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Thermal expansion and Debye temperature of Ti–Zr–Ni quasi-crystal

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Thermal expansion coefficient and Debye temperature of single-phase $Ti_{41.5}Zr_{41.5}Ni_{17}$ quasi-crystal have been determined from changes in the positions and intensities of X-ray diffraction lines within 80–300 K temperature range. The thermal expansion of the icosahedral crystal has been found to be isotropic. The average thermal expansion coefficient and Debye temperature have been determined to be $\alpha = 8 \cdot 10^{-6}$ K^{-1} and $\Theta_D = 340$ K.

Рентгенографически по изменению положения и интенсивности дифракционных линий в интервале температур 80–300 К определены коэффициент термического расширения и температура Дебая однофазного квазикристалла $Ti_{41.5}Zr_{41.5}Ni_{17}$. Установлено, что тепловое расширение икосаэдрического квазикристалла имеет изотропный характер. Значения среднего коэффициента теплового расширения и температура Дебая соответственно равны $\alpha = 8 \cdot 10^{-6}$ K^{-1} и $\Theta_D = 340$ K.

Icosahedral quasicrystals (QCs) are highly ordered metallic phases with structure characterized by the presence of 5-fold symmetry axes [1]. Ti–Zr–Ni QCs based on Bergman cluster are attributed to the 2nd class of known stable QCs. Their unusual structure assumes special physical properties. So, it is well known that QCs are able to absorb a considerable amounts of hydrogen forming a solid solution [2]; the parameters of hydrogen diffusion have been investigated [3]; superconductivity has been found [4, 5]; mechanical properties and elastic-plastic deformation mechanism have been studied [6, 7]. However, the thermal-physical properties of QCs remain a poorly investigated field [8]. This concerns first of all the characteristics defined by the lattice dynamics, namely, thermal expansion, square-root deviations, characteristic Debye temperature, etc. This work is aimed at determination of the thermal expansion coefficient (α) and Debye temperature (Θ_D) for titanium-zirconium-nickel alloy of $Ti_{41.5}Zr_{41.5}Ni_{17}$ composition using X-ray diffraction method.

The studed objects were thin ribbons prepared by quenching on rotating wheel in pure argon atmosphere. The techniques of sample preparation and structure attestation of QCs are described in [3–7]. The samples of $\leq$50 μm thickness and 2 to 4 mm width mounted on a copper plate were placed in an original vacuum chamber put on the diffractometer goniometer. Vacuum in the chamber was not worse than 10^{-2} Pa. The sample temperature was varied from room value to liquid nitrogen boiling point and controlled by a chromel-copel thermocouple. The X-ray diffraction spectra were taken simultaneously from the QC and from copper plate as a reference using filtered Cu irradiation. For QC examination, three reflections lying along 2-fold [0/0 0/0 0/2] axis, and two reflections with diffraction vector directed along 5-fold [0/0 1/0 0/1] axis were chosen, as well as (400) and (420) reflections from copper. The QC reflection indices are given in two-index (N, M)

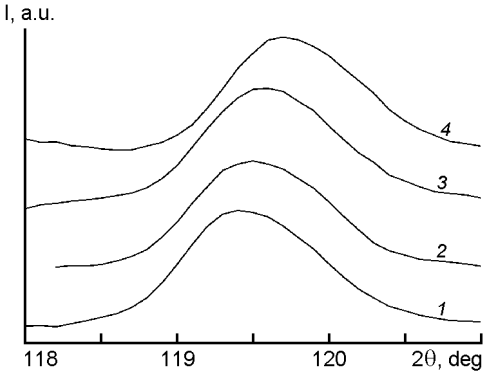

Fig. 1. The quasicrystalline phase (136,220) diffraction maximum position and intensity at temperature (K): 300 (*1*); 223 (*2*); 183 (*3*); 73 (*4*).

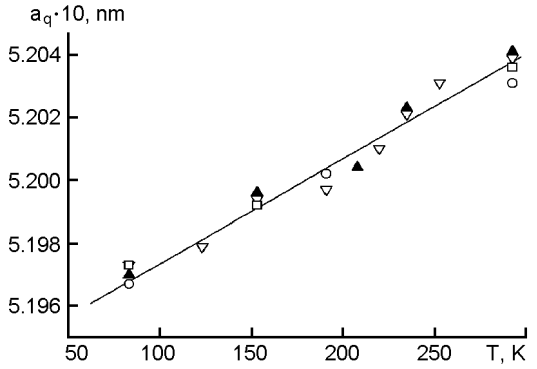

Fig. 2. Temperature dependence of quasi-crystallinity parameter, obtained by repeated scanning of (136,220) reflection (open symbols), and of (72,116) reflection (shaded symbols).

Cahn's notation [9], for example, (72, 116) or (136, 220).

Temperature dependences of diffraction line positions and integral intensities were analyzed. The quasi-crystallinity parameter (or the quasi-lattice period) aq was calculated from line positions using the equation

$$a_q = \frac{\lambda \cdot \sqrt{N + \tau M}}{4\sin\theta \cdot \sqrt{1 + \tau^2}}. \quad (1)$$

Then, thermal expansion coefficient was determined from the expression

$$\alpha = \frac{\Delta a_q}{\Delta T} \cdot \frac{1}{a_q}. \quad (2)$$

The total square-root atomic displacements $\overline{U^2}$ were calculated by analyzing the integral intensity angular dependence for multiple reflection orders along the two chosen directions. Static $\overline{U_s^2}$ and dynamic $\overline{U_d^2}$ constituents were separated using $\overline{U^2}$ temperature dependence plot extrapolating to 0 K.The characteristic Debye temperature Θ_D was determined in Debye approximation from Debye-Waller factor e^{-2M} of intensity formula using temperature variation of diffraction maxima integral intensity as well as the dynamic atomic displacements [10]. Every sample was analyzed during several heating/cooling cycles.

The preliminary X-ray phase analysis within the wide range of diffraction angles has shown that in the samples chosen, only the icosahedral quasi-crystalline phase was present. It is characterized by a *P*-type unit cell and quasi-crystallinity parameter a_q from 0.52045 to 0.52065 nm. As the temperature drops, diffraction peaks were observed to shift towards larger angles, and the intensities thereof increase (Fig. 1). The quasi-crystallinity parameter temperature dependence for a typical sample is shown in Fig. 2.

It should be noted that the temperature range under study is lower than synthesis temperature and corresponds to the phase stability area. In this temperature range, the experimental data are found to be approximated well by a linear dependence. The quasi-crystallinity parameter values calculated for different crystallographic directions are well fitted by a single dependence. From the plot slope, the linear thermal expansion coefficient is found to be isotropic and equal to $(7...8)\pm0.5\cdot10^{-6}$ K^{-1}. The value dispersion for different samples may be caused by different structure perfection and, in particular, by differences it the phason defect density, as it was observed for $Al_{65}Cu_{23}Fe_{12}$ QCs [11], as well as by residual macro-strain effect. In the substantially stress-free samples, the results obtained for opposite ribbon sides coincide (Fig. 3), and α is close to $8\cdot10^{-6}$ K^{-1}. For copper reference, the experimental average value α_{Cu} was $13.3\pm0.5\cdot10^{-6}$ K^{-1}. Since in the temperature range under study, α_{Cu} varies from 8.3 to $16.7\cdot10^{-6}$ K^{-1} according to table data as a sufficiently reliable. It may be noted that the value obtained is close to reference data for titanium-zirconium alloys [12].

The calculation of square-root atomic displacements made taking into consideration the corrections for angular and atomic multipliers for two pairs of the reflections (18,29) and (72,116), as well as (20,32) and (116,220), has shown that $\overline{U^2}$ value is the same for atoms positioned in the planes

both with 5-fold and 2-fold symmetry axes, and is $4.2 \cdot 10^{-4}$ nm^2 at room temperature. The value obtained is close to the data for coarse-crystalline metal samples [13]. The results obtained at $T = 80$ K also have given the single $\overline{U^2}$ value of $3.1 \cdot 10^{-4}$ nm^2. Then, it follows from the temperature dependence that static displacements are about $2.7 \cdot 10^{-4}$ nm^2. The dynamical displacements at room temperature can be obtained as a difference, and then the characteristic temperature may be estimated according to the expression

$$\Theta_D = \left(9h^2T / (\overline{U_d^2}\,\pi^2 mk)\right)^{1/2}, \qquad (3)$$

where m is the reduced mass; k, the Boltzmann constant; h, the Plank constant. Note that the expression (3) is valid for temperatures T which do not differ considerably from Θ_D. Such estimation determines the value of characteristic temperature as $\Theta_D \approx 370$ K. The characteristic temperature refinement was carried out using variation of (136,220) and (72,116) reflection integral intensity under temperature decrease from $T_1 = 300$ K to $T_2 = 80$ K. The choice of the reflections was caused, first, by low sensitivity to phason defects, and second, by the fact that these reflections characterize different crystallographic directions. The value Θ_D was determined from the expression

$$\ln\frac{I_{T_1}}{I_{T_2}} = \frac{12h^2}{mk\Theta_D}\left[\frac{\Phi(x_1)}{x_1} - \frac{\Phi(x_2)}{x_2}\right] \cdot \frac{\sin^2\theta}{\lambda_2}, \qquad (4)$$

where $\Phi(x)$ is the Debye function (taken from [14]), and $x = \Theta_D/T$. From the calculations, the characteristic temperature was found to be $\Theta_D = 320$ K for (72,116), and $\Theta_D = 360$ K for (136,220) reflections, respectively. For five samples, the Debye temperature value was determined to be within the range from 300 to 360 K. It should be noted that the samples in initial state had different structure perfection that manifested itself as differences in intensity, width, and positions of diffraction maxima. We explain the Θ_D value dispersion just by that fact. A conclusion can be drawn that, according to the X-ray diffraction data, $Ti_{41.5}Zr_{41.5}Ni_{17}$ icosahedral quasicrystal has the Debye characteristic temperature $\Theta_D = 340 \pm 20$ K. The value is found to agree well with other data [4, 5], where the Debye temperature was used as fitting parameter for electrical resistance temperature dependence. The reliability of the presented results is supported as well by the fact that for copper internal reference, the value $\Theta_D = 310$ K was obtained which is in excellent accordance with X-ray data from [15] ($\Theta_D = 315$ K).

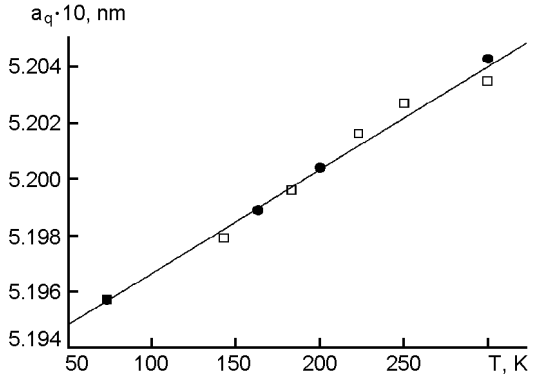

Fig. 3. Temperature dependence of quasi-crystallinity parameter, obtained by (136,220) reflection scanning from the opposite sides of the sample. Shaded symbols correspond to the side contacted with quenching drum; open symbols, to the ribbon free side.

At last, let us discuss the isotropy of atomic oscillations and of Debye temperature in the icosahedral quasi-crystals. A similar effect was observed before in Al–Pd–Mn QC [16]. We think this fact to be not surprising for icosahedral quasicrystals. It is known that for crystals, the $2M$ value (in the Debye-Waller factor e^{-2M}) is usually calculated using a model taking into account only atomic interactions of the first (or several first) coordination spheres. In the Debye approximation, the frequencies of three oscillation branches depend on wave vector in the same manner. That condition is the better fulfilled, the better the reciprocal lattice is inscribed into sphere. In this sense, the Ti–Zr–Ni QC with structure based on Bergman cluster including three spherically symmetric atomic shells where each atom is surrounded by icosahedron of its neighbors, satisfies the Debye theory completely. The cluster forming atoms oscillate together. Zirconium atoms should play the main role, because they form the second shell and enter the third one. That is may be the reason that the obtained QC characteristic temperature is close to the value for pure zirconium and only a little lower than for titanium and nickel. This may mean that metallic bonding type prevails in the structure.

Thus, using X-ray diffraction in temperature range from 80 to 300 K, thermal expansion coefficient, square-root atomic displacements, and Debye characteristic temperature have been determined for icosahedral $Ti_{41.5}Zr_{41.5}Ni_{17}$ quasi-crystal, and it has been shown that these thermal-physical characteristics are isotropic. It is established that in the temperature range under study, an average linear thermal expansion coefficient is $\alpha = 8\pm0.5\cdot10^{-6}$ K^{-1}, while Debye temperature being $\Theta_D = 340\pm20$ K.

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Теплове розширення і температура Дебая Ti-Zr-Ni квазікристала

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Рентгенографічно за зміною положення та інтенсивності дифракційних ліній в інтервалі температур 80–300 K визначено коефіцієнт термічного розширення та температуру Дебая однофазного квазікристала $Ti_{41.5}Zr_{41.5}Ni_{17}$. Встановлено, що теплове розширення ікосаедричного квазікристала має ізотропний характер. Значення середнього коефіцієнту теплового розширення та температура Дебая відповідно дорівнюють $\alpha = 8\cdot10^{-6}$ K^{-1} і Θ_D= 340 K.