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TEMPERATURE DEPENDENCE OF DECAGONAL QUASICRYSTALS HEAT CAPACITY

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The heat capacity of decagonal quasicrystals of the Al–Co–Cu or Al–Co–Ni alloys was calculated at the temperatures of 600, 700, and 900 K in this work. The expression for the heat capacity of the quasicrystals was obtained based on the Debye model. For the quasicrystals, the linear "excessive" heat capacity is observed in the range of temperatures between 400 to 600 K which means the deviation from the 3R Dulong-Petit value. The heat capacity at a temperature of 900 K is about 28.4 J/mol·K which is higher than the Dulong-Petit value (~ 25 J/mol·K). The "excessive" heat capacity relates to the peculiarities in the decagonal quasicrystal anisotropy. These crystals are quasiperiodic in the *x* and *y* directions, and periodic in the *z* direction. As a result, there is a difference in the dispersive laws in the different directions. The Debye temperature values have essential influence on the temperature dependencies of the heat capacity of the decagonal quasicrystals. Thus, the higher the Debye temperature and the larger "excessive" heat capacity, the more stable are considered the quasicrystals exposed to the temperature effects.

Keywords: quasicrystals, anisotropy, the Debye model, dispersive law, temperature heat capacity dependence, "excessive" heat capacity.

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1. Introduction

Since the first discovery of stable decagonal quasicrystals (the D-phases) in the slowly solidified Al–Co–Cu and Al–Co–Ni alloys, many papers dealing with solidification process, stability and anisotropy in physical properties (ten-fold periodic direction versus two-fold quasiperiodic direction) have been published [1–3]. The heat capacity of decagonal quasicrystals is of special interest. This feature is directly connected with the distribution of vibration energy among oscillators – vibrational degrees of freedom. Besides, heat capacity obeys the Gruneisen law and depends on linear expansion coefficient. From these considerations, the conclusion can be made that heat capacity is responsible for the quasicrystal resistance to temperature effects such as those that occur during the contact of the quasicrystals with molten metal alloys [4]. The experimental studies [5,6] showed that the quasicrystals have so called "excessive" heat capacity at a temperature of about 470 – 550 K. The increase in the "excessive" heat capacity reaches maximum in the temperature range between 1000 to 1200 K and acquires value of about 33 J/mol·K. With the following increase in a temperature, the "excessive" heat capacity starts decreasing up to quasicrystal structure fracture. However, explanation of such heat capacity behavior of the quasicrystals is scarce. Therefore, the aim of this paper is to consider the effect of temperature on the heat capacity of the decagonal quasicrystals, since its role for the stability of the D-phases has been assumed.

2. Results and discussion

To calculate the temperature dependence of the heat capacity of the decagonal quasicrystal phases of the Al–Co–Cu and Al–Co–Ni alloys from the positions of the theory of high anisotropic crystals, the methods of the Debye model have been used.

They apply substitution of the upper integration limits by the finite values – the Debye frequency ~ ω_D or the corresponding wave vectors.

For anisotropic solid, free energy can be written as

$$F = \frac{8VT}{(2\pi)^3} \int_0^{kz_{\max}} dk_z \int_0^{\chi^2_{\max}} \ln\left(1-\exp\left(-\frac{\hbar}{T}\sqrt{u_z^2k_z^2+\gamma^2\chi^4}\right)\right)2\pi\chi d\chi \qquad (1)$$

where V – volume, u_z – acoustic wave velocity, k_z – wave vector in the z direction, γ – group velocity, χ – stiffness coefficient.

Expression (1) considers the peculiarities in the quasicrystal anisotropy. Thus, in the k_xk_y plane, the dispersive distribution that is similar to the Debye distribution in the three-dimensional space can be applied, such as $const\ \pi\chi^2\ \left(\chi^2 = k_x^2 + k_y^2\right)$. In the z direction the dispersive distribution is $const\ k_z$.

For anisotropic decagonal quasicrystals, the atomic interaction is stronger in the *dxdy* plane than that in the z direction. For inner integral, we obtain the following expression

$$\frac{\pi T}{\gamma\hbar}\int_0^x \ln\left(1-e^{-z}\right)dz = 4\frac{\pi T}{\gamma\hbar}\left[x\ln\left(1-e^{-x}\right)-\int_0^x \frac{zdz}{e^z-1}\right], \qquad (2)$$

where $z = \frac{\hbar}{T}\sqrt{a+\gamma^2\chi^4}$, a – factor ~ $u_z^2k_z^2$, $x = \frac{\hbar}{T}\sqrt{a+\gamma^2\chi^4_{\max}}$ – the integration limit.

On expanding into a series of e^z up to a third term and e^x up to a second term, we obtain for (2)

$$\frac{\pi T}{\gamma\hbar}\left[x\ln x - 2\ln\left(1+\frac{x}{2}\right)\right] \qquad (3)$$

For further integration in the direction of the wave vector k_z, we additionally expand the function $\ln\left(1+\frac{x}{2}\right)$ into a series up to a fourth term. Considering the low values of some coefficients in the square terms of the dispersive frequency law, the terms of the fourth order cannot be ignored. Then, the inner integral of expression (1) can be given by

$$\frac{\pi T}{\gamma\hbar}\left(x\ln x - 2\left[\frac{x}{2}-\frac{x^2}{8}+\frac{x^3}{24}-\frac{x^4}{64}\right]\right). \qquad (4)$$

To integrate over k_z, we additionally substitute variables

$$x = \frac{\hbar}{T}\sqrt{u_z{}^2k_z^2+b}\text{, where } b = \gamma^2\chi^4_{\max}.$$

Then, considering the coefficient before the double integral of expression (1), we obtain

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

where $y=\frac{\hbar}{T}\sqrt{u_z{}^2k_{z\max}^2+b}$.

On integrating by parts, we can write

$$\int_0^y x\ln x dx=\frac{1}{2}y^2\ln y-\frac{1}{4}y^2 \qquad -2\int_0^y\frac{x}{2}dx=-\frac{1}{2}y^2$$

$$2\int_0^y\frac{x^2}{8}dx=\frac{1}{12}y^3 \qquad -2\int_0^y\frac{x^3}{24}dx=-\frac{1}{48}y^4 \tag{6}$$

$$2\int_0^y\frac{x^4}{64}dx=\frac{1}{160}y^5$$

For free energy

$$F=\frac{VT^3}{\pi^2\gamma u\hbar^2}\left[\frac{y^2}{2}\ln y-\frac{3}{4}y^2+\frac{1}{12}y^3-\frac{1}{48}y^4+\frac{1}{160}y^5\right] \tag{7}$$

considering that $y=\frac{\hbar}{T}\sqrt{u^2k_{z\max}^2+\gamma^2\chi_{\max}^4}=\frac{\hbar}{T}L$, we obtain

$$F=\frac{VL^2}{2\pi^2\gamma u}\left[T\ln\hbar L-T\ln T-\frac{3}{2}T+\frac{1}{6}\hbar L-\frac{1}{24}\frac{\hbar^2L^2}{T}+\frac{1}{80}\frac{\hbar^3L^3}{T^2}\right]. \tag{8}$$

Entropy is given by

$$S=-\frac{\partial F}{\partial T}=\frac{VL^2}{2\pi^2\gamma u}\left[-\ln\hbar L+\ln T+\frac{5}{2}-\frac{1}{48}\frac{\hbar^2L^2}{T^2}+\frac{2}{80}\frac{\hbar^3}{T^3}L^3\right]. \tag{9}$$

Then, from expressions (8) and (9), internal energy can be found as

$$E=F+TS=\frac{VL^2}{2\pi^2\gamma u}\left[T+\frac{1}{6}\hbar L-\frac{1}{12}\frac{\hbar^2L^2}{T}+\frac{3}{80}\frac{\hbar^3L^3}{T^2}\right]. \tag{10}$$

Correspondingly, heat capacity can be given by

$$C_V=\frac{\partial E}{\partial T}=\frac{VL^2}{2\pi^2\gamma u}\left[1+\frac{1}{12}\frac{\hbar^2L^2}{T^2}-\frac{3}{40}\frac{\hbar^3L^3}{T^3}\right], \tag{11}$$

where the expression $\hbar L=\hbar\sqrt{u^2k_{z\max}^2+\gamma^2\chi_{\max}^4}$ has meaning that is similar to the Debye temperature.

Expression (11) consists of three terms, two of them depend on temperature and have opposite signs. This consideration leads to the “excessive” heat capacity in the certain temperature range. Besides, this feature essentially depends on the generalized Debye temperature. In Fig. 1 the temperature dependencies of calculated heat capacity of the decagonal quasicrystals of the Al–Co–Cu and Al–Co–Ni alloys are shown.

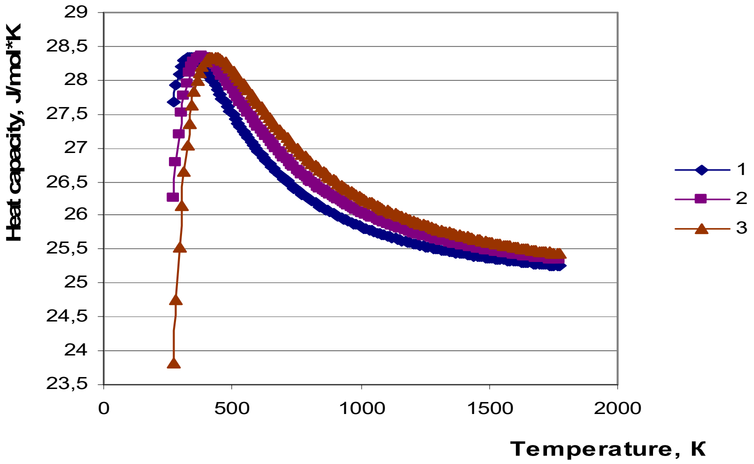

Fig. 1. The temperature dependencies of the calculated heat capacity of the decagonal quasicrystals of the Al–Co–Cu and Al–Co–Ni alloys at the following Debye temperatures: 1 – 600 K; 2 – 700 K; 3 – 900 K.

3. Conclusions

For the heat capacity of the decagonal quasicrystals of the Al–Co–Cu and Al–Co–Ni alloys, the deviation from 3*R* value (the Dulong–Petit law) can be assumed. The heat capacity at the temperature of 1000 K is about 28.4 J/mol·K which is higher than the Dulong–Petit value (~ 25 J/mol·K). The increase in the "excessive" heat capacity of the quasicrystals approaches to the linear dependence in the range of temperature between 400 to 600 K, which is in good agreement with the experimental dependencies obtained by authors [5,6]. According to the energy equipartition law, the "excessive" heat capacity of the quasicrystals distributes among the larger number of freedom degrees as compared to that of crystal phases. As a result, the resistance of the quasicrystals to temperature effects, i.e. their stability, is higher than that of periodic crystals.

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