

DEBYE'S TEMPERATURE AND DIMENSIONAL BORDER BETWEEN MACRO – AND NANO STATES

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Abstract: Debye's temperature θ_D is the temperature border between areas, $C_V^\mu(T)$ has constant value and, when $T < \theta_D$, begins to decrease monotonically. θ_D is the crystal parameter, which allows to calculate the dimensional border between macro- and nano-states. The statement which is found in scientific discussions that θ_D depends on temperature is incorrect because it contradicts modern crystal-physical theories. The numerical value θ_D is defined experimentally and is related to the structure of crystals and to the processes taking place in them.

KEYWORDS: DEBYE'S TEMPERATURE, DEBYE'S PARAMETERS, NANOSTATE, MAXIMUM SIZE OF NANOPARTICLES.

1. Introduction

In classical thermodynamics the molar thermal capacity of substance at the constant volume equals $C_V^\mu = 3R$ where $R = 8,31441 \text{ J} / (\text{K} \cdot \text{mol})$ (a universal gas constant).

$C_V^\mu = \text{const}$ when cooling down to the temperature called θ_D Debye's temperature which is substance parameter.

At $T = \theta_D$, with the fall of temperature C_V^μ begins to decrease monotonically. At $T < \theta_D$ the classical description of thermodynamic processes in a crystal should be replaced with quantum. The value θ_D is connected with other Debye's parameters, for example, with Debye's frequency w_D which depends on structural and chemical parameters of the substance.

Besides the parameter w_D concepts of Debye's energy E_D , a Debye's impulse P_D and the Debye's size λ_D (Debye's wavelength) are introduced. All these parameters are analytically connected with each other.

The definitions θ_D on the basis of the known parameters of substance are numerous, which demonstrates that in any model it is impossible to consider all possible characteristics of a condition of substance. In Debye's theory a formula

$$\theta_D = \frac{\hbar}{k} w_D = \frac{\hbar}{k} \bar{U} (6\pi^2 \cdot n)^{1/3} \quad \text{where } k, \hbar - \text{ Boltzmann and}$$

Planck's constants respectively, \bar{U} – the average acoustic speed, n – the number of atoms in a unit of volume, required additional analysis.

The aim of the work is to prove that θ_D is a parameter of a substance, determined only by an experimental $C_V = f(T)$ function. Metal crystals were taken as the object of the study.

2. Classical theory of thermal capacity

In the classical theory of thermal capacity atoms are modeled as absolutely rigid spheres, which have three degrees of freedom of movement. At a temperature $T > \theta_D$ energy of $E=kT$ is the share of one degree of freedom of the movement of such atom.

That is the number of atoms in one mole is equal to A (to Avogadro's number), one mole of a substance "contains" energy [1]:

$$E = 3AkT = 3RT \quad (1)$$

Thermal capacity at constant volume equals $C_V^\mu = dE / dT = 3R = 24,94 \approx 25 \text{ J} / \text{K} \cdot \text{mol}$.

3. Quantum theory of thermal capacity

The development of cryogenic technologies at the beginning of the 20th century made it possible to analyze changes of thermal capacity $C_V^\mu = f(T)$ at low temperatures [2, 3]. The experimental dependence C_V^μ on temperature is given in figure 1.

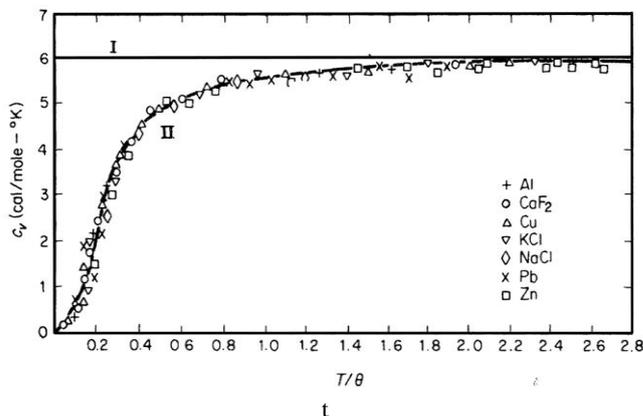


Fig 1. – The generalized dependence $C_V = f(T / \theta_D)$ [3]

To explain the dependence $C_V^\mu = f(T)$ at $T < \theta_D$ A. Einstein and P. Debye considered quantum models [2, 4] approximately at the same time independently of each other. Both of these scientists noted what at $T < \theta_D$ atoms cannot be considered as spheres (or points). Each atom is the quantum oscillator with its own wave number (q) and, therefore, with its own frequency (w). A. Einstein based on the assumption of homology of atoms and considered that all atoms are quantum oscillators with an identical frequency (w_E).

P. Debye assumed that wave vectors of atoms in the space of a wave vector are evenly distributed in the sphere with a radius (w_D), that is at $w > w_D$ the classical description should be applied, and at $w < w_D$ – the quantum description.

In this case

$$\theta_D = \frac{\hbar}{k} w_D \quad (2)$$

The total number of wave vectors (P) depends on the number of atoms, moreover

$$P \approx \frac{4}{3} \pi (P_D)^3 \quad (3)$$

Therefore, the number of wave vectors in a spherical layer with a radius $P(w) \div P(w + dw)$ equals

$$dP(w) \approx 4\pi P(w)dw \quad (4)$$

or

$$dP(w) \approx 4\pi w^2 dw \quad (5)$$

Distribution of frequencies in Einstein's model is described by the condition:

$$P_E = \delta(w - w_E) \quad (6)$$

where δ is the Delta function [1].

At low temperatures in Debye's model the role of electronic processes increases. At $T \approx \theta_D$ an electronic contribution to thermal capacity is small though heat conductivity is generally caused by the electrons that are currently available [5].

So at $T < \theta_D$ atoms are quantum oscillators. At low temperatures interaction between atoms is carried out by means of excitement of quantum electronic gas, that we should speak of "electronic jelly" at $T < \theta_D$ which exists in crystals.

Dynamic excitement at the same time is carried out by means of quasiparticles of phonons and plasmons [6]. Debye's temperature was considered by some authors as the peculiar "adjustable" parameter allowing to reach bigger consent between theoretical and experimental values C_V^{μ} [4, 7, 8]. There was a statement that Debye's temperature depends on temperature [9]. Many scientists pointed out that the statement is illogical, for example [5, 10].

Now θ_D is considered as the parameter of properties of substance and it is included in various reference books. The main criterion of θ_D is the experiment studying the function $C_V^{\mu} = f(T)$. The temperature point of deviation C_V^{μ} from $3R$ -line and therefore θ_D cannot be defined precisely. As, for example, it is impossible to determine the temperature of "fluidifying" of glass precisely. The stronger are inequalities $T < \theta_D$ or $T > \theta_D$ the more strictly works the corresponding approximations.

Functions $C_V^{\mu} = f(T)$ in Debye's and Einstein's theories are described by rather close, but still different curves which differ by the value exceeding an experiment error. The search of the functions $C_V^{\mu}(T)$ more coinciding with an experiment is still continued. For example, in [11] phenomenological function is offered:

$$C_V(T) = \frac{C_V}{\exp\left[a \cdot \Delta(T) \cdot \left(\frac{\theta - T}{T}\right)\right]} \quad (7)$$

where coefficient of linear connection $a = 0,0817$.

The analytical dependence of $C_V(T)$ looks like:

$$C_V(T) = \frac{C_V}{\exp\left[0.0817 \cdot \Delta(T) \cdot \left(\frac{\theta_D}{T} - 1\right)\right]} \quad (8)$$

At $T \leq \theta_D$ the formula (8) looks like:

$$C_V(T) = \frac{C_V}{\exp\left[0.0817 \cdot \left(\frac{\theta_D}{T} - 1\right)\right]} \quad (9)$$

At $T > \theta_D$, $C_V(T) = C_V = const.$

The curve dependences of $C_V(T)$ received for various $\left(\frac{T}{\theta}\right)$ on

the corresponding values of function of Debye and Einstein [12], on the values calculated by a formula (8) and also – on the basis of experimental data are given in figure 2 [3]. Distribution of points throughout the whole temperature interval and especially on the allocated sites (inserts) shows that function (8) more corresponds to experimentally received values, than calculations using the formula of molar thermal capacity at the constant volume:

$$C_V = \frac{\partial U}{\partial T} = 9R \left(\frac{T}{\theta}\right)^3 \int_0^x \frac{e^{-x} x^4}{(e^x - 1)^2} dx.$$

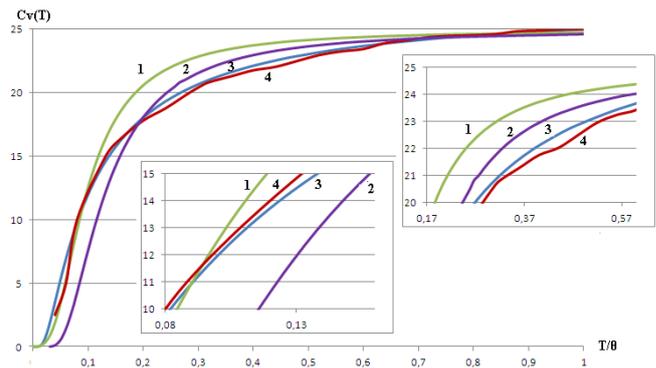


Fig 2. – Thermal capacity C_V of various substances depending on the substance temperature relation to its Debye's temperature. 1 – on Debye's formula, 2 – on Einstein's formula, 3 – calculate by formula (8), 4 – curve on experimental data [3]. Source: [11].

From the presented schedules it is clear that the theoretical curve calculated by formula (8) has bigger consent with an experiment.

4. Debye parameters of crystals

Other parameters of a condition of substance are also connected with Debye's temperature. If internal energy at $T = \theta_D$ (Debye's energy) is designated as E_D , then the Debye's frequency w_D , a Debye's impulse P_D and Debye's temperature θ_D are connected with it.

This connection is described by the condition:

$$E_D = \hbar w_D = k \theta_D = \frac{P_D^2}{2m} \quad (10)$$

The Debye's impulse at $T < \theta_D$ corresponds to model of "electronic jelly", however, at $P = P_D$ it is possible to use adiabatic approximations of a free electron with an effective mass of m^* . As in these conditions thermal oscillation of ions (atoms) have much smaller energy than the energy of plasmons, with a certain extent of approximations it is possible to consider that $m^* = m_e$ where m_e is the mass of an electron [5, 6].

According to de Broil's condition $P_D = \frac{h}{\lambda_D}$, the value λ_D can be

considered as the particle size at which there is a change of mechanisms of course of physical processes. Therefore, at the sample sizes $r > \lambda_D$ (r is the particle size), macroscopic methods of the analysis are applicable. At $r < \lambda_D$ the sample size begins to affect the value of parameters of physical properties. Thus $\lambda_D = L_0$ defines the dimensional border between macro- and nano states. At $r > L_0$ a particle is in a macroscopic state, at $r < L_0$ – in a nanostate. The stronger the specified inequalities are, the more corresponding state is observed. From the condition (10) follows:

$$k\theta_D = \frac{P_D^2}{2m}, \quad (11)$$

but λ_D is considered along a certain direction, for example, along axis x . As $P^2 = P_x^2 + P_y^2 + P_z^2$, for isotropic substance.

$$P^2 = 3P_x^2 = \frac{3h^2}{\lambda_D^2}. \quad (12)$$

Taking it into account according to conditions (6, 10), the value $\lambda_D = L_0$ will take the following form:

$$L_0 = \frac{\sqrt{1,5h}}{\sqrt{km}} \theta_D^{-1/2} = C\theta^{-1/2}. \quad (13)$$

As C is determined from tabular values, put them in the formula and get $C = 2,3 \cdot 10^{-7} m \cdot K^{1/2}$, i.e., (13) takes the following form:

$$L_0 = 230 \cdot \theta_D^{-1/2} [nm] \quad (14)$$

In [13] it is shown that the numerical values θ_D calculated by the formula (13) and the values θ_D received experimentally do not exceed 10%.

Table 1. – Structural and chemical characteristics of atoms of metals, θ_D – tabular and calculated by formula (15).

Name element	symbol	N_0	$a, \text{Å}$	$r_a, \text{Å}$	L_0, nm	n $4/a(\text{m}^3)$	$\theta_{D(\min)}, K$ $\theta_{D(\max)}, K$ [1, 5, 8, 16]	θ_D, K , calculated by a formula $\theta_D = \sqrt[3]{\frac{U(6\pi^2 n)}{h}} / k$
Aluminium	Al	13	4,04955	1,43	11,6	0,060234E+30	375 – 428	415,7
ν – Iron	Fe	26	3,6467	1,29	11,2	0,082482E+30	355 – 470	466,5
Nickel	Ni	28	3,5238	1,25	11,9	0,091417E+30	375 – 450	442,2
Copper	Cu	29	3,6147	1,275	13,0	0,084692E+30	315 – 343	330,8
Silver	Ag	47	4,08591	1,44	15,7	0,05864E+30	215 – 229	219,4
Platinum	Pt	78	3,9238	1,385	15,2	0,066212E+30	230 – 240	234
Gold	Au	79	4,07832	1,44	17,6	0,058968E+30	164 – 170	157,2
Lead	Pb	82	4,9500	1,75	24,6	0,03298E+30	88 – 105	85

Values θ_D for low temperatures of silver crystals are given in work [2]. At temperature change of a crystal (from 1.4 K to 124.20 K) θ_D grows from values (from 165 K to 225 K). At the same time the connection between properties of a crystal and Debye's temperature is described by the condition [2]

$$\theta_D = \sqrt[3]{\frac{U(6\pi^2 n)}{h}} / k, \quad (15)$$

In the formula (15) temperature of example is absent. However U and n depend on temperature. Acoustic speed as it is shown, for example, in works [7, 14] decreases as the temperature rises. As there the temperature increase in volume takes place at the same time, n also decreases as temperature of the sample increases. The provided data contradict each other as according to one model θ_D increases, and to the other decreases. From this it follows that Debye's temperature, first, does not depend on the temperature of the sample, and secondly, is an inner property of a crystal and can be determined only by experimental curve dependence of thermal capacity of a crystal on temperature ($C_V(T)$). The inflection point on a curve $C_V''(T)$ corresponding to value θ_D is not strictly fixed as experimental function $C_V''(T)$ is differentiated on T in all points of the temperature interval including θ_D .

According to [5], the idea of dependence θ_D on object temperature is deprived of any basis. θ_D is the substance parameter independent of temperature as, for example, the number of nucleons in a nucleus, Fermi's level, energy of electronic levels, width of the forbidden zone, etc. does not depend on T .

The analysis of the existing sources shows that the values θ_D given in various sources can differ from each other [2, 3, 5]. However θ_D , and value n are defined by methods independent from each other.

Therefore, it is necessary to analyze the definition of θ_D based on values of other parameters determined by the known methods [15, 16].

Acoustic speed is connected with θ_D and density of atoms, which is described by condition (15).

The maximum and minimum values θ_D for metals taken from references [1, 5, 8, 16] and also calculated by a formula (15) θ_D for some metals are given in table 1.

The technique of determining acoustic speed is often not described. In some cases the values θ_D which are experimentally determined by various authors differ from those found in reference books. In metals acoustic speed significantly depends on processing to which the sample was subjected: rolling, forging, annealing. The value n is determined by results of structural and diffraction experiments.

It can be concluded from the analysis made, that θ_D and n can be used as assessment of effective (idealized) value of acoustic speed, i.e. \bar{U} is determined by results of thermodynamic and structural and physical parameters (θ_D and n). The provided table suggests that θ_D , determined by a curve ($C_V(T)$) a table value and calculated by the formula $C_V^H = f(\bar{U}, n)$ differ from each other at the relative size which is not exceeding 5%. Average acoustic speed \bar{U} – was defined with longitudinal and cross acoustic waves.

5. Conclusion

Debye's temperature has to be considered as a temperature point on an experimental curve $C_V^H = f(T)$ when the constant value $C_V^H = 3R$ begins to decrease monotonously. The temperature point of transition from constant value C_V^H to temperature area of reduction C_V^H is also called Debye's temperature. Upon transition through Debye's temperature at a research of thermal physical properties of a crystal it is necessary to use methods of the quantum theory $T < \theta_D$ or classical $T > \theta_D$. The stronger these inequalities are, the better the corresponding approximations "works".

From the condition $k\theta_D = \frac{P_D^2}{2m} = \frac{\hbar^2}{2m\lambda_D^2}$ the dimensional

border is received $\lambda_D = L_0$ between macro- and nano states

$$L_0 = 230 \cdot \theta_D^{-1/2} [nm].$$

It is established that Debye's temperature – θ_D allows to calculate average effective value of acoustic speed.

The results of the work can be used in theoretical studies of properties of crystals and the acoustic phenomena in crystal materials. They can also be used by experts in the field of nanotechnologies.

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