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# Assessment of thermal expansion coefficient for pure metals

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ABSTRACT

In this paper, thermal expansion coefficients of 42 pure metallic elements were evaluated on the basis of empirical and theoretical methods and the adjusted Debye–Grüneisen model. In Debye–Grüneisen model, Debye temperature was regarded as an undetermined constant. Parameters in the model were determined via the nonlinear least square fit method through MATLAB program. Besides, for pure metallic elements with phase transition, segment fitting can be realized and the computational results fit experimental data well; meanwhile, reliable forecast for high-temperature or low-temperature thermal expansion can be provided, and a set of average Debye temperatures based on thermal expansion coefficients have been obtained.





## Q4 1. Introduction

Thermal expansion is the basic physical property. It has great theoretical and practical value to study the law of thermal expansion coefficients that indicate the thermal property of new alloys [1]. Over the past century, large amounts of experimental information on thermal expansion have been accumulated and sometimes reviewed.

Debye–Grüneisen model was adjusted in this paper by treating Debye temperature $\Theta_D$ (limit Debye temperature of 0 K is taken for $\Theta_D$) in the Debye–Grüneisen model as undetermined constant to evaluate 42 metallic elements on the basis of the nonlinear least square method through MATLAB program to correctly describe the thermal expansion coefficient.

Evaluation methods for thermal expansion: (1) the empirical model. Empirical models include polynomial or spline polynomial functions of temperature [2–4]. These expressions are sensitive to the order of the polynomial and unfortunately the coefficients have no physical meaning. Therefore, such functions are not appropriate for predicting or extrapolating the expansion to temperatures that are outside the range of measurement. Lu et al. [5] adopted the method of empirical formula to estimate thermal expansion of pure metallic elements in bcc, fcc and hcp structures, systematically and comprehensively fitted the thermal expansion curves via a large number of data through the CALPHAD method, and gained satisfying results; however, they have not estimated data below room temperature. (2) The theoretical model. These approaches utilize the lattice dynamics or equation of state considerations to represent the thermal expansion. Coefficients for these approaches are usually determined by least-square fitting of the experimental data. Such fitting coefficients, with reliable experiments, do have real physical significance and thus should provide more reliable high temperature thermal expansion predictions [6]. Nix and Macnair [7,8] adopted Debye–Grüneisen equation to estimate thermal expansion of metals including thermal expansion coefficients below room temperature, and obtained satisfying fitted curves, but only with few estimated elements; moreover. The limit Debye temperature of 0 K was adopted as Debye temperature in the Debye–Grüneisen model, but actually Debye temperature is a variable [9] and the authors also mentioned that better fitted curve could be obtained by changing Debye temperature. However, they did not realize it from algorithm.

## 2. Theoretical methods

An approximate relation between the coefficient of volume expansion and the temperature is given by Grüneisen's equation [4]

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{1}$$

$$\beta = \frac{C_V}{Q_0[1-k(U/Q_0)]^2} \tag{2}$$

where $C_V$ is the molar heat capacity at constant volume, $U$ is the energy of the lattice vibrations, and $Q_0$ and $k$ are constants. If the Debye temperature $\Theta_D$ is known, both $C_V$ and $U$ may be calculated at any temperature $T$ from the equations

$$C_V = 3R\left[12\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{y^3\,dy}{e^y-1} - 3\frac{\Theta_D/T}{e^{\Theta_D/T}-1}\right] \tag{3}$$

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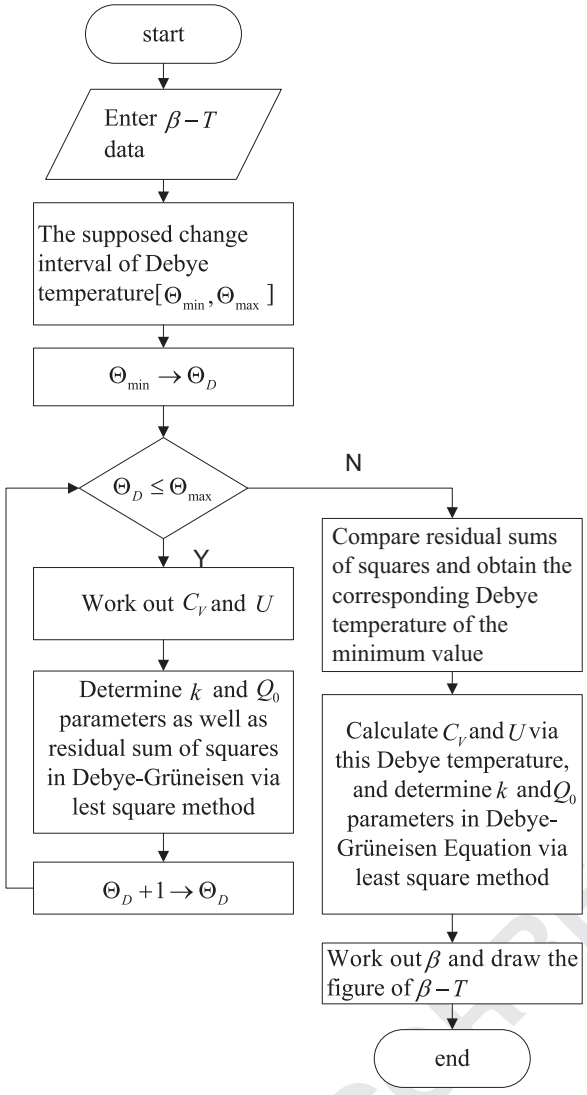


**Fig. 1.** Program flowchart of assessment process of thermal expansion coefficient.

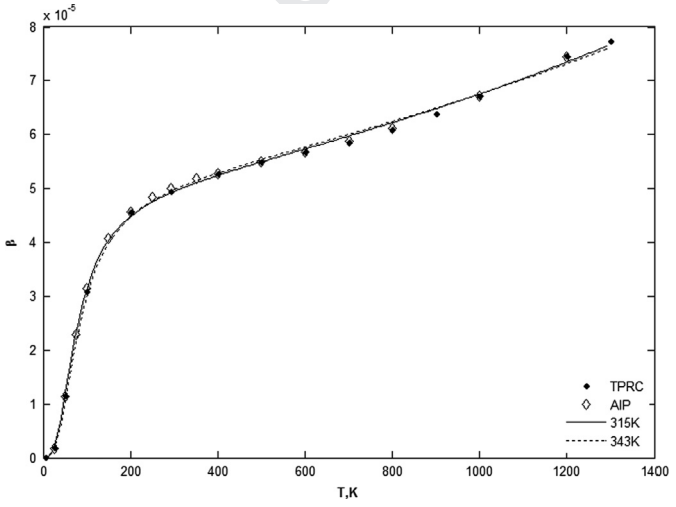


**Fig. 2.** Comparison between volume expansion coefficients and experimental values fitted under the 0 K limit Debye temperature and the average Debye temperature of Cu.

$$U = \int_0^T C_V \, dT \tag{4}$$

## 3. Calculation process

Data of thermal expansion coefficients evaluated in this paper come from two manuals which are TPRC and AIP [10]. In the TPRC data series, Touloukianet et al. [2] have collected and tabulated major experimental investigations before 1973, and listed recommended values of the macroscopic linear expansion and linear thermal expansion up to the melting points of the materials concerned. Other

**Table 1**
Comparison of residual sum of squares between the 0 K limit Debye temperature and the average Debye temperature of Cu.

| Debye temperature of Cu | RESNORM |
|---|---|
| 343 K (0 K limit Debye temperature $\Theta_D$ of Cu) | 34.7086 |
| 315 K (average Debye temperature $\overline{\Theta}$ of Cu) | 14.4343 |

**Table 2**
Assessed parameters in Eq. (2) for thermal expansion coefficient.

| Element | Structure | $k$ | $Q_0$ (kJ/mol) | $\overline{\Theta}$ (K) | $\Theta_D$ (K) |
|---|---|---|---|---|---|
| Ag | fcc | 3.6897 | 472.6139 | 214 | 225 |
| Al | fcc | 4.4516 | 379.106 | 367 | 428 |
| Au | fcc | 4.6685 | 639.1281 | 161 | 165 |
| Be | hcp | 2.618 | 476.6529 | 957 | 1440 |
| Bi | hcp | 0.0866 | 633.1196 | 121 | 119 |
| Ca | fcc | 1.7932 | 386.3696 | 231 | 230 |
| Cd | hcp | 3.7944 | 307.0226 | 112 | 209 |
| Co | hcp | 4.6481 | 624.3493 | 388 | 445 |
| Co | fcc | 2.2879 | 625.7783 | 385 | 385 |
| Cr | bcc | 7.9455 | 971.7697 | 750 | 630 |
| Cu | fcc | 3.5344 | 511.9897 | 315 | 343 |
| Fe | bcc | 0.2853 | 608.3791 | 488 | 470 |
| Fe | fcc | 0.2061 | 340.6442 | 420 | 420 |
| Ge | fcc | 5.0997 | 1286.255 | 515 | 374 |
| Hf | hcp | 8.5687 | 1477.475 | 160 | 252 |
| In | hcp | 8.9887 | 354.3489 | 109 | 108 |
| Ir | fcc | 7.4105 | 1308.14 | 287 | 420 |
| Li | bcc | 2.674 | 181.0102 | 434 | 344 |
| Mg | hcp | 4.0105 | 356.7582 | 307 | 400 |
| Mn | bcc | 6.4731 | 389.7182 | 490 | 410 |
| Mo | bcc | 14.0361 | 1958.922 | 219 | 450 |
| Na | bcc | 0.9866 | 121.1927 | 300 | 158 |
| Nb | bcc | 3.1596 | 1115.179 | 307 | 275 |
| Ni | fcc | 2.7276 | 578.1584 | 440 | 450 |
| Os | hcp | 5.5187 | 1610.491 | 250 | 500 |
| Pb | fcc | 3.6917 | 332.0544 | 89 | 105 |
| Pd | fcc | 4.2628 | 720.8621 | 283 | 274 |
| Pt | fcc | 5.1792 | 976.3254 | 226 | 240 |
| Re | hcp | 3.797 | 1306.291 | 315 | 430 |
| Rh | fcc | 7.3312 | 981.3101 | 224 | 480 |
| Ru | hcp | 9.2628 | 1302.515 | 234 | 600 |
| Sb | hcp | 2.1217 | 768.8687 | 183 | 211 |
| Sc | hcp | 3.6194 | 792.7256 | 476 | 360 |
| Si | fcc | 2.2038 | 1887.789 | 1101 | 645 |
| Sn | hcp | 8.5492 | 469.0371 | 164 | 200 |
| Ta | bcc | 11.0824 | 1653.603 | 158 | 240 |
| Th | fcc | 4.6252 | 782.6518 | 163 | 163 |
| Ti | hcp | 4.7097 | 898.7748 | 422 | 420 |
| Ti | bcc | 6.8934 | 1074.047 | 300 | 300 |
| V | bcc | 5.9149 | 946.3259 | 395 | 380 |
| W | bcc | 9.2307 | 2027.944 | 291 | 400 |
| Y | hcp | 3.9089 | 816.8919 | 275 | 280 |
| Yb | bcc | 3.2559 | 368.0229 | 195 | 120 |
| Zn | hcp | 1.7497 | 291.5521 | 181 | 327 |
| Zr | hcp | 10.4648 | 1460.968 | 286 | 291 |
| Zr | bcc | 6.6146 | 1240.919 | 212 | 212 |



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