Semi-empirical evaluation of linear coefficient of thermal expansion of metals

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Abstract. The paper considers various semi-empirical methods of the linear coefficient of thermal expansion (CTE), $\alpha$, calculation. Debye-Grüneisen model was used as a basis and adjusted by taking account of thermodynamic (molar heat capacity, enthalpy) and elastic (Young, bulk, and shear moduli, Poison ratio) characteristics of metals. The formulas for numerical calculations of CTE are derived using: (1) elastic longitudinal modulus, (2) microscopic constants, and (3) enthalpy. CTE were calculated for 25 metals, Ge and Si, and five hexagonal single-crystals in directions perpendicular and parallel to the principle crystallographic axis. Theoretical values of $\alpha$ show good agreement with the experimental ones.

1. Introduction

Modern materials, including metals and alloys, are to operate in a wide temperature range. In this regard, their properties stability, determined by the fundamental physical property, the linear coefficient of thermal expansion (CTE), $\alpha$, is of particular importance. As mentioned in [1, 2], the problem of calculating the of thermal expansion based on an accurate calculation of potential energy from first principles is challenging. CTE evaluation is a complex task, but it can be performed based on measurements of the ultrasound velocity, i.e. longitudinal and transverse frequencies of the lattice modes, from which all the elastic characteristics (Young, bulk, and shear moduli) are then calculated. Using elastic constants we can estimate thermodynamic ones [4-8] and evaluate CTE via proposed empirical formulas. Several semi-empirical approaches for calculating the linear coefficient of thermal expansion of metals are proposed in the paper.

2. Theoretical aspects

In [3] we had proposed formula (1), based on the Grüneisen equation [4] and taking into account the interdependence of elastic constants, for calculation of the linear coefficient of thermal expansion, $\alpha$:

$$
\alpha = \frac{1}{2} \frac{(1-2\mu)C_v}{(1+\mu)GV} \gamma 
$$

(1)
where $V$ is the volume of solid, $G$ is the shear modulus, $C_V$ is the molar heat capacity at the constant volume, $\mu$ is the Poisson ratio, and $\gamma$ is the Grüneisen constant.

If we consider thermal expansion (compression) as a reversible thermal elastic process of changing the volume (and the length) of a solid, then for polycrystalline solids, we can write the equation for CTE as follows:

$$\alpha = \frac{1}{2} \frac{C_V}{E_l} \gamma'$$

where $E_l$ is the elastic longitudinal modulus, defined as $E_l = B + 4/3G$ ($B$ is bulk modulus); the coefficient $\gamma'$ is close to $\gamma$ (the Grüneisen constant), but not always equal to it; here $\gamma'$ is expressed as $\gamma' = (1 + n\mu)$, where $\mu$ is the Poisson's ratio reflecting the ratio of transverse and longitudinal elastic strains, and $n = 0, 1, 2, 3$. Let us denote the energy of the elastic wave as $e_l = E_l \cdot V$, whereby one can calculate the binding energy $E_B$ as it was shown in [5]. The values of linear coefficients of thermal expansion, $\alpha$, calculated according to formulas (1) and (2), in comparison with theoretical ones are listed in Table 1.

Note, that equation (2) is universal it applies to the calculation of the thermal expansion of single crystals, it can be written through microscopic constants as follows:

$$\alpha = \frac{1}{2} \frac{C_V}{c_{l_{ij}}V} \gamma'$$

where $c_{l_{ij}}$ is the longitudinal elastic modulus along the directions in the crystal; $\mu$, as shown in [7 6], can be expressed as:

$$\mu = \frac{c_{12}}{c_{l_{ij}} + c_{12}}$$

Equation (4) gives fairly accurate results, comparable with a similar values for polycrystals. The calculated values of $\alpha$ for five hexagonal single crystals in directions perpendicular and parallel to the crystallographic main axis are listed in Table 2.

Underneath we give another approach to the problem - we express $\alpha$ in terms of the binding energy and the energy of a longitudinal elastic wave as follows:

$$\alpha = \nu \cdot C_V \left( \frac{1}{e_l \cdot E_B} \right)^{1/2}$$

where $e_l = E_l \cdot V$ ($E_l$ is the longitudinal elastic modulus of polycrystals), $E_B$ is the binding energy, multiplying factor $\nu$ possess values from 0.4 to 0.5 for metals. It was estimated was that $\nu$ corresponds to the relaxed Poisson's ratio, $\mu_m$, that can be evaluated according the McLaren empirical formula at the critical point (melting, as well as, polymorphic and martensitic transition point) [5-8]:

$$\mu_m \equiv 0.83\mu_0 + 0.14$$

From equations (2) and (5), the significant consequence follows that $\alpha$ inversely as the square root of the product of the energy of the longitudinal elastic wave by the binding energy multiplied by the Poisson's ratio relaxed to $T_m$, and for $\mu_m = 0.5\gamma'$ $\alpha$ directly depends on the square root of this relation. Such an expression for $\gamma'$ justifies the empirical coefficients in Tables 2 and 3, and the coefficient $\nu$ in equation (5) acts as the relaxation coefficient.
We note that the binding energy $E_B$ itself can be expressed in terms of the kinetic energy of a longitudinal elastic wave relaxed to $T_m$, as was shown in [5], and the equations of this work are suitable for both metals and covalent crystals, i.e. have a universal character.

We will try to give CTE thermodynamic calculation directly from the expression for internal energy. As noted, the problem of accurate evaluation of $\alpha$ quantity (and not its order) by decomposing the potential energy has not yet been successful. Earlier [8, 9] we use the Einstein equation for free energy, that includes static compression (or expansion) energy, to calculated the relative elongation values of metals. According to (7), one can write the total internal energy, including static compression energy, as follows:

$$u = E_v + \frac{\Delta V^2}{2\chi V}$$

where $\chi$ is the compressibility, $\Delta V = VT + V_0$, and $E_v$ is the energy of the three-dimensional oscillator. $E_v$ is calculated according to equation (8):

$$E_v = E_0 + \frac{3Nh\nu}{e^{\frac{kT}{h\nu}} - 1}$$

We deduce (9) from equation (7) while substituting the bulk compression modulus:

$$\beta = \frac{1}{T} \frac{2(u - E_v)}{BN\Delta V}$$

Since by the condition $u > E_v$, the sign of the coefficient $\beta$ will depend on whether the volume increases or decreases during heating. To calculate the quantity $\alpha$, tentatively let $u$ be the thermal enthalpy (heat content) $H_T$, which tends to zero as $T \rightarrow 0$, we also transform the second term of equation (8), multiplying the numerator and denominator by $V_0$, and thus we have:

$$\alpha = \frac{1}{3T} \left( \frac{2(H_T - E_v)}{BV_0} \right)^{1/2}$$

We denote the difference $(H_T - E_v)$ by $e_{\beta}$ - the energy required to change the volume during heating by 1 K (equations (9) and (10)). We put in equation (8) for the second term of the thermal part of the energy $\nu = \nu$, rel. The first term (zero energy) is calculated taking into account the work of Pippard on anharmonic vibrators [10] as follows:

$$E_0 = \left( 1 + \frac{1}{2} n \right) \frac{1}{2} h\nu_D$$

where $n$ can take values 0, 1, 2, 3.

The obtained results show satisfactory agreement between the calculated and experimental values of $\alpha$ at 300 K (and at high temperatures for copper), see Table 3. The enthalpy $H_T$ is taken from [11], and the quantities $\Theta_D$ and $\Theta_{rel}$ are calculated from elastic constants at room temperature.

### 3. Practical Implementation

Table 1 shows the calculated values of $\alpha$ according the equations (1) (proposed in [3]) and (2). The agreement between the calculated and the experimental values is satisfactory, except for Ir and Re, for which $\alpha_{calc}$ significantly less than $\alpha_{exp}$, this is probably due to a strong effect of impurities on CTE that was noted for these two metals [12]. The remarkable thing is that our semi-empirical approach results fit better the experimental ones than that derived from the first principles [2].
Table 1. Thermodynamic and elastic characteristics of 25 metals, germanium and silicon, and the calculated values of the coefficient of thermal expansion ($\alpha_{\text{calc}}$) in comparison with experimental ones ($\alpha_{\text{exp}}$).\(^a\)

| Element | $\alpha_{\text{exp}}$ | $\alpha_{\text{calc}}$ | $\alpha_{\text{calc},\perp}$ |
|---------|----------------------|------------------------|-----------------------------|
| Li      | 3.55                | 3.41                  | 13.63                       |
| Na      | 1.20                | 1.08                  | 7.21                        |
| K       | 0.74                | 0.63                  | 3.99                        |
| V       | 0.48                | 0.47                  | 155.87                      |
| Nb      | 0.26                | 0.25                  | 187.5                       |
| Ta      | 0.137               | 0.136                 | 206.1                       |
| Mo      | 0.250               | 0.248                 | 285.2                       |
| W       | 0.132               | 0.131                 | 338.3                       |
| Fe\(^b\) | 0.447           | 0.421                 | 173.1                       |
| Ca      | 0.63                | 0.612                 | 16.6                        |
| Ni\(^b\) | 0.44               | 0.400                 | 186.5                       |
| Cu      | 0.384               | 0.373                 | 137.2                       |
| Ag      | 0.235               | 0.226                 | 100.1                       |
| Au      | 0.131               | 0.126                 | 172.1                       |
| Al      | 0.913               | 0.883                 | 76.4                        |
| Pb      | 0.128               | 0.120                 | 40.37                       |
| Pd      | 0.240               | 0.230                 | 192.3                       |
| Pt      | 0.130               | 0.126                 | 274.8                       |
| Ir      | 0.126               | 0.125                 | 370.2                       |
| Be\(^b\) | 1.983           | 1.916                 | 125.8                       |
| Mg      | 1.020               | 0.989                 | 33.26                       |
| Re      | 0.130               | 0.128                 | 363.33                      |
| Ti\(^b\) | 0.520           | 0.503                 | 123.56                      |
| Zn      | 0.389               | 0.373                 | 58.39                       |
| Cd      | 0.231               | 0.220                 | 43.6                        |
| Si\(^b\) | 0.705           | 0.702                 | 98.1                        |
| Ge      | 0.320               | 0.319                 | 75.4                        |

\(^a\) Notes are referenced using alpha superscripts.
\(^b\) $C_T$ and $C_V$ - in J/K.
\(^c\) $d$ - in GPa.
\(^d\) $\gamma$ - in $10^{-6}$ K$^{-1}$.
\(^e\) $\gamma_{\text{exp}}$ - experimental data from [12, 13].
\(^f\) $\gamma_{\text{calc}}$ - values of $\gamma$ calculated according to formula (1), from [3].
\(^g\) $\alpha_{\text{calc}}$ - calculated values of $\alpha$ from [2].

The results of CTE calculations for five hexagonal single crystals in directions perpendicular and parallel to the principal crystallographic axis, as well as the quantities $\gamma'_{\parallel}$ and $\gamma'_{\perp}$ (provided $c_{\perp} = c_{||}$, \(<100>\), and $c_{\perp} = c_{\perp\parallel}$, \(<100>\)) according to the formula (3) are given in Table 2. We note the satisfactory agreement between theoretical and experimental values of CTE.
Table 2. The calculated values of the CTE for hexagonal single crystals, at 300 K.a

| Element | $C_{ij}$ | $\gamma'|$ | $\alpha_{calc}|$ | $\alpha_{exp}|$ | $C_{ij}$ | $\gamma'|$ | $\alpha_{calc}|$ | $\alpha_{exp}|$ |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Be      | 307.5   | 1+3$\mu$ | 7.7     | 8.0     | 357.0   | 1       | 4.9     | 5.0     |
| Ti      | 162.4   | 1+$\mu$  | 9.5     | 9.6     | 180.7   | 1       | 6.3     | 5.7     |
| Mg      | 60.82   | 1+3$\mu$ | 25.9    | 24.7    | 63.8    | 1+3$\mu$| 24.8    | 26.8    |
| Zn$^b$  | 163.6   | 1+3$\mu$ | 13.8    | 13.2    | 63.5    | 1+2$\mu$| 61.3    | 63.5    |
| Cd$^e$  | 115.2   | 1+3$\mu$ | 19.6    | 19.6    | 51.19   | 1+2$\mu$| 56.0    | 54.0    |

Notes are referenced using alpha superscripts.

$^a$Notes are referenced using alpha superscripts.

$^b$C$\ell$ - in GPa.

$^c$-$\alpha$ - in $10^{-6}$ K$^{-1}$.

$^d$-$\alpha_{exp}|$ - from [12, 13].

$^e$-$\alpha$|$^*=\alpha$/2; for Zn and Cd 1/2 is omitted.

$^f$we take $E_l$ instead of $C_{||}$ for Cd.

The theoretical values of $\alpha$, calculated according the equation (10), show the satisfactory agreement with experimental ones. For Cu we can note agreement both at 300 and at 200 K (copper), see Table 3. We use the values of enthalpy $H_T$ from [11, 12], and calculate the quantities of $\Theta_D$ and $\Theta_t$ from the elastic constants at room temperature.

Table 3. The results of CTE, $\alpha$, calculations using the enthalpy equation (10), at 300 K.a

| $\Xi\alpha$-T | $H^c$ | $\Theta_D$ | $\Theta_{rel}$ | $B^d$ | $n$ | $\epsilon|B^c$ | $\alpha_{calc}|$ | $\alpha_{exp}|^{c,d}$ |
|--------------|-------|-----------|---------------|-------|----|-------------|----------------|----------------|
| Cu           | 7.076 | 330       | 238           | 137.0 | 1  | 0.112       | 16.85          | 16.75          |
| Cu$^b$       | 34.723| 200       | 184           | 100.8 | 1  | 3.273       | 24.0           | 24.60          |
| Ag           | 6.768 | 215       | 154           | 100.1 | 0  | 0.153       | 19.1           | 18.9           |
| Au           | 7.341 | 140       | 100           | 172.1 | 1  | 0.158       | 14.9           | 14.0           |
| Pb           | 7.669 | 90        | 49            | 40.37 | 1  | 0.219       | 27.0           | 28.5           |
| Ti           | 7.815 | 385       | 270           | 123.56| 1  | 0.419       | 8.8            | 8.3            |
| K            | 8.173 | 92        | 69            | 3.993 | 3  | 0.555       | 87.0           | 83.3           |
| Nb           | 7.284 | 286       | 180           | 187.5 | 1  | 0.368       | 6.7            | 7.2            |

Notes are referenced using alpha superscripts.

$^a$Notes are referenced using alpha superscripts.

$^b$Cu at 200 K.

$^c$H$T$ and $\epsilon^B$ - in J/gr-mol.

$^d$B - in GPa.

$^e$-$\alpha$ - $10^{-6}$ grad$^{-1}$.

$^f$-$\alpha_{exp}$ - from [12, 13].

4. Conclusions
We propose new semi-empirical methods for calculating the thermal expansion coefficient using the thermodynamic and elastic characteristics of metals. The calculation results are in good agreement with experimental data.

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