

Correlation between thermal expansion and heat capacity

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Abstract

The theoretically predicted linear correlation between the volume coefficient of thermal expansion and the thermal heat capacity was investigated for highly symmetrical atomic arrangements. Normalizing the data on these thermodynamic parameters to the Debye temperature gives practically identical curves from zero kelvins to the Debye temperature. This result is consistent with the predicted linear correlation. At temperatures higher than the Debye temperature the normalized values of the thermal expansion are always higher than the normalized value of the heat capacity. The correlation detected has significant computational advantage since it allows calculating the volume coefficient of thermal expansion from one experimental value by using the Debye function.

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1. Introduction

The volume coefficient of thermal expansion (α_V) is described as

$$\alpha_V = \frac{1}{V} \left(\frac{dV}{dT} \right)_P \quad (1)$$

where V is the volume, T is the temperature, and P is the pressure. The volume coefficient of thermal expansion is temperature dependent, requiring numerous experiments for its complete description. The experiments are time-consuming and technically difficult at extreme temperatures.

The theory of thermal expansion is well defined. The volume expansion can be determined by calculating the anharmonic term of the lattice vibration (e.g. [1,2]). This traditional approach has been challenged by a simple classical model [3,4] which gave good or excellent agreement with the experimental data for Ne, Ar, Kr, and Xe. In these calculations it was assumed that the potential is of Lennard-Jones type and that the mean value of the interatomic distance ($\langle R \rangle$) can be used to calculate the thermal expansion:

$$[\alpha(T)]_{P=0} = \frac{1}{R_0} \left[\frac{d\langle R(T) \rangle}{dT} \right]_{P=0} \quad (2)$$

The mean interatomic distance to a good approximation is proportional to the mean vibrational energy per atom in a solid [2]. The thermal energy of a system (Q^{thermal}) is the product of the mean vibrational energy of an atom and the number of atoms in the system. The zero-term energy of the atoms is not included in the thermal energy. Introducing a constant (a) allows one to substitute for the mean interatomic distance the thermal energy of a system. Eq. (2) can be rewritten then as

$$[\alpha(T)]_{P=0} = \frac{a}{n} \left[\frac{dQ^{\text{thermal}}(\langle R(T) \rangle)}{dT} \right]_{P=0} \quad (3)$$

where n is the number of moles.

The molar thermal heat capacity $c(\varphi)^{\text{thermal}}$ is defined as

$$\begin{aligned} c(\varphi)^{\text{thermal}} &= \frac{1}{n\delta T} \int_T^{T+\delta T} \delta Q(\varphi)^{\text{thermal}} \\ &= \frac{1}{n} \frac{dQ(\varphi)^{\text{thermal}}}{dT} \end{aligned} \quad (4)$$

where $\varphi = g$ (gas), s (solid), l (liquid). Combining Eqs. (3) and (4) gives

$$[\alpha_V(T)]_{P=0} = a \left[c(s)^{\text{thermal}} \right]_{P=0} \quad (5)$$

The molar thermal heat capacity is pressure independent. The pressure has an effect on the equilibrium separation (R_0) of the atoms, which is incorporated in the constant. The pressure effect on R_0 can be accommodated by assuming that the

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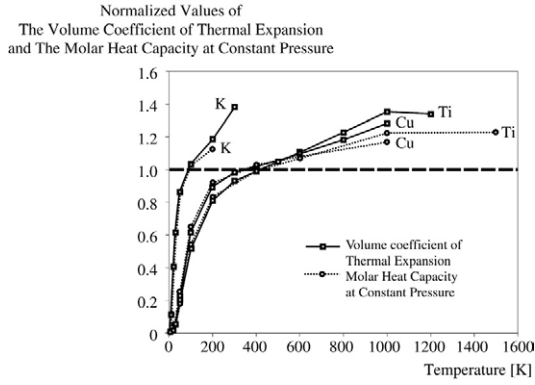


Fig. 1. Normalized values of the volume coefficient of thermal expansion and the molar volume heat capacity at constant pressure as a function of temperature for K, Cu, and Ti.

introduced constant (a) is pressure dependent:

$$[\alpha_V(T)]_P = a_P [c(s)^{\text{thermal}}] \quad (6)$$

The pressure up to a few GPa has a minor effect on the heat capacity [5]. In this pressure range the molar thermal heat capacity can be replaced with the constant pressure molar heat capacity:

$$[\alpha_V(T)]_P = a_P [c(s)]_P \quad (7)$$

Eq. (7) predicts a linear correlation between the volume coefficient of thermal expansion and the molar heat capacity at constant pressure. This correlation will be considered in detail.

2. Correlation between the volume coefficient of thermal expansion and the molar heat capacity

Experimental data for highly symmetrical monatomic arrangements [6] Ag, Al, Au, Ba, Co, Cr, Cu, Fe, K, Ni, Pb,

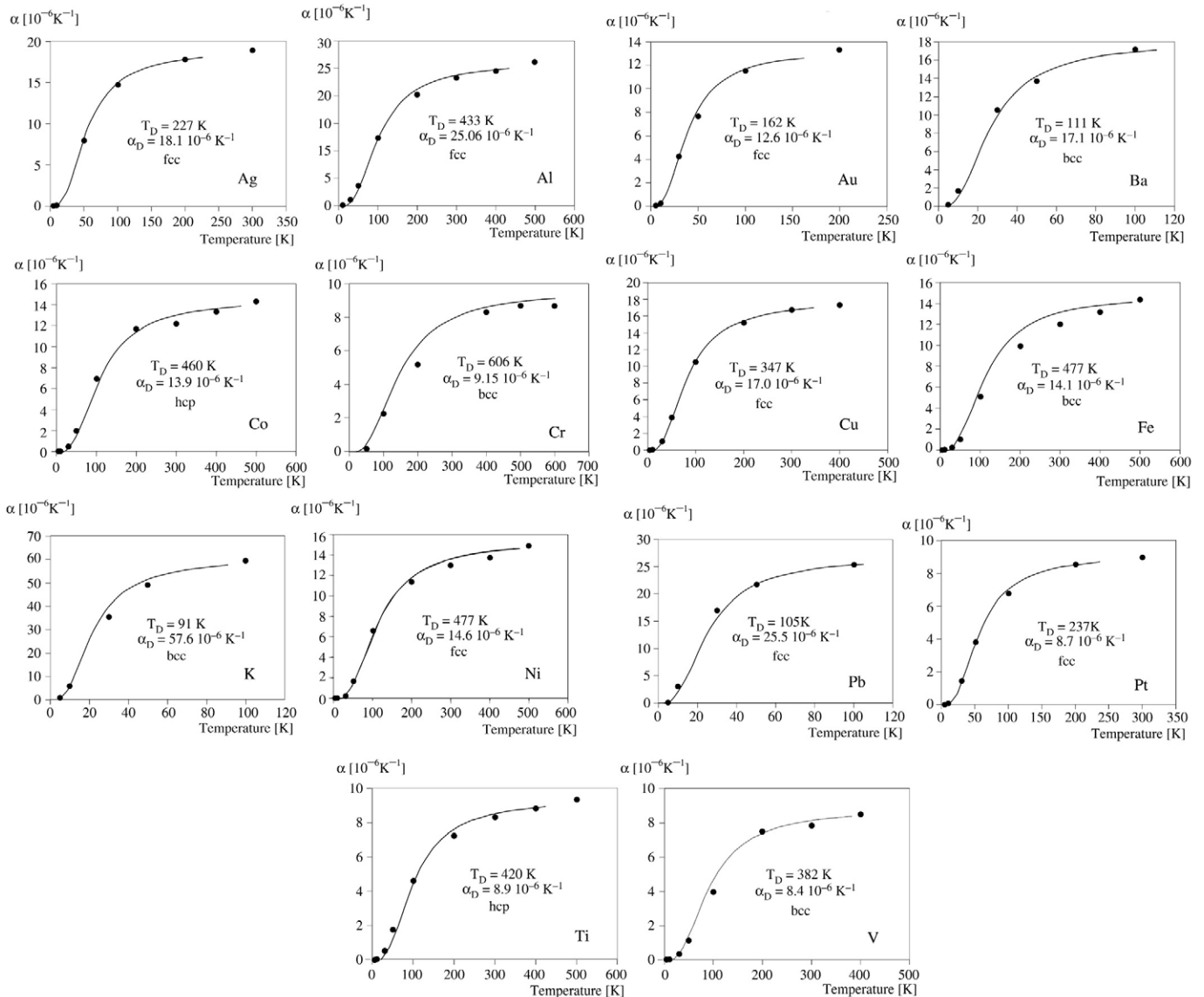


Fig. 2. The solid lines are the calculated volume coefficients of thermal expansion while the dots represent the experimental values [6].

Pt, Ti, V have been used to investigate the predicted correlation between the volume coefficient of thermal expansion and the molar heat capacity at atmospheric pressure. The experimental values of these two thermodynamic parameters were not necessarily determined at the same temperature. In order to make these parameters comparable, the two data sets were normalized to the Debye temperature. It has been found that the normalized values of the volume coefficient of thermal expansion and the heat capacities are practically identical below the Debye temperature. Above the Debye temperature the normalized values of the volume coefficient of the thermal expansion are higher than the normalized values of the heat capacity. The characteristic behavior is shown in Fig. 1. These results are interpreted as follows. The identity of the curves of the normalized values of the volume coefficient of thermal expansion and the molar heat capacity at atmospheric pressure confirms the predicted linear correlation between these thermodynamic parameters from zero kelvins to the Debye temperature. The higher normalized values of the volume coefficient of thermal expansion above the Debye temperature might be the result of the additional expansion caused by lattice vacancies [7,8].

3. Computational advantages

Employing the linear correlation detected between the volume coefficient of thermal expansion and the molar thermal heat capacity allows calculating the volume coefficient of thermal expansion from any experiment. Using Eq. (6) for two different temperatures and dividing the first equation by the second one gives

$$\left[\frac{\alpha_V(T_1)}{\alpha_V(T_2)} \right]_P = \frac{c(s)_{T_1}^{\text{thermal}}}{c(s)_{T_2}^{\text{thermal}}}$$

and
$$[\alpha_V(T_2)]_P = \frac{[\alpha_V(T_1)]_P}{c(s)_{T_1}^{\text{thermal}}} c(s)_{T_2}^{\text{thermal}}. \quad (8)$$

The pressure effect is canceled out in Eq. (8) by the division. The molar thermal heat capacity can be calculated by using the Debye function [9]:

$$c(s)^{\text{thermal}} \approx c(s)^{\text{Debye}} = 3Rf$$

$$f = 3 \left(\frac{T}{T_D} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (9)$$

and

$$x = \frac{h\omega}{2\pi k_B T} \quad \text{and} \quad x_D = \frac{h\omega_D}{2\pi k_B T} = \frac{T}{T_D} \quad (10)$$

where R is the universal gas constant, h is Planck's constant, ω is the frequency, ω_D is the Debye frequency and T_D is the Debye temperature. This equation has to be evaluated numerically [10].

Using the experimental value of the volume coefficient of thermal expansion at the Debye temperature ($\alpha(T_D)$) the volume coefficient of thermal expansion was calculated between zero kelvins and the Debye temperature. The calculated and the experimental values are plotted in Fig. 2. On the basis of visual inspection, we can say that the correlations are excellent for elements (Ag; Al; Au; Cu; Ni; Pb; Pt) with face centered cubic structure, very good for Co and Ti with hexagonal close packed structure and good for elements (Ba; Cr; Fe; K; V) with body centered cubic structure.

4. Conclusions

The theoretically predicted linear correlation between the volume coefficient of thermal expansion and the heat capacity has been confirmed for highly symmetrical monatomic arrangements.

The detected correlation allows calculating the volume coefficient of thermal expansion from an experiment conducted at a preferred chosen temperature.

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