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Linear coefficient of thermal expansion and Debye temperature of PbTe at high temperatures

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The linear coefficient of thermal expansion and the Debye temperature of PbTe in the high-temperature range have been investigated using X-ray diffractometry. The studies were carried out on samples of two types: single crystal and PbTe powder, synthesized separately. Both types of samples showed fairly similar results in all measurements.

It has been established that in the temperature range 293−773 K the linear thermal expansion coefficient is constant and for powder: $\alpha = 20.1 \cdot 10^{-6} \pm 0.9 \cdot 10^{-6}\,\mathrm{K}^{-1}$ and for single crystal: $\alpha = 19.7 \cdot 10^{-6} \pm 0.8 \cdot 10^{-6}\,\mathrm{K}^{-1}$.

The Debye temperature measured in the temperature range 293−573 K equal to 105 ± 3 K

Keywords: lead telluride, linear thermal expansion coefficient, Debye temperature.

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1. Introduction

Despite the fact that the linear coefficient of thermal expansion (α) and the Debye temperature (Θ_D) are among the most important characteristics of a solid, at present their values are not unambiguously determined for PbTe. The first studies of the thermal expansion of PbTe belong to the middle of the 20th century [1,2], and continue into the 21st century [3–8]. Most of the known literature data are measured at low temperatures.

Information about the value of the linear coefficient of thermal expansion of PbTe at high temperatures is of great practical importance in creation of thermoelectric elements for conjugation of working and switching materials. In order to prevent contact failure when the temperature changes during the operation of the thermoelement, it is necessary that the working and switching materials have close values of the linear coefficient of thermal expansion.

The upper limit of operating temperatures of thermoelectric generators based on PbTe reaches 500°C. At higher temperatures, PbTe exhibits significant volatility, which leads to rapid degradation of devices. The knowledge of the α value at operating temperatures will enable to scientifically substantiate the selection of switching materials in the design of thermoelectric elements based on PbTe.

In connection with the above, the first task of this article is to determine the linear coefficient of thermal expansion of PbTe at temperatures from 293 K to 773 K.

As the analysis of the literature shows, starting from the middle of the last century [9–12] and up to the present [13–22], active studies of the PbTe Debye temperature continue all over the world, however, the values obtained by different methods and authors turn out to be significantly different from each other.

In this regard, the second task of this article is to determine the Debye temperature of PbTe.

2. Methods of production and research of samples

All measurements were carried out on two types of PbTe samples: a single crystal and a powder preparation, which were synthesized separately.

Synthesis and growth of PbTe single crystals were carried out in quartz ampoules evacuated to 10^{-3} Pa from elementary components with purity of 99.999% (materials of Sigma-Aldrich Corporation). The lead surface was preliminarily cleaned from oxides by etching in an acetic acid solution.

The initial components were alloyed at a temperature of 1373 K for 3 h, and then the PbTe crystals were grown by the method of directed crystallization in a vertical two-zone furnace. The crystal growth direction coincided with the [100] crystallographic direction. The elemental composition was monitored by local X-ray spectral microanalysis using the INCAx-sight attachment for a Jeol JSM-6380LV scanning electron microscope. All synthesized samples had a composition close to stoichiometric, within a narrow region of PbTe homogeneity. The resulting samples were sawn into washers perpendicular to the growth axis. To remove disturbed near-surface layers, the washers were subjected to mechanical and then chemical polishing in an ammonium peroxide solution.

The PbTe powder preparation was synthesized in a separate ampoule from the same initial materials and by the same method as the single crystal, but without the stage of directional crystallization. Next, a fine powder was prepared from the obtained PbTe ingot. To prepare the powder, the synthesized PbTe ingot was crushed in a corundum mortar under a layer of anhydrous ethanol, which largely prevents the oxidation of powder particles. Then, the excess alcohol layer was poured off, and the resulting suspension was immediately placed in a cuvette and pumped out in the diffractometer vacuum chamber. At the same time, the remaining alcohol quickly evaporated. This method of preparation of the PbTe powder preparation prevents both oxidation and possible preferential orientation of particles.

The study of the linear coefficient of thermal expansion and the Debye temperature of PbTe was carried out using ARL X'TRA X-ray diffractometer in a vacuum chamber evacuated to a residual pressure of 10^{-3} Pa, equipped with a heater. Filtered Cu $K\alpha$-radiation with Bragg–Brentano focusing was applied in these experiments. Measurements were performed with a 0.02° pitch of 2ϑ.

The heating rate of the samples was about 0.04 K/s. Before the start of recording each diffraction pattern, the samples were kept for 30 min at a given constant temperature.

To find α, the period of the cubic crystal lattice was measured in a certain temperature range

$$\alpha = \frac{a_T - a_{293}}{a_{293}(T - 293)}, \tag{1}$$

where a_{293} and a_T are — the period of the PbTe lattice at „reference" temperature (293 K) and some temperature T, respectively.

To calculate the lattice period of the PbTe powder preparation, in order to increase the accuracy, the Nelson–Riley extrapolation function was used, applied to the full set of all diffraction pattern reflections [23]. The (600) reflection was taken to calculate the lattice period of a single crystal. The correction for the ample holder expansion during heating was taken into account for this diffractometer.

To find the Debye temperature, we used the technique described in [23], based on the analysis of the Debye–Waller factor. It is necessary to measure the integral intensities I_1 and I_2 of one reflection (hkl) at two temperatures T_1 and $T_{\{}2\}$, under the same geometric conditions. In this case, the equation is satisfied

$$\ln(I_1/I_2) = \frac{12h^2}{km\Theta}\left[\frac{\Phi(\Theta/T_2)}{\Theta/T_2} - \frac{\Phi(\Theta/T_1)}{\Theta/T_1}\right]\frac{\sin^2\vartheta}{\lambda^2}, \tag{2}$$

where $\Phi(\Theta/T)$ is Debye function; h is Planck's constant; k is Boltzmann's constant; m is mean atomic mass; ϑ is diffraction angle; λ is X-ray wavelength.

For cubic crystals: $\sin^2\vartheta/\lambda^2 = \sum h_i^2/4a^2$, where $\sum h_i^2$ is the sum of squared Miller indices, a is lattice period.

Then equation (2) takes the form

$$\ln(I_1/I_2) = \varphi(T_1, T_2, \Theta) \cdot \sum h_i^2, \tag{3}$$

where

$$\varphi(T_1, T_2, \Theta) = \frac{3h^2}{a^2km\Theta}\left[\frac{\Phi(\Theta/T_2)}{\Theta/T_2} - \frac{\Phi(\Theta/T_1)}{\Theta/T_1}\right]. \tag{4}$$

Equation (3) at fixed temperatures T_1 and T_2 is a linear function in the coordinates $\ln(I_1/I_2) - \sum h_i^2$ passing through the origin. For the PbTe powder sample, the Debye temperature was determined by measuring the intensities of all reflections of the diffraction pattern. Using the slope of the experimental dependence, approximated by linear regression in accordance with equation (3), the value $\varphi(T_1, T_2, \Theta)$ was found. Next, for temperatures T_1 and T_2, the dependence of $\varphi(T_1, T_2, \Theta)$ on Θ was calculated, which was used to determine the Debye temperature.

In the case of a PbTe single crystal, only one (600) reflection was used to find the Debye temperature, the intensity of which was measured at different temperatures. The choice of this reflection is due to the fact that as the interplanar distances decrease, the effect of temperature on the intensity of the reflections increases. Therefore, the (600) reflection was selected as the analyzed reflection of the single crystal, since it corresponds to a small interplanar distance, but has a rather high intensity.

3. Experimental results and discussion

Figure 1 shows the profiles of the (600) reflections of a PbTe single crystal at various temperatures. A similar picture was also observed for the diffraction patterns of the powder preparation, however, the intensity of the reflections was significantly lower than that of a single crystal, and the reflections did not split into a doublet.

As can be seen in Fig. 1, when heated, the reflections shift towards smaller angles and their intensity decreases. The temperature dependences of the cubic lattice period obtained in this article for a single crystal and a PbTe powder preparation are shown in Fig. 2. Both experimental dependences are approximated by linear regressions and practically coincide with each other.

Using standard procedures for estimating the boundaries of confidence intervals (with 95% confidence probability) for the linear regression coefficients (Fig. 2), an estimate of the absolute random errors of the linear coefficient of thermal expansion for the PbTe powder preparation was obtained: $\alpha = 20.1 \cdot 10^{-6} \pm 0.9 \cdot 10^{-6}\,\mathrm{K}^{-1}$, and for PbTe single crystal: $\alpha = 19.7 \cdot 10^{-6} \pm 0.8 \cdot 10^{-6}\,\mathrm{K}^{-1}$.

The linear coefficient of thermal expansion of lead telluride was studied in the articles [1,2] at very low temperatures and up to close to room temperature. Strelkov's quartz dilatometer was used in the article [1]. The studied samples were synthesized from components with a low degree of purity (99.99%). It was found that α grows from $9.02 \cdot 10^{-6}\,\mathrm{K}^{-1}$ at 30 K to $19.8 \cdot 10^{-6}\,\mathrm{K}^{-1}$ at 240 K, and further up to 350 K does not change. In the article [2] the capacitance method was used in the temperature range from 4.2 to 303.2 K. At $T = 300$ K, $\alpha = 20.4 \cdot 10^{-6} \pm 0.4\,\mathrm{K}^{-1}$,

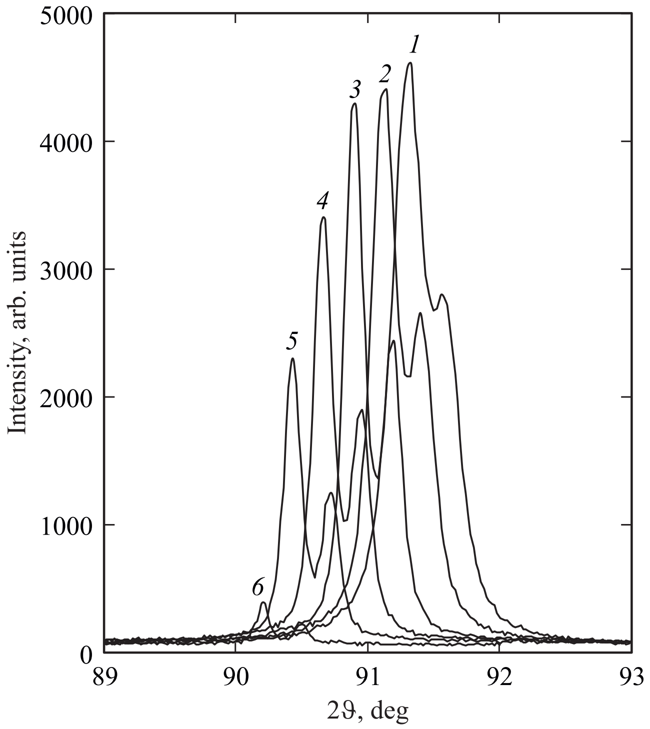

Figure 1. Profiles of the (600) reflections of a PbTe single crystal at different temperatures: *1* — 293 K, *2* — 373 K, *3* — 473 K, *4* — 573 K, *5* — 673 K, *6* — 773 K.

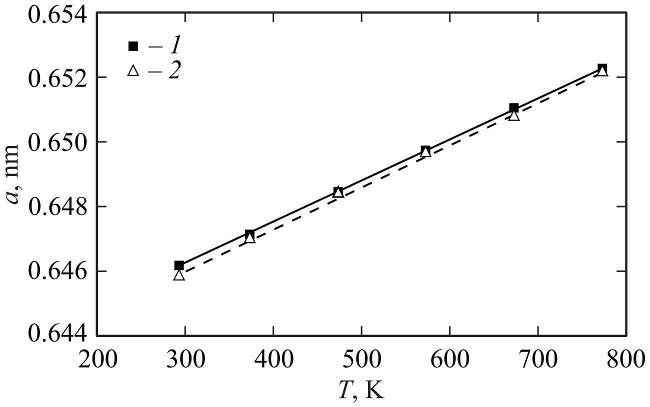

Figure 2. Temperature dependence of the cubic lattice period a of a single crystal (*1*) and powder preparation (*2*) PbTe.

which is only slightly larger than the value obtained in the article [1].

The article [3] provides the temperature dependence of the PbTe lattice period as a quadratic function: $a(T) = 6.444 + 1.04 \cdot 10^{-4}T + 8.10 \cdot 10^{-8}T^2$ defined on the temperature interval 150–600 K. Substituting this dependence into formula (1), we find that at 300 K, $\alpha = 23.45 \cdot 10^{-6}\,\mathrm{K}^{-1}$, and at 773 K, it reaches $29.37 \cdot 10^{-6}\,\mathrm{K}^{-1}$. It is obvious that such a noticeable increase of α with increasing temperature differs significantly from the results obtained in this article. Perhaps this discrepancy is due to the fact that in the article [3] the temperature dependence of the lattice period is approximated by quadratic regression over a very wide temperature range, including the low-temperature region, where the linear coefficient of thermal expansion really increases with increasing temperature [1,2].

In the article [4] the temperature dependence of the lattice period is approximated linearly on the interval 300–1000 K, therefore, α is constant and equals $20.1 \cdot 10^{-6}\,\mathrm{K}^{-1}$. Thus, the results obtained in the article [4] are in very good agreement with the results of the this article.

The value α at 300 K, obtained in the article [5] using neutron diffractometry on PbTe powder, which turned out to be $18.12 \cdot 10^{-6}\,\mathrm{K}^{-1}$, differs noticeably. However, in [6], the same method found: $\alpha = 19.91 \cdot 10^{-6}\,\mathrm{K}^{-1}$ at 300 K, which agrees well with this article.

It should be noted that other modern studies also showed good agreement with the value α obtained in this article at 300 K. So in [7], using X-ray diffraction, it was found that $\alpha = 19.6(6) \cdot 10^{-6}\,\mathrm{K}^{-1}$, and in the article [8], the theoretical growth within the local density approximation without spin-orbital interaction showed the value $\alpha = 19.36 \cdot 10^{-6}\,\mathrm{K}^{-1}$. The advantage of the method used in this article (X-ray diffractometry) for determining the linear coefficient of thermal expansion is that the change in the distance between the atomic planes of the crystal is actually determined, which is almost independent of the state of the sample at a higher level of organization of the crystalline substance — microstructures: size of crystallites, their mutual orientation, inclusions of impurity phases, etc. Therefore, such a „classical" method as dilatometry shows a more significant dependence on all these listed parameters.

From a theoretical point of view, it can be noted that, as is known from the literature [1,2], α continues to increase with increasing temperature at temperatures significantly exceeding the Debye temperature, up to room temperature. However, this growth is gradually slowing down. In this article, it has been established that a further increase in temperature above room temperature does not lead to an increase in the linear coefficient of thermal expansion. It can be assumed that in the studied temperature range, the constancy of thermodynamic quantities is achieved, depending on the contribution of the anharmonicity of lattice vibrations, which determine the Gruneisen relation. First of all, the temperature dependence α is determined by the temperature dependence of the molar heat capacity, which tends to constant values with increasing temperature.

Let's move on to finding the Debye temperature. Figure 3 shows an example of the experimental dependence of $\ln(I_1/I_2)$ on $\sum h_i^2$ for PbTe powder, while Figure 4 shows the corresponding example of the dependence of $\varphi(T_1, T_2, \Theta)$ on Θ.

The calculation results of the Debye temperature based on the ratios of the (600) reflection intensities of a single crystal and for all PbTe powder preparation reflections are provided in the table. The calculation does not include measurements of the reflection intensity at 673 and 773 K, since at these

X-ray Debye temperature of PbTe (powder and single crystal) determined in the temperature range from 293 to 573 K

Temperatures Samples, T_1, T_2 [K]	Single Crystal PbTe. Reflection (600)	Powder PbTe. All Reflections.
	Debye temperature, Θ_D [K]	
293, 373	103	104
293, 473	105	106
293, 573	105	107

temperatures an abnormally sharp decrease in intensity was observed, which may be due to the noticeable volatility of PbTe at these temperatures under vacuum conditions. A significant increase in the vacancies concentration can lead to a more significant decrease in the intensity of X-ray reflections than due to thermal vibrations alone.

As can be seen in the table, both types of samples — single crystal and powder preparation, show similar values of the Debye temperature.

The absolute random error Θ_D can be estimated by estimating the confidence interval boundaries for the tangent of the slope of the linear regression (Fig. 3). Further, based on this estimate, one can find the range of the Debye temperature variation. For the example shown in Fig. 3 and Fig. 4, the Debye temperature turned out to lie in a very narrow corridor of 107.1 ± 0.4 K with a confidence probability of 95%. The errors calculated in this way in determining the Debye temperature for all samples and temperature intervals did not exceed ± 1 K. Therefore, the table shows the values Θ_D, rounded to integral units.

Since, as can be seen in the table, the X-ray Debye temperature is practically independent of the single-crystal or polycrystalline state of PbTe, the results can be averaged over all measurements. The arithmetic mean Debye temperature, averaged over all measurements, gives $\overline{\Theta}_D = 105 \pm 3$ K with 95% confidence.

The literature data on the Debye temperature of PbTe have a fairly wide range of values. The methods by which the Debye temperature of PbTe was determined by different authors can be divided into diffractive and non-diffractive. The first group includes X-ray and neutron diffractometry. And the second, more numerous group includes methods based on the study of thermal conductivity, heat capacity, reflection of ultrasonic pulses and ultrasonic velocity, nuclear inelastic scattering, and neutron scattering.

The results obtained by different authors using diffraction methods for bulk PbTe single crystals and polycrystals (powders) range from $\Theta_D = 87(1)$ K [4] (X-ray diffractometry) up to $\Theta_D = 135.9(7)$ K [7] (X-ray diffractometry).

In the [6], using neutron diffraction on a PbTe powder preparation, the value $\Theta_D = 127.8(4)$ K was obtained, and using X-ray diffraction on a PbTe single crystal, the value $\Theta_D = 129.2$ K was obtained. These results are very close to [5], where $\Theta_D = 129(2)$ K (neutron diffraction). Taking into account the results of this work, it should be considered

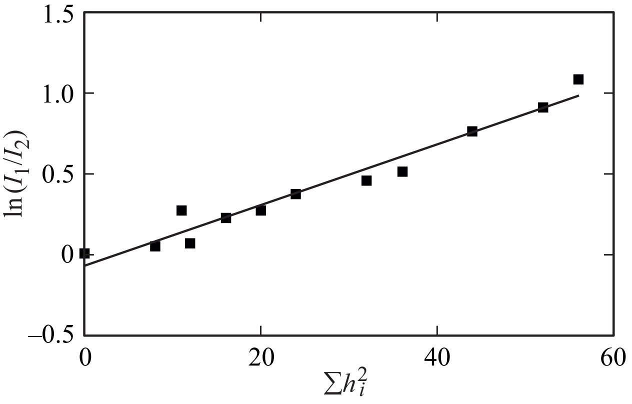

Figure 3. Experimental dependence of $\ln(I_1/I_2)$ on $\sum h_i^2$ for PbTe powder at $T_1 = 293$ K and $T_2 = 573$ K.

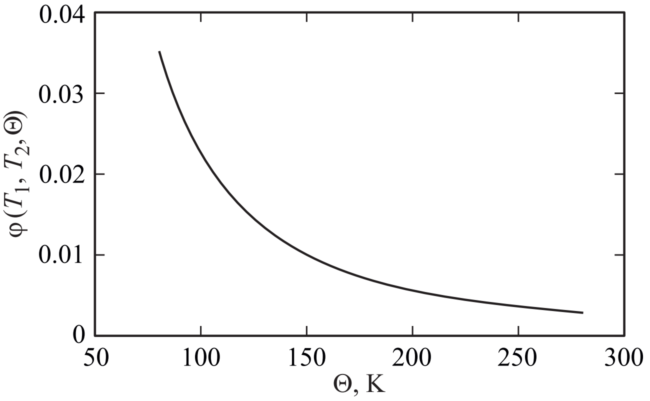

Figure 4. Calculated dependence of $\varphi(T_1, T_2, \Theta)$ on Θ for PbTe at $T_1 = 293$ K and $T_2 = 573$ K.

that the value Θ_D obtained in [4] is, most likely, greatly underestimated.

An extraordinary result was obtained in the article [15], where the Debye temperature of bulk and nanosized PbTe dendritic crystals was studied using X-ray diffraction and phonon spectrum analysis at a temperature close to room temperature one. It was found that for bulk PbTe crystals, $\Theta_D = 115$ K, but for nanosized dendritic crystals, PbTe increases to 156 K (according to calculations based on the Debye–Waller factor). An increase in Θ_D upon going to nanosized objects is, generally speaking, an unusual result, because nanomaterials are characterized by a larger specific surface, which means that vibrations of surface atoms can significantly attenuate the intensity of diffracted X-rays. This implies an increase in the Debye-Waller factor, and hence a decrease in the Debye temperature calculated based on it.

Non-diffraction methods show the Debye temperature of PbTe from 95 K (neutron scattering) [16] to 170(5) K (nuclear inelastic scattering) [17].

The Debye temperature found in the articles [9,10] turned out to be 125 and 130 K, respectively. In these articles, the specific heat capacity of PbTe was measured at a constant volume in the region of low temperatures. The Debye model of the frequency distribution of phonons was used. It was found in the article [10] that in the interval 20−80 K the dependence $\Theta_D(T)$ slowly increases, while in the interval 80−130 K it remains almost constant at the level ~ 130 K.

Taking into account the real phonon spectrum, studied in the article [11] by the method of neutron spectroscopy, enabled to calculate Θ_D based on the technique shown in [12]. As it turned out, the Debye temperature calculated in the article [11] on the basis of the experimental distribution of vibrations over frequencies differs from that obtained in the article [10] on the basis of the Debye distribution, by 5% down. In this case, the calculated dependence $\Theta_D(T)$ passes through a minimum at a temperature of about 10 K. The maximum value of $\Theta_D \sim 170$ K is reached at 0 K. At temperatures 80−200 K, the Debye temperature remains almost constant at ~ 125 K.

Calculation of the Debye temperature based on the experimental distribution of phonons, carried out in the article [13] using the method [14], showed a value of 136 K.

By studying the reflection of ultrasonic pulses, $\Theta_D = 163$ K, [18] was obtained, and by studying the speed of ultrasonic waves: 136 K [19] and 143 K [20]. Calculations based on lattice vibration spectra showed $\Theta_D = 152$ K [21].

It can be concluded that among non-diffraction methods, the results of this article coincide to the greatest extent with the result obtained in the article [22], where the Debye temperature was found by the method of studying thermal conductivity, equal to 105 K.

The fundamental reason leading to the error in determining the Debye temperature based on the X-ray diffrometry used in this article and the analysis of the − Waller Debye factor is the construction of a model for attenuation of the X-ray intensity based on the assumption that each atom (or ion) vibrates isotropically and perfectly independent of surrounding atoms (Debye approximation). For such crystals, the Debye−Waller factor is determined in terms of the mean square of the total displacement of atoms from the equilibrium position $M = 8\pi^2\langle U^2\rangle \sin^2\vartheta/3\lambda^2$. A more precise consideration requires knowledge and consideration of the spectrum of elastic vibrations of crystal atoms. In addition, to improve accuracy of determining the Debye temperature by X-ray methods, one should take into account thermal diffusion scattering, which can have a complex character of temperature dependence, — first increase, and when a certain temperature is reached, — decrease, and for reflections with different indices hkl, this temperature can be different.

4. Conclusion

Using high-temperature X-ray diffractometry, it was found that the linear coefficient of thermal expansion of PbTe in the temperature range 293−773 K is constant and practically does not depend on the polycrystalline or single-crystal state of the sample. For PbTe powder: $\alpha = 20.1 \cdot 10^{-6} \pm 0.9 \cdot 10^{-6}\,\mathrm{K}^{-1}$, and for PbTe single crystal: $\alpha = 19.7 \cdot 10^{-6} \pm 0.8 \cdot 10^{-6}\,\mathrm{K}^{-1}$. Generally, it can be said that the obtained values are in good agreement with the results of many other authors, who, however, in most cases, studied only the low-temperature region.

From an applied point of view, the constancy of the linear coefficient of thermal expansion at high temperatures and its independence from the polycrystalline or single-crystal state in the operating temperature range of thermoelectric generators based on PbTe opens up wide opportunities in the search for switching materials for creating these devices.

In this article, one of the most important characteristics in solid state physics, the Debye temperature for PbTe, is refined, in terms of which there is a rather wide scatter in the literature data. In the present study, it was found that in the temperature range 293−573 K, the average value $\overline{\Theta}_D = 105 \pm 3$ K.

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Conflict of interest

The author declares that he has no conflict of interest.

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