz}{e^z-1}\right], \tag{21}$$

where $z = \hbar/T\sqrt{a+\gamma^2\chi^4}$, a -parameter $\sim u^2k_z^2$, $x = \hbar/T\sqrt{a+\gamma^2\chi^4_{\max}}$ - integration boundary. The coefficient 3 in (21) takes into account small oscillations of sites of the lattice lying in the integration plane in three directions. After expansion in series e^z up to the third term and e^x to the second term, we get the expression

$$\frac{\pi T}{\gamma\hbar}\left[x\ln x - 6\ln(1+\frac{x}{2})\right]. \tag{22}$$

For the further integration in the direction of the wave vector k_z, we further expand the function $\ln(1+x/2)$ up to the sixth term. Then the inner integral of the expression (20) will be of the form of

$$\frac{\pi T}{\gamma\hbar}\left[x\ln x - 6(\frac{x}{2}-\frac{x^2}{8}+\frac{x^3}{24}-\frac{x^4}{64}+\frac{x^5}{160}-\frac{x^6}{384})\right]. \tag{23}$$

Next, we make an additional substitution of the variable $x = \hbar/T\sqrt{u^2k_z^2+b}$, where $b = \gamma^2\chi^4_{\max}$ – parameter, $y = \hbar/T\sqrt{u^2k^2_{z\max}+b}$.

Then, taking into account the coefficient in front of the double integral in (20), we obtain

$$F = \frac{VT^3}{\pi^2\gamma u\hbar^2}\left[\int_0^y x\ln x dx - 6\int_0^y (\frac{x}{2}-\frac{x^2}{8}+\frac{x^3}{24}-\frac{x^4}{64}+\frac{x^5}{160}-\frac{x^6}{384})dx\right]. \tag{24}$$

After integration, the free energy will take the form

$$F = \frac{VL^2}{2\pi^2\gamma u}\left[T\ln\hbar L - T\ln T - \frac{7}{2}T + \frac{1}{2}\hbar L - \frac{1}{8}\frac{\hbar^2L^2}{T} + \frac{3}{80}\frac{\hbar^3L^3}{T^2} - \frac{3}{240}\frac{\hbar^4L^4}{T^3} + \frac{3}{672}\frac{\hbar^5L^5}{T^4}\right], \tag{25}$$

where $L = \sqrt{u^2k^2_{Z\max}+\gamma^2\chi^4_{\max}}$.

From here, we find the entropy of the decagonal quasicrystalline phase:

$$S = 3R\left(-\ln\theta + \ln T + \frac{9}{2} - \frac{\theta^2}{8T^2} + \frac{6\theta^3}{80T^3} - \frac{9\theta^4}{240T^4} + \frac{12\theta^5}{672T^5}\right). \tag{26}$$

The factor $VL^2/2\pi^2\gamma u$ is similar in meaning to the Debye sphere $(V/(2\pi)^3 4/3)\pi k_D^3 \approx 3R$. The factor $\hbar L$ is similar to the Debye temperature.

2. Results and discussion

Using our findings, we calculate the Debye temperature of the quasicrystalline and crystalline phases of the alloys. For this purpose, we substitute in (26) and (18) the values of the phase entropies obtained by the information-and-statistical method at the temperature of 300 K. From the resulting equality, we calculate the Debye temperature of the phases. The obtained Debye temperatures for crystalline and quasicrystalline phases of the alloys are given in Table 3. The papers [28, 29] point to a wide range of values of the Debye temperatures of quasicrystalline phases of the Al-Co-Cu and Al-Co-Ni alloys values of the Debye temperature of $Al_{65}Co_{20}Cu_{15}$ vary from 22 K to 400 K, respectively, according to [28]. The Debye temperature of $Al_{73}Co_{17}Ni_{10}$ is 123 K, and for $Al_{71}Co_{13}Ni_{16}$ it is 589 K, according to [29]. Moreover, according to [30] the Debye temperature of the Al-Co-Ni d-phase is 545 K.

No experimental data relating to determination of the total entropy of the $Al_{65}Co_{20}Cu_{15}$ and $Al_{72}Co_{18}Ni_{10}$ quasicrystalline alloys are found in the literature, since the configurational component of the entropy is determined by calculation. However, the proposed information-and-statistical method was used earlier to determine the entropy of the WC and W_2C crystalline phases of the W – C alloy [22]. In this case, the calculated entropy values agree satisfactorily with the reference ones. Somewhat different approach to the estimation of integration and approximation constants was

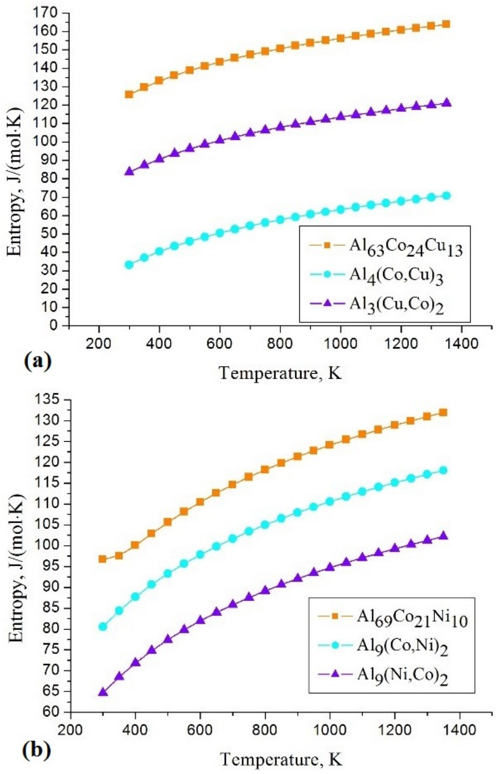

Figure 4. Dependence of the entropy on the temperature of alloy phases: (a)- $Al_{65}Co_{20}Cu_{15}$, (b) - $Al_{72}Co_{18}Ni_{10}$.

used in [22]. Besides, for the crystalline phases of simple alloys the obtained values of the entropy agree satisfactorily with the reference values at 298 K (Table 4).

The advantage of the proposed algorithm for the determination of the phase entropies is the possibility to calculate the phase entropy at higher temperatures using expressions (18) and (26). Thus, the dependencies for quasicrystalline and crystalline phases of the alloys under study have been constructed (Fig. 4). Fig. 4 shows that the phase entropy increases monotonically with rising temperature, which indicates complying with the law of the entropy increase. It is also evident that the entropy of quasicrystalline phases at all temperatures is higher than the entropy of crystalline phases. This phenomenon results from the fact that statistical weight of the realization of quasicrystalline structures is much higher than statistical weight of the realization of crystalline structures.

Therefore, the algorithm proposed for determination of the entropy and Debye temperature can be used in practice for various phases, including quasicrystalline phases.

3. Conclusion

To calculate the entropy of the quasicrystalline alloy phases, the digitized images of the phases were scanned using the computer program. Elements of the digital matrix of values of the light absorption coefficient obtained by scanning displayed the spatial configuration of phases in the alloys. Dividing the combined distribution of the probability density of the absorption coefficients into individual Gaussians corresponding to the phases, we calculated the mean-square deviation for each phase. The calculations took into account that the dependence of the logarithmic representation of the normal distribution function takes the form of a quadratic function. Using the found mean-square deviations, we calculated the entropy of the relevant phases at 300 K, and the light absorption coefficient was the distribution factor determining the entropy in the Einstein formula.

The obtained values of the phase entropy at 300 K were further used to calculate the Debye temperature of the phases. Decagonal quasicrystals have an anisotropic structure. It is assumed that anisotropy manifests itself in the difference of the dispersion laws in the xy plane and in the direction of the z axis, which is described by the model of anisotropic crystals. Based on this model, an expression describing the dependence of entropy on the temperature and the Debye temperature of phases was found. From here, the Debye temperature of quasicrystalline phases of the Al-Cu-Co and Al-Ni-Co quasicrystals was calculated. Then, using the found expression and values of the Debye temperature, we calculated the entropy of the phases at higher temperatures. Therefore, using the presented methods of calculation, we can determine the Debye temperature and the entropy of quasicrystalline phases. Since the entropy values of quasicrystalline structures are higher than the entropy values of crystalline structures, the obtained data can be used to determine the relative content of quasicrystalline phases in the film coatings. The knowledge of these quasicrystal properties provides additional opportunities for implementation of the task of creating the film coatings resistant to thermal loads.

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Authors Contribution
Authors have contributed equally in preparing and writing the manuscript.

Availability of data and materials
The datasets generated (or analyzed) during the current study are available from the corresponding author on reasonable request.

Conflict of interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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