



Calculation of Thermophysical Characteristics from First Principles

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Abstract

Using the pseudopotential method and the quasi-harmonic approximation, the following are calculated: the coefficient of linear thermal expansion (CLTE), the Debye temperature and their temperature dependencies. The temperature dependence of both characteristics, after approximation, is presented in analytical form. The results were compared with known tabular data. To check the reliability of the results, the calculations were carried out for pure metals as well. The difference between the calculated and tabular data does not exceed 7.3%. The presented model for calculating the CLTE of multielement alloys adequately reflects the results of thermal expansion of materials, considering such effects as phase transitions or the appearance of a second phase.

Keywords: Coefficient of linear thermal expansion; temperature dependence; pseudopotential method; quasi-harmonic approximation; debye temperature

Introduction

Along with hardness and strength, thermophysical characteristics (Debye temperature and coefficient of thermal expansion) are of primary importance when classifying materials by their properties. In [1], the Debye temperatures of nickel-based alloys were determined by fitting (to obtain the temperature dependence of the force constants), which have values of 150–200 K. The results of theoretical calculations of the Debye temperature for the same alloys, but with the addition of the element Cu (FeCoNiCu, FeCoNiCuCr, FeCoNiCuMn) are in the range 400-470K [2]. As is known, the physical characteristics of alloys in the first approximation can be estimated according to the rule of mixtures, from which it follows that the results obtained in [1] contradict the rule of mixtures. Also, the acceptance of the Debye temperature as a material constant is questionable, since, it is associated with quantities such as elastic moduli and lattice parameters, which are temperature dependent. A similar temperature dependence of the Debye parameter was noted in [3]. To assess the residual stresses in materials, knowledge of the values of their thermal expansion coefficient and its temperature dependence is required. Experimental determination of the thermal characteristics of materials is a problem for multi-element alloys and materials

with a complex structure. There is a disagreement in the data on the temperature dependence of the physical and mechanical characteristics [1,2,4]. Often, to assess the temperature dependence of a particular physical characteristic of alloys, empirical formulas are used with the method of fitting to some known experimental data [1,2]. An analysis of the results of these works confirms the difficulty of determining the temperature dependence of the physical and mechanical characteristics of metal alloys, borides, composites, both experimentally and theoretically. The purpose of this work is to estimate the thermal expansion coefficient, Debye temperature and their dependence on temperature from first principles. The work uses the method of a priori pseudopotential [5] as the most suitable for the conditions of ab initio and speed of calculations.

Theory and Method Of Calculation

To calculate the physical characteristics of materials (metals, multi-element metal alloys, borides, eutectic composites), the value of the energy of the electron-ion system is required. The total energy of the electron-ion system of a crystalline material can be represented as the sum of U_0 - the energies of the electron-ion system at a temperature $T = 0$ and U_T - the energy of thermal

vibrations of ions at nonzero temperature. When calculating the energy of the electron-ion system of crystals at zero temperatures, the pseudopotential method is used, and the energy of thermal vibrations can be considered using the Einstein model [6]. According to Einstein's model, atoms in a crystal lattice vibrate at the same frequency, the value of which is proportional to the stiffness of the material. The average value of the lattice vibration energy is determined by the equality

$$U_T = \sum \frac{h\omega_q}{q \exp(h\omega_q / kT) - 1} \quad (1)$$

where the summation is carried out over all types of oscillations, and ω_q is the oscillation frequency (according to Einstein's model, $\omega_q = \omega$ for all q).

To calculate the energy U_T , you need the value of the vibration frequency, which is associated with the dynamics of the crystal lattice.

The lattice dynamics is described using the Lagrange formalism, where the kinetic and potential energy of the vibrating atom is expressed through the displacement of the atom from the equilibrium position. When calculating the energy of thermal vibrations ($T \neq 0$), we use the quasi-harmonic approximation in combination with the method of a priori pseudopotential; as a result, we obtain the dependence of the energy of the electron-ion system on temperature through the unit cell volume $U = U(\Omega(T))$ [7]. The developed model in the quasi-harmonic approximation allows, within the framework of the harmonic approximation, to calculate the parameters of the crystal lattice during thermal expansion, and then the corresponding physical and mechanical characteristics of materials. Strength and elastic characteristics represent the derivatives of the total energy with respect to the lattice parameter.

Calculation and Discussion

The coefficient of linear thermal expansion

The lattice parameter in the equilibrium state, depending on temperature, is determined from the minimum energy of the electron-ion system. Thermal expansion coefficient is calculated by

Table 1: Coefficients of linear thermal expansion of alloys with fcc and bcc structure, calculated using formula (2) and experimental data (in parentheses).

	Ni	NiCoCr	NiCoCrFe	NiCoCrFeGa	FeCrCoNiGa
	fcc			bcc	fcc
T, K	$\alpha \cdot 10^6, K^{-1}$				
100	9,04	9,28	10,03	10,34	11,60
200	10,75	11,03	11,929	12,30	13,81
300	11,89 (11,75) [8]	12,21 (13) [1]	13,2 (14,2) [1]	13,60 (13,3) [9]	15,27
400	12,78	13,12	14,19	14,63	16,41
500	13,51	13,87	15,0	15,47	17,35

the formula:

$$\alpha = \frac{a_T - a_0}{T \cdot a_0} \quad (2)$$

Here a_T , a_0 are the parameters of the crystal lattice at temperatures T and at zero temperature.

In the case of anisotropy, the CLTE of the material can be represented in the form of generalized curves

$$\bar{\alpha} = \frac{2\alpha_a + \alpha_c}{3}$$

where α_a and α_c - are the CLTEs along the a and c axes, respectively.

The calculation results for some materials are presented in Table 1. For all metals, the calculated CLTE values and their temperature dependences are consistent with the tabular data and data from [8], except for the NiCoFe alloy. According to experimental data, the FeCoNi alloy has an almost constant CLTE at temperatures above 200 K. This is explained by the fact that FeCoNi is a two-phase alloy containing a small amount of a centered cubic body (BCC) in an FCC matrix.

According to the results of our calculations, the CLTE value of the FeCrCoNiGa alloy is in good agreement with the experimental data from [9] up to a temperature of 750K. And at temperatures above 750K a high increase in the thermal expansion coefficient is observed in the experiment, which is associated with a possible structural bcc - fcc transition [9]. Taking this factor into account, the CLTE of the FeCrCoNiGa alloy with an fcc lattice was estimated Table 1. The fcc alloy has a higher CLTE value compared to the same bcc alloy. According to the data of [9] at $T = 900$ K its value reaches $22.75 \cdot 10^{-6} K^{-1}$, and according to our calculations, $\alpha = 20.1 \cdot 10^{-6} K^{-1}$. The divergence of the results obtained from ab initio methods and experiment is less than 11.6%. It can be argued that the presented CLTE calculation model for multielement alloys adequately reflects the results of thermal expansion of materials, considering such effects as phase transitions or the appearance of a second phase. A relationship is observed between the calculated CLTE values and the material melting point T_{max} .

600	14,14 (14,6) [8]	14,52 (14,8) [1]	15,7 (16,3) [1]	16,19 (16,2) [9]	18,17
700	14,70 (14,98) [8]	15,09 (15) [1]	16,32 (16,5) [1]	17,121 (17,3) [9]	18,88
800	15,28	15,62	16,87	17,43 (19,3) [9]	19,5
1000	16,07 (16,03) [8]	16,49	17,84	18,42	20,12
1200	16,82	16,78	18,67	19,37	20,64

(Figure 1) shows the dependence $Y = \alpha \cdot T_{max}$ of metals and multi-element alloys on the parameter T/T_{max} . The same dependence of the function Y on the relative temperature parameter is obtained for metals and metal alloys considered in this work. As a result of mathematical analysis, two approximating functions were obtained

that describe the functional dependence $Y = \alpha \cdot T_{max}$ on $x = T/T_{max}$:

$$\alpha \cdot T_{max} = 0,0 - 0,01966 \cdot \exp(-3,833T/T_{max}) \tag{3}$$

$$\alpha \cdot T_{max} = 0,032 \cdot (T/T_{max})^{1/4} . \tag{4}$$

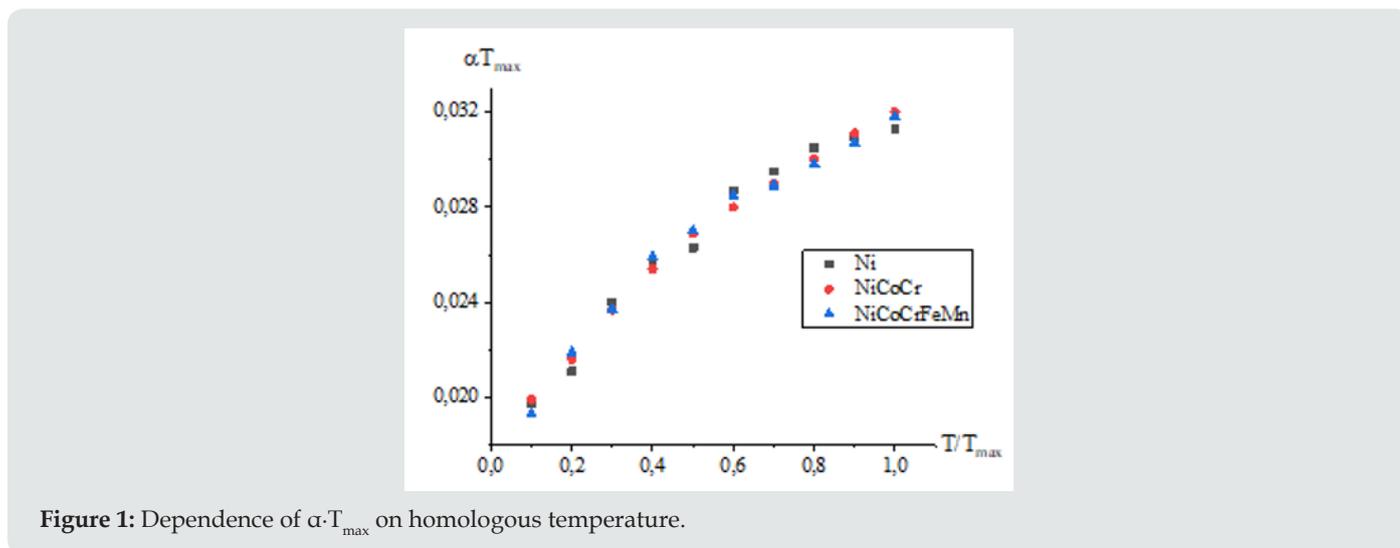


Figure 1: Dependence of $\alpha \cdot T_{max}$ on homologous temperature.

Formula (3) is close to the empirical formula that was introduced in [10] to describe the temperature dependence of CLTE for austenitic steel in the temperature range 100-1600K, with the only difference that the Debye temperature was used instead of the parameter T_{max} . The second approximation is simpler. When choosing an approximating function in the second case, the empirical relation was used $\alpha = 0,13232 \cdot T_{max}^{-5/4}$ to estimate the CLTE of metals with a cubic structure at room temperatures, which was proposed in [11]. The results obtained using approximations (3) and (4) agree with each other by 99%. We apply formula (4) to estimate the CLTE of borides, and in parallel calculate the CLTE from first principles. For eutectic composites, the calculation was carried out using the modified rule of mixtures [5]. In the usual

rule of mixtures for calculating physical characteristics, interfacial interaction is ignored. The averaged CLTE of a composite is defined as the sum of the LCTEs of the components considering their volume fraction [12,13]:

$$\alpha_k = \alpha_A \cdot \delta_A + \alpha_B \cdot \delta_B .$$

The results of CLTE calculations for borides and eutectics are presented in Table 2 For borides, the results obtained using relation (4) agree with experiment [14] and with the data obtained by us from first principles. In the case of composites, the maximum difference in CLTEs between calculated from first principles and using formula (4) is less than 7%.

Table 2: Calculated CLTE values for borides.

	ZrB2		LaB6		LaB6 - ZrB2	
	Theory	Formula (4)	Theory	Formula (4)	Formula (4)	Theory
T, K	$\alpha \cdot 106, K$					
100	4,045	4,024	4,963	4,905	5,0814	5,0272
300	5,37 (5,9) [14]	5,512	6,472 (6,4)[14]	6,588	6,5875	65,312
500	6,065	6,052	7,436	7,413	7,5985	7,2575
750	6,684	6,609	8,246	8,202	84,094	81,025
1000	7,187	7,139	8,870	8,783	9,0361	84,723

Debye Temperature

In Debye's theory, the frequency of acoustic waves is related to the speed of sound (s) and the wave number (q_{max})

$$\omega_D = s \cdot q_{max} \tag{5}$$

The presence of optical phonons is neglected, and the Brillouin zone is replaced by a sphere of the same volume:

$$q_{max} = (9\pi / 2)^{1/3} / r_s; 4\pi r_s^3 / 3 = a, \tag{6}$$

'a' is the crystal lattice parameter, and q_{max} represents the total number of allowed vectors in the Wigner - Seitz cell. The speed of propagation of vibrations is determined from the relation [6]

$$s = \sqrt{\alpha^* / \rho}. \tag{7}$$

Here ρ is the density of matter, α^* - force constant, which is determined through the second derivative of the interatomic interaction energy with respect to displacements at the point of equilibrium position of the atom.

The Debye temperature is determined from the relation [6]:

$$k_B \theta_D = \hbar \cdot s \cdot q_{max} \tag{8}$$

Suppose that the generated elastic wave due to the vibrations of atoms propagates along the crystallographic directions (x, y or z axis), then the speed of propagation of elastic waves in isotropic

bodies can be written in the form:

$$s = \sqrt{E/\rho} \tag{9}$$

where 'E' is the modulus of elasticity at T = 0.

All physical characteristics (lattice parameter, elastic moduli, speed of sound) are determined at temperature $T_0 = 0$ for crystals and are presented in Tables 3,4,5. Experimental data obtained by other authors are also presented, and in parentheses there are known tabular values [8]. Calculations confirm the stability of the fcc structure for all alloys considered here Table 3 and the bcc structure Table 4. The Debye temperature for metals (Ni, Fe, Hf) was calculated using the same method. From the examples given, Hf has an hcp lattice. The calculated values of the elastic modulus and lattice parameter are consistent with experiment (the maximum difference between the calculated and experimental data is less than 7.3%) [5]. The elastic modulus for materials with a cubic crystal lattice is isotropic along the crystallographic directions (001) (along the x, y, z axes). To calculate the modulus of elasticity with an hcp lattice of Hf or TiB₂, we assign these materials a cubic lattice, keeping the volume of the unit cell per two atoms for Hf or 3 in the case of TiB₂. This approximation makes it possible to calculate the modulus of elasticity along the coordinate axes and obtain good results for the Debye temperature. The calculated values of the speed of sound and Debye temperature for pure metals are consistent with the tabular data.

Table 3: Calculated values of the lattice parameter, elastic modulus, speed of sound and Debye temperature for metals and multi-element metal alloys with fcc crystal lattice.

	a, nm		E, GPa			s, m/c	θ_D , K	
	Theory	[13].	Theory	[13]	[1]			
Ni	0,3530	0,3524	201,5	199		4960 (4970) [8]	389,0	(375)[8]
NiCo	0,3535	0,35345	217,9	217	216	4953	376,4	
NiCoCr	0,3561	0,3559	227,8	226	235	5233	399,6	
NiCoCrFe	0,3571	0,35719	215,3	215	214	7150	546,2	
NiCoCrFeMn	0,3602	0,3599	202,4	202		7088	541,3	

Table 4: Calculated values of the lattice parameter, elastic modulus, sound speed and Debye temperature of metals and metal alloys with a bcc crystal lattice.

	a, nm		E, GPa		s, m/c	θ_D , K	
	Theory	[14]	Theory	[14]			
Fe	0,2865	0,2861	200	(210) [8]	5035 (4910) [8]	520	(464) [8]
Hf	0,3544	0,3542	140	(136) [8]	3240	271	(252) [8]
TZrVNbTa	0,3317	0,3304	123	117	3870	341	
WNbMoTaV	0,3197	0,3205	180	176	3830	354	
TiZrVNbTaMo	0,3338	0,3340	157	135	4370	388	
TZrVNbHf	0,3401	0,3358	98	86	3540	308	

Table 5: Calculated values of the lattice parameter, elastic modulus, sound speed and Debye temperature of carbides and borides.

	a, nm		E, GPa		s, m/s	θ_D , K	
	Theory	[8]	Theory	[8]		Theory	[8]
Diamond	0,3563	0,3572	1100	900-1000	15110	2480	2200-2460
SiC	0,3619	0,3615	400	380	10893	1468	1200-1430
TiC	0,4329	0,4327	500	494	989	755	590
TiB ₂	0,3018;	0,3023;	605,8	540-550 [15]	1160	2312	-
	0,3245	0,3220					
ZrB ₂	0,3210;	0,3150;	530,86	430-495 [15]	933	1750	-
	0,3550	0,3530					
LaB ₆	0,4177	0,4153	495,64	487 [15]	1024	1449	-

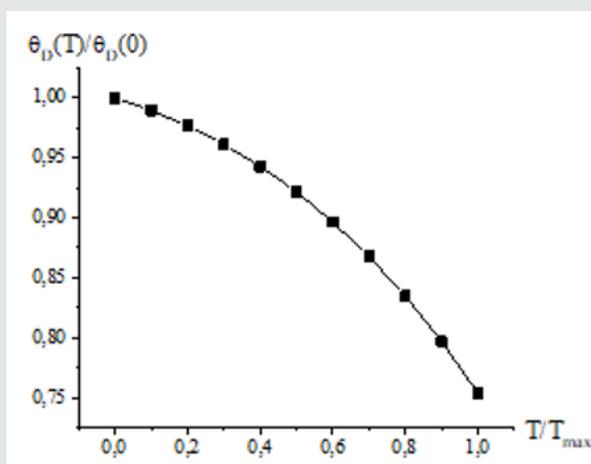
Debye temperature depends on temperature through the elastic modulus and lattice parameter (formulas 5-9). The calculated data Tables 3,4,5 refer to the temperature $T = 0$ K. The temperature dependence of the Debye parameter can be represented as:

$$k_B \theta_D = h \cdot s(T) \cdot q_{\max}(T) \quad (10)$$

or, taking into account the temperature dependence of the elastic moduli [15] and the coefficient of thermal expansion, we have:

$$\theta_D(T) = \theta_D(0) \sqrt{1 - 0,2 \frac{T}{T_{\max}} - 0,24 \left(\frac{T}{T_{\max}}\right)^2} \sqrt{1 + 0,032 \left(\frac{T}{T_{\max}}\right)^4} \quad (11)$$

The calculation results are presented in (Figure 2). The temperature dependence of the Debye parameter depends on two competing factors arising, respectively, on Young's modulus and lattice parameter. If the first factor decreases rapidly with increasing temperature, then the second factor slowly increases. Based on the results of our calculations of the temperature dependence of the Debye parameter (in the first approximation), only the temperature change in Young's modulus can be considered.

**Figure 2:** Debye relative temperature $\theta_D(T)/\theta_D(0)$ versus T/T_{\max} .

Summary

The coefficient of linear thermal expansion of metals, metal multielement alloys, borides and eutectic boride-boride systems calculated from first principles (using the method of pseudopotentials and quasi-harmonic approximation) is presented in an analytical form depending on the melting point. With the help of the obtained formula, bypassing complex quantum-mechanical calculations, it becomes possible to estimate the CLTE for the family of the mentioned materials. From ab initio calculations, a formula

was obtained that describes the temperature dependence of the relative Debye temperature $\theta_D(T)/\theta_D(0)$ on T/T_{\max} for different classes of materials.

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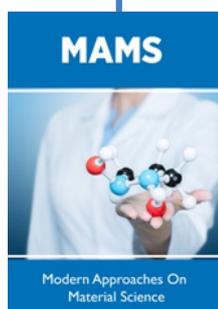
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