Transactions of Materials Research 1 (2025) 100015

Contents lists available at ScienceDirect

Transactions of Materials Research

journal homepage: www.sciencedirect.com/journal/transactions-of-materials-research

Prediction of thermal expansion of solids in wide temperature range by heat capacity

Meibo Tang, Xiuhong Pan, Weijie Deng, Kun Chen, Huan He, Jinghong Fang, Jinqi Ni, Xuechao Liu *

State Key Laboratory of Functional Crystals and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 201899, China

ARTICLE INFO

Keywords:
Thermal expansion
Heat capacity
Thermal property

ABSTRACT

We employ the unified heat capacity model to predict thermal expansion in the temperature range from several Kelvin to melting temperature. A generic method is first established to get thermal expansion only by the experimental heat capacity in a series of materials, which is well in agreement with the experimental results of thermal expansion. The method is important to predict the temperature-dependent thermal expansion, and is helpful for further understanding the physical nature of thermal properties in solids.

1. Introduction

The temperature (T) dependent volumetric thermal expansion β (or volume V) is an important property of materials in applications, and is also of interest theoretically and experimentally [1–6]. In solid state physics, thermal expansion originates from the anharmonic energy, which results in a greater average separation between atoms when the temperature increases [3]. The coefficient of volumetric thermal expansion β of materials is very low, usually in the order of 10^{-5} K^{-1} at room temperature. Thus, accurate data of thermal expansion in wide temperature range is often scarce because of experimental difficulties. The uncertainty of experimental thermal expansion β at high temperatures (above 1000 K) is especially large.

Due to the difficulty of accurate thermal expansion' measurement, reliable semiempirical or theoretical models are developed to evaluate or predict thermal expansion, especially at high temperatures [7]. Correlations between different properties of materials has always been of practical interest, and also is an important method to predict thermal expansion by other physical properties. For example, Garai calculated the thermal expansion in metals by the linear correlation between thermal expansion and heat capacity [8]. Wang et al. predicted the high temperature thermal expansion of NaCl by the feature of βKV (K: isothermal bulk modulus) [9]. Digilov evaluated the temperature-dependent thermal expansion in some solids by lambert function [10]. Inaba estimated the thermal expansion in fluorite-type compounds using the Morse potential and Debye model [11]. Lu et al. evaluated the thermal expansion in transition cubic metals by Calphad method which is based on the Debye-Gruneisen model [12]. Drebushchak et al. calculated the thermal expansion by Lennard-Jones potential and thermodynamic equation [13]. The theoretical models play a central role in describing the high temperature thermal expansion in solids. The empirical models or methods reported so far are complex and are inadequate for predicting thermal expansion of general materials in a wide temperature range. Therefore, theoretical prediction of temperature-dependent thermal expansion in general materials is still of challenge.

Recently, the studies show that there is universal correlation between thermal expansion and heat capacity C_p in a series of reference materials [14,15]. A new heat capacity model was developed, and it well explained the behavior of heat capacity in temperature range from 0 K to melting temperature [16]. In the new model, heat capacity below melting temperature can be expressed as [17].

$$C_p = 1.5Rf_D + E\beta, \tag{1}$$

where R is the gas constant, E is the volume-energy constant, and f_D is Debye function. The total heat capacity C_p includes two parts: the kinetic heat capacity $1.5Rf_D$ and potential heat capacity $E\beta$. There are only two parameters: constant E and Debye temperature θ in Eq. (1). The parameters E and θ are dependent on the compositions of a matter, and can remain unchanged at different temperatures, even at different states (for example, solid state, liquid state, supercooled liquid state, and disordered glass state) [18].

When the temperature-independent parameters E and θ in materials are known, thermal expansion can be directly obtained by the

* Corresponding author.
E-mail address: xcliu@mail.sic.ac.cn (X. Liu).

https://doi.org/10.1016/j.tramat.2025.100015
Received 26 March 2025; Received in revised form 7 April 2025; Accepted 7 April 2025
Available online 9 April 2025

experimental heat capacity in Eq. (1). So thermal expansion can be directly predicted only by heat capacity. Debye temperature is studied widely, and can be determined by different experimental methods. The parameter E in the model is difficultly determined by other experimental results. If the value of thermal expansion at room temperature is known, the temperature-independent parameter E can be approximately determined by the heat capacity and thermal expansion at room temperature.

In this work, we calculate thermal expansion of a series of solid materials only by experimental heat capacity in a wide temperature range from 0 K to melting temperature. The calculated thermal expansions by Eq. (1) are well consistent with the experimental data in the reference solid materials and other solid materials. The method is important to get thermal expansion for general materials in applications and helpful to further understand the volume effect on heat capacity.

2. Collating and analyzing experimental data

The experimental data in a series of solid materials are surveyed. The investigated materials contain metals (W, Ta, Mo, Pt, Be, Cu, Al, Ag, and Au), chemical compounds (Al_2O_3, MgO, and KCl). The heat capacity data of Ag are from Ref. [19], Au from Ref. [20], and KCl from Ref. [21]. The heat capacity data of other materials are from Ref. [14].

Fig. 1 shows the temperature-dependent heat capacity below melting temperature in the reference solid material Cu. The experimental results of heat capacity are exhibited by blue half-filled dots. Debye temperatures θ is determined with two methods. First, when the experimental heat capacity is equal to $1.5R$, the corresponding temperature is equal to 0.2488θ. Thus, Debye temperature of Cu is about 313.2 K at $C_p = 1.5R$. Secondly, the experimental data of heat capacity below $3R$ and thermal expansion can also determine the parameters E and θ (303.7 K for Cu) by Eq. (1). The calculated heat capacity below melting temperature by $3Rf_D$ with different Debye temperatures θ is also shown in Fig. 1 (black solid line for $\theta = 313.2$ K, and red solid line for $\theta = 303.7$ K). The values of Debye temperature by different methods are similar. Hence the calculated heat capacities with the different θ are similar (the black solid line is close to the red solid line). Below about 200 K, the calculated heat capacity is well close to the experimental heat capacity. At high temperatures, the calculated heat capacity $3Rf_D$ deviates from the experimental heat capacity. The higher the temperature is, the larger the difference between the experimental and calculated heat capacity $3Rf_D$ is.

When Debye temperature is determined at $C_p = 1.5R$ ($\theta = 313.2$ K for Cu, 940.1 K for Al_2O_3), the kinetic heat capacity $1.5Rf_D$ below melting temperature can be calculated. Heat capacity and thermal expansion can be accurately measured at room temperature (300 K). Therefore, by Eq. (1), the parameter E in potential heat capacity $E\beta$ can be calculated by the experimental thermal expansion and heat capacity at room temperature [C_p(300 K) = 25.17 J/mol/K for Cu, 17.14 J/mol/K for Al_2O_3; $1.5Rf_D$(300 K) = 11.83 J/mol/K for Cu, 8.08 J/mol/K for Al_2O_3; β(300 K) = 50.1 K^{-1} for Cu, 16.94 K^{-1} for Al_2O_3; mol: g-atom]. Because the parameter E in a material is a constant, the E in Eq. (1) can be approximately obtained by the experimental results at room temperature. If the thermal expansion at low temperatures is known, we can also fit the experimental thermal expansion and heat capacity at low temperatures by Eq. (1), and get the parameters θ and E ($\theta = 303.7$ K for Cu, 870.6 K for Al_2O_3; E = 0.2504 MJ/mol for Cu, 0.4211 MJ/mol for Al_2O_3). The temperature-dependent thermal expansion below melting temperature in the reference solid materials of Cu and Al_2O_3 are exhibited in Fig. 2. The experimental results of thermal expansion are shown by black dots. The calculated thermal expansion with different parameters is shown by solid lines. The calculated thermal expansion by the parameter at $C_p = 1.5R$ is close to the experimental thermal expansion of both of the reference materials in the temperature range from 0 K to melting temperature. In Al_2O_3, calculated heat capacity by low temperature thermal expansion and heat capacity slightly deviates from the experimental values at high temperatures. As a whole, the calculated thermal expansions in the reference materials Cu and Al_2O_3 are consistent with the experimental values, especially below 300 K.

In the same way, Debye temperature is determined at $C_p = 1.5R$ and the temperature-independent parameter E is determined by the experimental values at room temperature in the materials (W, Ta, Mo, Pt, MgO, Be, and Al). Fig. 3 shows the experimental and calculated thermal expansion below melting temperature in the solid materials (half-filled dots: the experimental results; solid lines: calculated thermal expansion β below melting temperature through heat capacity C_p). Below about 2000 K, the calculated thermal expansion is well consistent with the experimental thermal expansion in the investigated materials (except Be), especially below 300 K. Above 2000 K, the calculated thermal expansion is larger than the experimental thermal expansion in the materials W, Ta, and Mo, which may be due to the large uncertainty of both the thermal expansion and heat capacity at high temperatures. As a whole, the calculated thermal expansions in the reference materials are well consistent with the experimental data.

The thermal expansion and heat capacity of KCl are obtained by statistical average and smoothing the many experimental data [21]. The recommended values exhibit trilinear behavior, which is different from

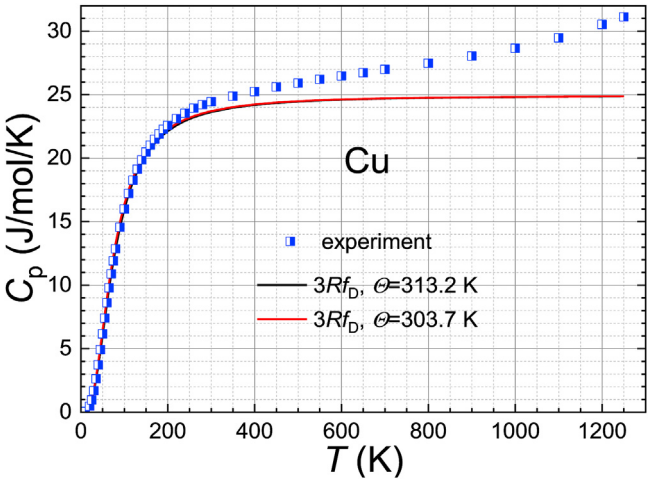

Fig. 1. Temperature-dependent heat capacity below melting temperature in the reference solid material of Cu. Blue half-filled dot: the experimental results; black and red solid lines: calculated heat capacity below melting temperature by $3Rf_D$ with different Debye temperatures θ.

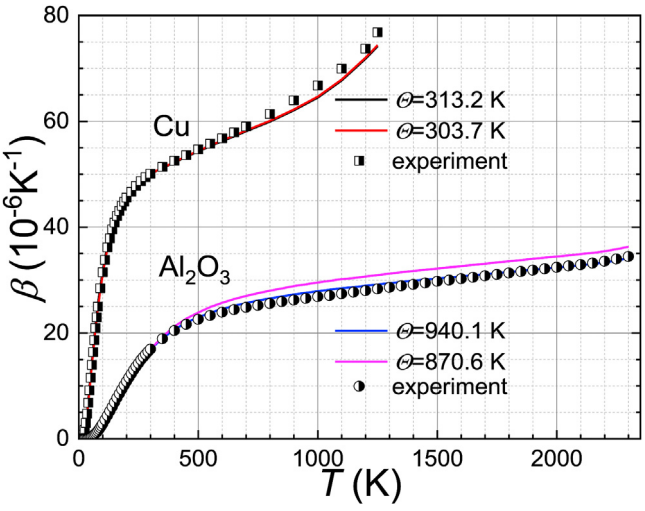

Fig. 2. Temperature-dependent thermal expansion below melting temperature in the reference solid materials Cu and Al_2O_3. Half-filled dots: the experimental results; solid lines: calculated thermal expansion β below melting temperature through heat capacity C_p.

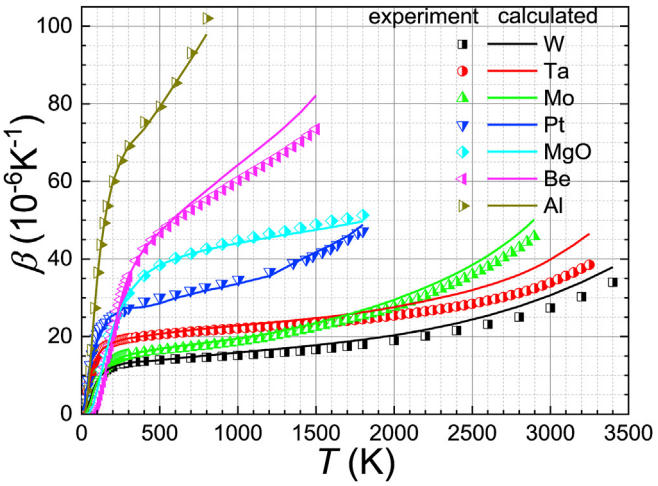

Fig. 3. Temperature-dependent thermal expansion below melting temperature in a series of reference solid materials. Half-filled dots: the experimental results; solid lines: calculated thermal expansion β below melting temperature through heat capacity C_p.

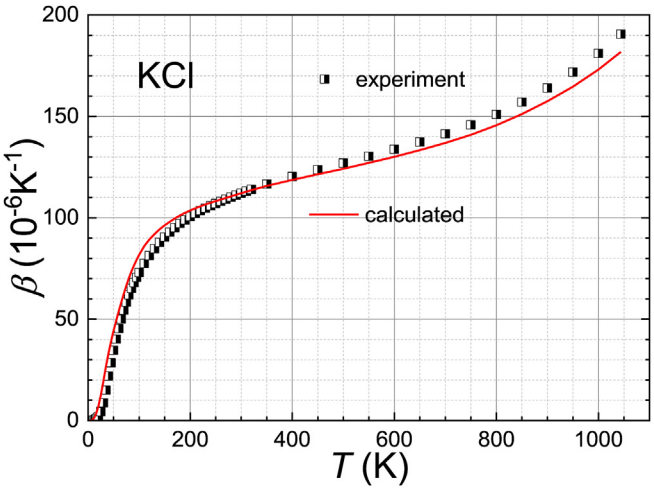

Fig. 4. Temperature-dependent thermal expansion below melting temperature in ionic solid KCl. Half-filled dots: the experimental results; solid line: calculated thermal expansion β below melting temperature through heat capacity C_p.

that in the reference materials (Cu, Al_2O_3, W, etc.). The thermal expansion versus heat capacity in KCl weakly deviates the linear behavior at low temperatures. We calculated thermal expansion with the same method in Fig. 3 by the recommended heat capacity of KCl. Fig. 4 exhibits the temperature-dependent thermal expansion below melting temperature in ionic solid KCl (half-filled dots: the experimental results; solid line: calculated thermal expansion). The calculated thermal expansion in KCl is slightly larger than the experimental values below 300 K, and is somewhat smaller than the experimental value above 300 K. Overall, the calculated thermal expansion of KCl in the wide temperature range is also close to the experimental data.

In our previously investigated materials, thermal expansion is known, and it is usually obtained by smoothing experimental data. To study the generality of Eq. (1), we select the materials only with sporadic data of thermal expansion: Ag and Au. The data of heat capacity is taken from Refs. [19,20]. Thermal expansion is calculated only by heat capacity (the temperature-independent parameter E is still calculated by the heat capacity and thermal expansion data at room temperature). Fig. 5 shows the calculated temperature-dependent thermal expansion below melting temperature in metal solids Ag (a) and Au (b), respectively (solid lines). The data of the experimental thermal expansion β below melting temperature (half-filled dots) in Ag (or Au) is taken from Refs. [22–30], and is not smoothed here. Like other materials, the calculated thermal expansion in Ag and Au is well consistent with experimental thermal expansion at low temperatures. The calculated thermal expansion lies between different experimental thermal expansions at high temperatures. The results further confirm that the calculated thermal expansion by the new model is reasonable and is consistent with the experimental results in the materials.

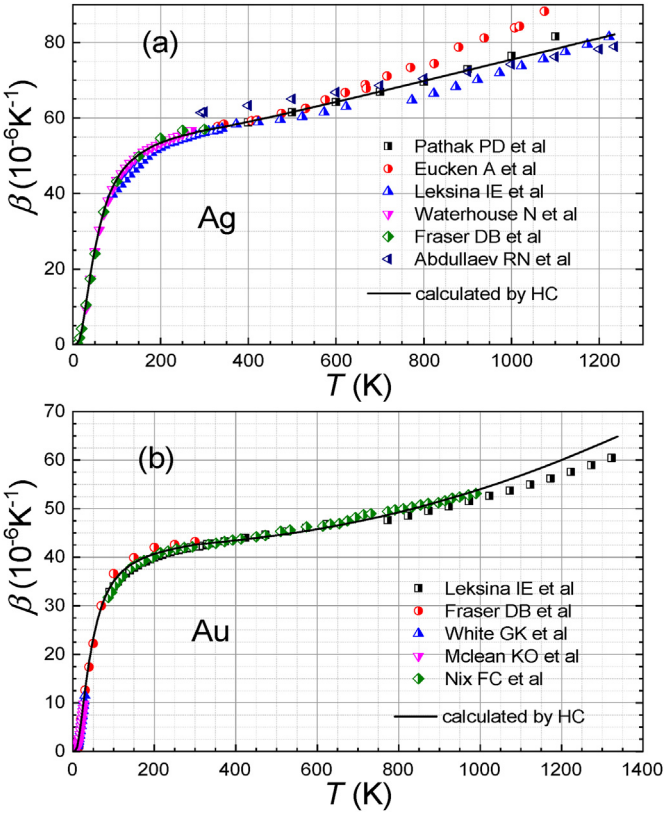

Fig. 5. Temperature-dependent thermal expansion below melting temperature in metal solids: (a) Ag and (b) Au. Half-filled dots: the experimental results; solid lines: calculated thermal expansion β below melting temperature through heat capacity C_p.

3. Discussion

There are two famous equations about both thermal expansion and heat capacity in thermodynamics. A well-known relationship between thermal expansion β and heat capacity is $C_p = C_v + KVT\beta^2$, where C_p is the constant-pressure heat capacity (or experimental heat capacity), C_v is the constant-volume heat capacity, and K is the isothermal bulk modulus. The relation is mainly used to explain the excess heat capacity due to anharmonic effect. Another relationship is suggested by Gruneisen: $C_v = KV\beta/\gamma$, where γ is the Gruneisen constant. The Gruneisen equation provides a direct correlation between the heat capacity and thermal expansion. Based on the two basic equations, some semiempirical or theoretical models are developed to predict thermal expansion in materials. There are two parameter K and γ, which are temperature-dependent. The models to explain the thermal expansion in special materials are extremely complex [10–12]. The empirical models or methods are inadequate for predicting thermal expansion of general materials in the entire temperature range.

According to the unified model based on many experimental results, heat capacity in matters is dependent on both of the temperature and thermal expansion (or volume). The correlation between thermal

expansion and heat capacity is not dependent on the states of matters (for example, crystalline state, glass state, or supercooled liquid, etc.). Thus, the temperature and volume are two important dimension parameters in the new model. Previous models are in single temperature dimension. At the same time, the temperature-volume relation under constant pressure is an important property to simply distinguish the phase transition kinds [18]. Therefore, the temperature-dependent volume (or thermal expansion) is a critical experimental data in the new model, and it affects the heat capacity. Equation (1) also shows a general correlation between thermal expansion and heat capacity in general materials. Only based on the experimental heat capacity in the wide temperature range, thermal expansion in the corresponding temperature range can be calculated by Eq. (1). In the investigated materials, the calculated thermal expansion by the new model in a wide temperature range is well consistent with the experimental results, which also confirms that the new model is reasonable in general materials. The experimental heat capacity can be usually measured accurately. Thereafter, the thermal expansion in general materials can be predicted accurately by the experimental heat capacity.

There are two parameters θ and E in Eq. (1), which affect the calculated results of thermal expansion. The physical meaning of parameters was discussed in Ref. [19]. When the parameters are determined, thermal expansion at any temperature can be obtained by heat capacity at the corresponding temperature. Thermal expansion is difficult to be accurately measured mainly at high temperatures. The experimental heat capacity can be accurately measured relatively. Then, according to Eq. (1), thermal expansion can be calculated simply and accurately. We have shown how to calculate thermal expansion by heat capacity in a wide temperature range. If there is the data of heat capacity only at high temperatures ($C_p > 3R$), we can set $f_D = 1$ (due to $f_D \sim 1$ when the temperature is higher than the Debye temperature or $C_p > 3R$), and calculate $E\beta$ by Eq. (1). The parameter E in materials is constant and can be gotten by other parameters (for example, cohesive energy) [17], or by reference data of thermal expansion. Thermal expansion at corresponding temperature range can be determined by Eq. (1). Therefore, Eq. (1) has either scientific significance or engineering application importance.

4. Conclusion

In summary, based on the general correlation between thermal expansion and heat capacity, the thermal expansion in a series of materials is calculated, and the results are well consistent with the experimental data in a wide temperature range. When heat capacity in a material is known, thermal expansion can be simply and accurately predicted by Eq. (1). Thus, the new method of determining thermal expansion of general materials in a wide temperature range has important scientific and engineering significance.

CRediT authorship contribution statement

Meibo Tang: Writing – original draft, Investigation, Conceptualization. **Xiuhong Pan:** Funding acquisition, Formal analysis. **Weijie Deng:** Formal analysis. **Kun Chen:** Formal analysis. **Huan He:** Funding acquisition, Formal analysis. **Jinghong Fang:** Formal analysis. **Jinqi Ni:** Formal analysis. **Xuechao Liu:** Funding acquisition, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The work is financially supported by the National Key Research and Development Program of China (2021YFA0716304), the Shanghai Science and Technology Innovation Action Plan Program (23DZ2201500), the Space Application System of China Manned Space Program (KJZ-YY-NCL403, KJZ-YY-NCL406, and KJZ-YY-NCL01), and the National Key Research and Development Program of China (2022YFF0504600).

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