

The role of defects on thermophysical properties: thermal expansion of V, Nb, Ta, Mo and W

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Abstract

Thermophysical properties at high temperatures and pressures are difficult to measure. Many reviews have approximated experimental data with empirical polynomial functions. In the case of thermal expansion and molar volume, extensive results for refractory body centered cubic (BCC) metals have been published. A critical evaluation of these experimental data is essential for many other studies. We provide this evaluation in terms of models that interrelate the thermophysical properties, self diffusion, and high temperature thermal defects. Experimental and theoretical methods for measuring and representing thermal expansion and the limitations of such methods are also briefly reviewed. Results for V, Nb, Ta, Mo, and W fall into two distinct subgroups relating to their elemental positions in the periodic table. The thermal expansions for these elements are analyzed within the constraints of a simple vibrational model and its equation of state. This approach represented the thermal expansion as the contributions from a perfect crystal and the crystal's high temperature anharmonicity as well as its thermal defects. Quantitative expressions, neglecting electronic contributions, are provided for the coefficient of thermal expansion and the expansivities for these five BCC metals from near 20°K to their melting temperatures. Vacancy formation enthalpies and entropies are also estimated. Our vacancy thermodynamic results are compared with earlier predictions and results from positron annihilation, thermal expansion, and specific heat measurements. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Thermal defects are important for understanding and determining the thermophysical properties of materials at elevated temperatures and at high pressures. Diffusion, resistivity, positron annihilation, specific heat and thermal expansion experiments [1–5] provide clear evidence of their effects. In spite of this, many theoretical models assume that such effects are either small enough to be neglected or that they can be approximated within the constraints of an empirical interatomic potential. As reviewed by Hehenkamp [5], there are many techniques available for obtaining the formation parameters of vacancies such as electrical resistivity, specific heat, thermal expansion, positron annihilation, etc. However, all these approaches are indirect and involve at least one parameter which is either unmeasurable, or highly uncertain. Differential dilatometry, which simultaneously measures the macroscopic length change and the X-ray lattice parameter is the only direct method. It has been applied to many metals [5]. Unfortunately, due to the difficulty of making measurements at elevated temperatures, this technique has not been applied to body centered cubic (BCC) refractory metals. High temperature thermal expansion is the property most sensitive to the formation of thermal defects [6]. In this paper, the extensive data on the thermal expansion of the BCC refractory metals is reviewed in terms of a model that explicitly includes thermal defects.

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1.1. Lattice dynamics and thermophysical properties of materials

Each material at absolute zero is uniquely represented by the nature of its atoms, their spatial arrangement and the forces between them. In the rigid ion model it is assumed that the electron distribution is locked to the nuclei and is not affected by the lattice dynamics induced by increases in the temperature and pressure. However, as one investigates the state of matter at higher temperatures and pressures, it is anticipated that the majority of models will have increasing inaccuracies as responsible interatomic interactions are complex and not well understood. Shell representations also provide qualitative results for this difficult problem.

It is well known that the original Grüneisen relationship is valid over a fairly broad temperature range. When modified to include a temperature dependent γ this range may be extended from near absolute zero to the melting point. Unfortunately, the temperature dependence of γ is generally unknown at higher temperatures and is often assumed to be a constant. In the simplest situation, as temperature increases, atomic vibrations provide a dynamical means for maintaining the energy equilibrium without changing the symmetry of the system. This symmetry provides a specific mathematical framework for describing the distribution of the fully excited $3N$ frequencies of a mole of atoms or molecules. The higher the temperature the more excited the atoms become until all of the modes are fully excited. At that point the Grüneisen parameter, a quantitative measure of the anharmonicity, is generally considered to reach its high temperature limiting value, γ_{∞} .

In 1911, nearly a century ago, Einstein [7] introduced lattice dynamical calculations that applied approaches from the mechanics of solids to the atomic scale. He assumed only next nearest neighbor interactions and calculated the specific heat of monatomic solids with several simplifying assumptions. Born and Huang [8] provided many additional insights and fully developed the lattice dynamical theory of solids within the constraints of a rigid ion approach. Blackman [9], one of Born's students, provided a lattice dynamical theory of specific heat and, as illustrated later, redefined the Grüneisen parameter. His approach was physically meaningful and assumed that γ could be simplified as a number of average Blackman–Grüneisen parameters, each of which represents a given section of the phonon spectrum.

Theoretical calculations have been carried out for simplified one, two, and three dimensional lattices [10,11]. These provide useful physical insights, but yield very qualitative results for real materials because of the inherent difficulties in realistically representing interatomic forces. Simplified models of the vibration spectra, such as the modified multifrequency Einstein model and early Debye model shown in Fig. 1, require empirically determined variable characteristic temperature parameters to represent thermophysical properties over any extended temperature range. A schematic spectrum that represents a typical solid is also shown in Fig. 1. Thermal defect modes present in a typical spectrum are not included in the Debye model. Vibrational spectra for many materials can be found in the book of Bilz and Kress [12]. Quasi-harmonic models [13] utilizing perturbation techniques to shift the harmonic potential, i.e., expanding a Taylor series at each finite temperature, provide reasonable results for many simple materials from 0 K to approximately half of their Debye temperatures, θ_D .

The phonon spectrum can be measured with a reasonable degree of accuracy using neutron spectroscopy at low temperatures. Experimental spectra contain $3N$ vibrational modes where N is Avogadro's number. Neutron measurements provide phonon spectra for ascertaining the validity of interatomic force models when anharmonic contributions are relatively weak. The pressure dependence of the phonon spectra, rarely measured, can give significant information about anharmonicity. The mode Grüneisen parameters have been determined from the experimentally measured pressure dependence of Raman spectra for diamond and also for some other materials [14,15]. This approach is in

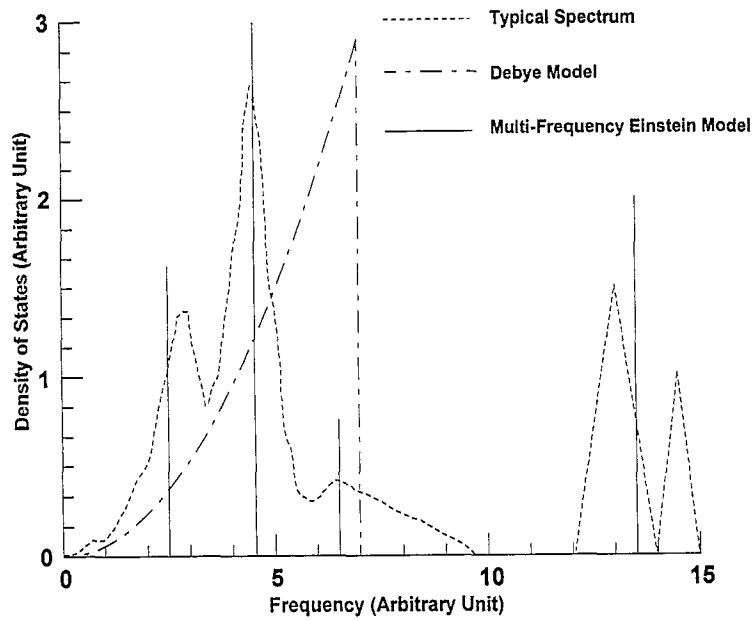


Fig. 1. Schematic of a vibrational spectrum.

excellent agreement with semiempirical methods for calculating the thermal expansion at high temperatures. At the highest temperatures, neutron spectroscopy measurements are difficult to interpret as the increasing anharmonicity and defect interactions further complicate the phonon spectrum.

1.2. Thermal expansion

Thermal expansion is an important characteristic property of all materials. It is directly related to the anharmonicity of the interatomic potential of a crystal. Because of this, it is an inherent part of the equation of state of solids. It is critical for understanding the nature of residual stresses in materials. Thermal expansion is closely related to other thermodynamic and mechanical properties, i.e., specific heat, elastic constants, self diffusion, etc. Therefore, it is difficult to discuss this property in isolation and an appropriate equation of state is useful for evaluating the self consistency of experimental data.

Thermal expansion is defined as the dimensional change occurring with a change in the temperature at constant pressure. In most cases, the coefficient of volumetric expansion:

$$\alpha_V = (\partial \ln V / \partial T)_P, \quad (1)$$

is discussed. Here, V is the volume, T the temperature, and P the pressure. The coefficient of linear expansion α_L is commonly utilized for cubic crystals or isotropic materials:

$$\alpha_L = \frac{1}{3} \alpha_V = (\partial \ln l / \partial T)_P. \quad (2)$$

From an atomistic perspective, the interactions can be represented by an interatomic potential as schematically illustrated in Fig. 2. At the lowest temperatures, the potential function is approximately harmonic. The interatomic distance remains close to r_0 , the interatomic separation at absolute zero, and the crystal dimensions do not change appreciably. With heating the increasing anharmonicity of the potential function results in an increase of the equilibrium distance and the corresponding molar volume.

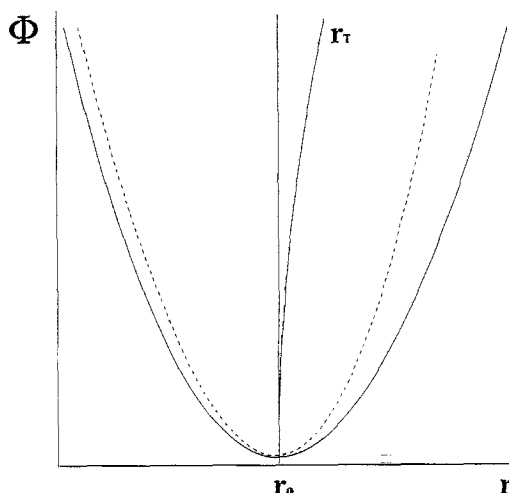


Fig. 2. Schematic of interatomic potentials and the equilibrium atomic position. The dashed line represents the harmonic potential and the solid line is the anharmonic potential. The r_T is the equilibrium position.

Thermal expansion can be represented by a symmetrical strain tensor α_{ij} . The α_{ij} are the six generalized coefficients of thermal expansion for a material with no symmetry, i.e., triclinic. At the other extreme, for an isotropic material, all α_{ij} 's are equal and, as indicated by Nye [16], the representation quadric is a sphere. Although many cubic materials are anisotropic in certain properties, in order to preserve crystal symmetry, their α_{ij} 's at a given temperature must remain equal to each other. The thermal expansion of hexagonal, tetragonal and orthorhombic crystals can be represented by ellipsoids whose two, and for the orthorhombic case three, maximum diameters are coincident with the unit cell axes. One must take special care when measuring thermal expansion of monoclinic and triclinic crystals as maximum thermal expansion is defined by the maximum ellipsoid diameters. Because of the reduced symmetry there is no a priori reason to expect these to coincide with chosen crystallographic axes. Several computer programs [17,18] provide systematic approaches to determine the α_{ij} 's.

Low temperature thermal expansion of materials has been reviewed by many authors [19–21]. Merchant et al. [22] reviewed the equations of state and thermal expansion of alkali halides based on work prior to 1973. Most thermal expansion data for materials prior to 1979 have been compiled by many investigators [23–25]. For the majority of materials it is observed that low temperature measurements, from cryogenic temperatures to the Debye temperature, are self-consistent and generally reliable. Unfortunately, because of the difficulties of high temperature experiments, elevated temperature data are often scattered or sparse. Therefore, reliable theoretical, semiempirical, and empirical models are necessary to evaluate and predict thermal expansion.

1.3. Methods of measurement

Thermal expansion coefficients of metals and ceramics range from 10^{-5} to $10^{-7}/^\circ\text{K}$. Detecting such changes requires sensitive methods as well as careful control of sample temperature. The volume can be experimentally measured by X-ray or neutron diffraction as a function of temperature with the thermal expansion then determined by differentiating some analytical function fit to the volume/temperature dependency. Becker [26] was one of the first to measure thermal expansion by this method. The interplanar spacings, d_{hkl} , can be calculated from Bragg's law $n\lambda = 2d \sin \theta$, where n is an integer, λ is the wavelength of the X-ray, and 2θ is the angle between the diffracted X-rays and the

direction of the incident X-ray beam on the sample. In X-ray diffraction, the absolute accuracy of the lattice parameter depends on a knowledge of the absolute value of the characteristic X-ray wavelength. High density materials have high absorption coefficients, which combined with the universally occurring high temperature broadening and reduction of intensity of X-ray diffraction profiles, reduce the precision of higher temperature X-ray temperature data. As Hart [27] has indicated, simultaneous X-ray and optical interferometry now provide a measure of the lattice parameter of silicon to ± 0.1 ppm. At this absolute accuracy it is clear that crystal imperfections and minute impurity levels will influence the results obtained. All lattice parameters for this review have been normalized to a Cu $K\alpha_1$ X-ray wavelength of 1.540597 Å. As summarized elsewhere [28], the literature for 298°K experimentally measured silicon lattice parameters is reviewed and the values are normalized with this absolute value of the Cu $K\alpha_1$ wavelength. The lattice parameter, 5.431066 Å, is believed to be accurate in absolute terms to at least 5 significant figures. Neutron diffraction measurements [29] have provided the high precision lattice parameters of high density materials such as the hexagonal polymorph of tungsten carbide. There, because neutron absorption was low, a large number of diffraction profiles were obtained and self consistently evaluated with a Reitveld analysis.

The early development of thermal expansion measurements can be found in Reeber [30]. Many thermal expansion measuring techniques have been developed and most are reviewed by Touloukian et al. [23,24]. A detailed review of the most sensitive low temperature relative and absolute methods was given by Barron et al. [21]. Thermal expansion and expansivity are either measured directly or are measured relative to a standard material. Here, several important methods are briefly reviewed. The interferometer was invented by Fizeau in the 1860's. He utilized it to accurately measure the thermal expansion of a variety of materials [31]. The technique, which has medium to high sensitivity, is based on the interference of monochromatic light reflected from two surfaces separated by a specimen, or from a specimen and a reference material. The interference condition can be represented by $2nL \cos \theta = N\lambda$. Here, n is the index of refraction, L the distance between the two surfaces, θ the incident angle, N the order of interference, and λ the wavelength of the light. The availability of low cost lasers makes this a convenient method to achieve accurate results from relatively small samples.

A simpler system, the push-rod dilatometer, transfers the expansion of the sample from the heated zone to a calibrated extensometer by means of a rod of a stable material such as alumina or fused silica [32]. Low temperature dilatometers are designed for ultrahigh sensitivity. They include: (1) the three terminal capacitor method of White [33], (2) the variable transformer method of Carr and Swenson [34], (3) the double-twisted strip, optical lever adaption of Shapiro et al. [35], and (4) the optical lever/photometric method of Andres [36] and Jones [37].

At higher temperatures, where the expansion is significantly higher, the diffraction profiles are broad, weak, and difficult to measure; sample temperature gradients are difficult to monitor and eliminate, and in general the quality of experimental data suffers. A clever interferometric method for high temperature-high speed observation, which rapidly self-heats the specimen from room to the maximum temperature of interest has been developed by Miller and Cezairliyan [38]. In their method, an electrical current pulse resistively heats the sample while it is being simultaneously measured. These workers have successfully applied this method to measure the specific heat and thermal expansion of most of the refractory metals to temperatures approaching the melting point [39,40].

1.4. Estimation and prediction of thermal expansion

1.4.1. Empirical relationships

Empirical models include polynomial or spline polynomial functions of temperature [23,24,41,42]. These expressions are sensitive to the order of the polynomial and unfortunately the

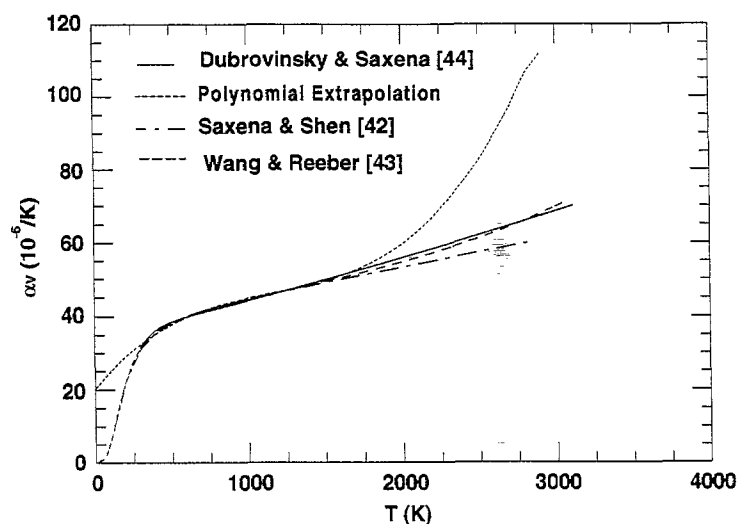


Fig. 3. Comparison of a polynomial, constrained polynomial, experimental results and the $\alpha_v K_T V$ model of thermal expansion for MgO.

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. This is illustrated in Fig. 3 where the coefficient of thermal expansion for MgO is given as an example. In Fig. 3, our most recent prediction of the temperature dependence of the coefficient of thermal expansion of MgO [43] is compared with some of the earlier polynomial expressions and recent experimental results [44]. It is clear that the polynomial relationship obtained by fitting room temperature to 1750°K data has unrealistic values when extrapolated to temperatures outside the data range [45]. A constrained polynomial [42] is better, but still deviates from our model, which at the highest temperature ranges is in excellent agreement with the recent experiments.

1.4.2. Theoretical methods

Theoretical approaches for predicting the high temperature thermodynamic parameters include interatomic potential approaches based on equations of state, first-principle lattice dynamical methods relying on approximate interatomic potentials and ab-initio nonempirical approaches that utilize quantum mechanics [46–64]. Early theoretical approaches have been reviewed by Barron et al. [21]. Each approach has its own assumptions, many are valid only over a limited temperature range. In some calculations, as indicated by Merchant et al. [22], “the parameters used for calculation have been obtained by curve fitting techniques, using not only the extensive phonon data measured by inelastic neutron scattering, but also the thermal expansion (and the temperature dependence of elastic constants) data which the models purport to predict.” These methods, to date, give mostly qualitative results and deviate from experiment at intermediate to high temperatures. Fig. 4 compares different ab-initio methods [60,61,64], recent experiments [44], and our predictions for MgO [43]. We can see that Agnon and Bukowinski’s [61] calculations deviate from experiment above 400°K. Isaak et al.’s [60] calculation is much lower than experiment over the whole temperature range. Inbar and Cohen’s [64] results are only correct at intermediate temperatures.

1.4.3. Semiempirical models

These approaches utilize the lattice dynamics or equation of state considerations to represent the thermal expansion [65–69]. Coefficients for these approaches are usually determined by least-square

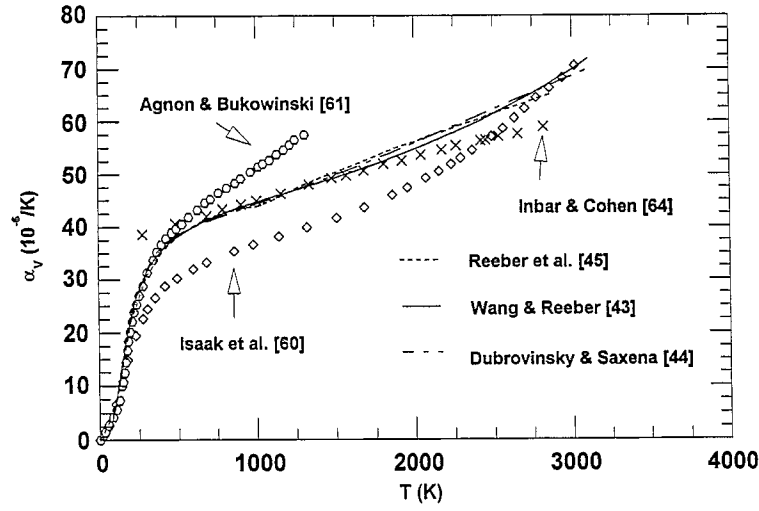


Fig. 4. Comparison of ab-initio thermal expansion models with the $\alpha_v K_T V$ model predictions for MgO (modified from Wang and Reeber [43]).

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.

According to the Mie-Grüneisen theory [70], the thermal expansion of a solid should be proportional to the specific heat C_V . This is known as the Grüneisen rule:

$$\alpha_v K_T = \gamma \frac{C_V}{V}. \quad (3)$$

Here, α_v is the coefficient of volume thermal expansion, K_T is the isothermal bulk modulus, γ is the Grüneisen parameter, C_V is the isochoric specific heat, and V is the volume. The Grüneisen parameter in its original and strictest sense is considered to be independent of temperature. This can not be true in a lattice. Within a quasi-harmonic approximation, the lattice is represented by a system of $3N$ loosely coupled harmonic oscillators and the vibrational frequencies only change with the volume. The Grüneisen parameter is then represented by the following expression [71]:

$$\gamma = \frac{\sum_{i=1}^{3N} \gamma_i C_i}{\sum_{i=1}^{3N} C_i}, \quad (4)$$

where:

$$\gamma_i = - \left(\frac{\partial \ln \omega_i}{\partial \ln V} \right)_T \quad (5)$$

is the i th mode Grüneisen parameter and:

$$C_i = k \left(\frac{\hbar \omega_i}{kT} \right)^2 \frac{\exp(\hbar \omega_i / kT)}{[\exp(\hbar \omega_i / kT) - 1]^2} \quad (6)$$

is the contribution to the specific heat C_V from the i th mode.

Wachtman et al. [65] and Suzuki [67] have followed the Grüneisen theory of thermal expansion based on the Mie-Grüneisen equation of state [70]:

$$PV + X(V) = \gamma E_{\text{vib}}, \quad (7)$$

where P is the pressure, $X(V) = (d\phi/dV)V$, ϕ is the potential energy as a function of volume only and E_{vib} is the thermal lattice vibrational energy. After applying a Taylor expansion to the second term in Eq. (7) with respect to the volume change $\Delta (= V - V_0)$ and restricting this to the second order, Eq. (7) can be represented by:

$$Y(T) - \kappa Y(T)^2 = \frac{E_{\text{vib}}}{Q_0}, \quad (8)$$

where:

$$Q_0 = \frac{K_0 V_0}{\gamma}, \quad (9a)$$

and

$$\kappa = \frac{1}{2} \left(\frac{dK_0}{dP} - 1 \right). \quad (9b)$$

Here, K_0 is the bulk elastic modulus at 0°K. At the zero pressure condition, the volume expansivity $Y(T)$ is defined as Δ/V_0 . A quadratic equation of $Y(T)$ is then obtained. An iterative method is applied to solve Eq. (8) for $Y(T)$ [70]:

$$Y(T) = \frac{E_{\text{vib}}}{Q_0 - \kappa E_{\text{vib}}}. \quad (10)$$

The coefficient of thermal expansion is then determined by differentiating Eq. (10) with respect to temperature. In this way, Wachtman et al. [65] and Suzuki [67] fit their expressions to experimental data and then extrapolated the results to higher temperatures. Wachtman et al. [65] represented the vibrational energy with a Nernst–Lindemann vibrational spectrum and Suzuki [67] utilized a simple Debye model. Later, Suzuki et al. [68] solved the real root of Eq. (8) for $Y(T)$ and obtained an improved expression for the expansivity:

$$Y(T) = \left[1 - \left(1 - \frac{4\kappa E_{\text{vib}}}{Q_0} \right)^{1/2} \right] \frac{1}{2\kappa}. \quad (11)$$

It must be noted that Suzuki's model (Eq. (11)) is based upon the Taylor expansion of the potential energy term in Eq. (7). Since only the second-order term is retained in the calculation and higher-order terms are omitted, this approximation must introduce errors at high temperatures and pressures. In a later work, Anderson [72] concluded that, for NaCl, Suzuki's approach is only useful to temperatures of about twice the Debye temperature. This restriction should also apply to other materials. With another approach, Reeber et al. [45] have estimated the thermal expansion of MgO and obtained results higher than Anderson's high temperature extrapolation [73].

The semiempirical lattice dynamics model based upon Eqs. (3) and (4) provides an alternate approach for representing the thermal expansion [66,74,75]. This modified Einstein model represents the vibrational spectrum with several Einstein frequencies. Ibach [74], and Lu and Wang [75] have respectively applied three fixed Einstein frequencies to fit thermal expansion data. Reeber [66], relying

on Blackman's [76] less rigorous but more physically significant definition of the Grüneisen parameter, has developed a least-square fitting method. There, both the Einstein frequencies and the mode Grüneisen parameters were determined from the fitting of reliable cryogenic and intermediate temperature expansivity or thermal expansion.

Considering that the γ_i vary slightly with temperature, Blackman [76] defined γ as:

$$\gamma = \frac{\int \bar{\gamma}_v \rho(\nu) E(h\nu/kT) d\nu}{\int \rho(\nu) E(h\nu/kT) d\nu}, \quad (12)$$

where $\rho(\nu)$ is the frequency distribution function and $\bar{\gamma}_v$ is the average between the two frequency contours ν and $\nu + d\nu$, while $E(h\nu/kT)$ is the Einstein function:

$$E\left(\frac{h\nu_i}{kT}\right) = \frac{\left(\frac{\theta_i}{T}\right)^2 \exp\left(\frac{\theta_i}{T}\right)}{\left[\exp\left(\frac{\theta_i}{T}\right) - 1\right]^2}, \quad (13)$$

where $\theta_i = h\nu_i/k$ is the i th Einstein temperature. Thermal expansion can be represented by:

$$\alpha_V = \frac{\gamma C_V}{K_T V}, \quad (14a)$$

$$\alpha_V = \frac{1}{K_T V} \int \bar{\gamma}_v \rho(\nu) E(h\nu/kT) d\nu, \quad (14b)$$

Reeber [66] further simplified Eqs. (14a) and (14b) with:

$$\alpha_V = \sum_{i=1}^n 3X_i E(h\nu_i/kT), \quad (15)$$

and the expansivity can be represented as:

$$\ln\left(\frac{V}{V_0}\right) = \left[\sum_{i=1}^n \frac{3X_i \theta_i}{\exp\left(\frac{\theta_i}{T}\right) - 1} \right]_0^T, \quad (16)$$

where n Einstein frequencies are applied to approximate the vibrational spectrum. $X_i = \gamma_i \rho_i / K_T V$ includes the effect of the bulk modulus, volume, frequency distribution and the Grüneisen parameter of the i th mode. The Einstein function, Eq. (15) approaches a limit at high temperatures. This method is applicable at low temperatures and also for materials with a weak temperature dependence of the product $K_T V$. Eqs. (15) and (16) have been critically applied to evaluate the experimental data and also to predict the thermal expansion of Group IV elements, II–VI, and III–V compounds [28,66,77,78]. Excellent agreement was obtained with experiments. Wang and Reeber [79] have recently extended Reeber's [66] original model to include a high-temperature parabolic relationship for predicting the thermal expansion of the alkali halides. Defect ordering within that structure has been proposed to explain this relationship [45].

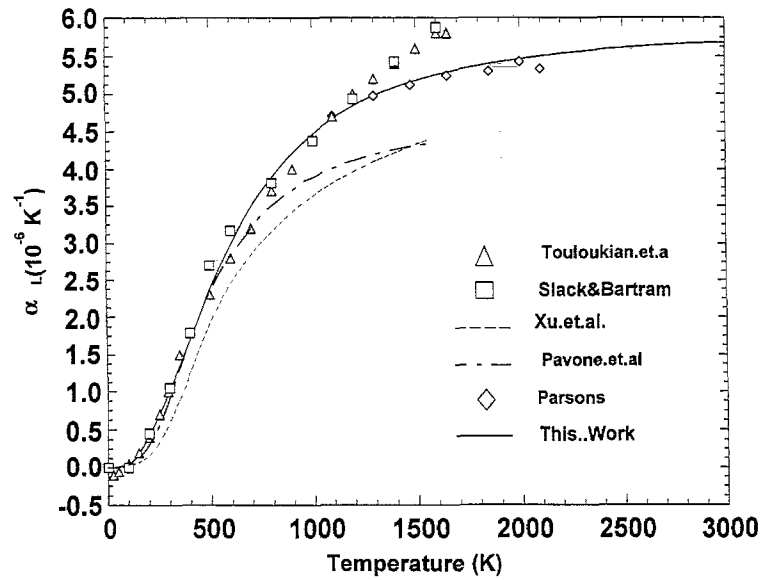


Fig. 5. Comparison of the diamond thermal expansion model with previous work (from Reeber and Wang [78]).

1.4.4. Other approaches

From the definition of the isothermal bulk modulus, K_T , mode Grüneisen parameters represented by Eq. (5) can be expressed as:

$$\gamma_i = K_T \left(\frac{\partial \ln \omega_i}{\partial P} \right)_T. \quad (17)$$

Measurement of the mode Grüneisen parameters γ_i permits the calculation of the Grüneisen parameter of a material within the constraints of the simple lattice dynamic model of Eq. (4). Parsons [14] has measured room temperature first and second order Raman spectra of diamond and calculated its Grüneisen parameters from cryogenic temperature to about 2000 °K. We have predicted the thermal expansion, molar volume, and specific heat for diamond [78] and the Grüneisen parameters determined for diamond are in good agreement with Parsons' [14]. Fig. 5 illustrates the thermal expansion comparison for diamond [78]. The model calculation that utilizes Parsons' Grüneisen parameter is the closest to our calculations. This method of determining the Grüneisen γ has also been utilized by Gillet et al. [15] to estimate the thermal expansion at high temperatures and pressures for MgSiO_3 , perovskite.

1.5. Defect contributions to thermal expansion at high temperature/pressure

Thermal defect contributions to the thermodynamic properties have been discussed extensively by Varotsos and Alexopoulos [80]. Here we provide a brief description of how defects contribute to the thermal expansion. As discussed by Schoknecht and Simmons [6], the Gibbs free energy of a real crystal can be written as:

$$G(T, P) = G^0(T, P) + \sum_{i,j} \{n_j g_{ij}(T, P) - kT \ln W_{ij}\}, \quad (18)$$

where G^0 is the Gibbs free energy of a perfect crystal, n_j is the number of defects of species j , g_{ij} is the formation Gibbs free energy of the defects including interactions among species i and j , and W_{ij} is the

number of ways of distributing n_j defects on the available sites. The equilibrium number of defects for species j is obtained from the minimum condition of the free energy:

$$\left(\frac{\partial G}{\partial n_j}\right)_{T,P} = 0. \quad (19)$$

For thermal defects, the volume of the crystal is expressed by:

$$V(P,T) = V^0(P,T) + \sum_{ij} n_j \nu_{ij}(P,T) \quad (20)$$

where $\nu_{ij} = (\partial g_{ij} / \partial P)_T$ is the formation volume of the defect j . The volume thermal expansion of the crystal can be written as:

$$\alpha_V V = \alpha_V^0 V^0 + \sum_{ij} \left[n_j \left(\frac{\partial \nu_{ij}(P,T)}{\partial T} \right)_P + \nu_{ij} \left(\frac{\partial n_j}{\partial T} \right)_P \right] \quad (21)$$

For simplicity, let's consider n thermal defects in a crystal of N atoms. From the equilibrium condition, one has the standard form:

$$n \approx N \exp \left(-\frac{g_P^f}{kT} \right). \quad (22)$$

Following the derivation of Varotsos and Alexopoulos [80], one finds the following expression:

$$\alpha_V V = \alpha_V^0 V^0 + n \nu_P^f \alpha_V^f + \frac{n \nu_P^f h_P^f}{kT^2}, \quad (23)$$

where α_V is the coefficient of thermal expansion of the real crystal, α_V^0 is the coefficient of thermal expansion of the perfect crystal, α_V^f is the coefficient of thermal expansion of the vacancy, ν_P^f is the formation volume of the vacancy, g_P^f and h_P^f are the formation free energy and enthalpy of the vacancy, respectively. From Eq. (6) we obtain exactly:

$$\alpha_V - \alpha_V^0 = \frac{n \nu_P^f}{N \Omega_P} \left(\alpha_V^f - \alpha_V^0 + \frac{h_P^f}{kT^2} \right), \quad (24)$$

where Ω_P is the mean volume per atom of the real crystal. When $\alpha_V^f - \alpha_V^0 \ll h^f / kT^2$, we have:

$$\Delta \alpha(P,T) \approx \frac{\nu_P^f h_P^f}{\Omega_P} \exp \left(-\frac{g_P^f}{kT} \right) \frac{1}{kT^2}. \quad (25)$$

In Eq. (25), the formation volume ν_P^f , formation enthalpy h_P^f , formation Gibbs free energy g_P^f , and volume per atom Ω_P are all functions of pressure. At constant temperature and low pressure, the Gibbs free energy can be expanded as a Taylor series [81]:

$$g_P^f - g_0^f = \left. \frac{\partial g_P^f}{\partial P} \right|_{P=0} P + \frac{1}{2} \left. \frac{\partial^2 g_P^f}{\partial P^2} \right|_{P=0} P^2 + O(P^3) = P \nu_0^f \left(1 - \frac{1}{2} \frac{P}{K_0^f} \right) + O(P^3), \quad (26)$$

and the formation enthalpy can be expressed as:

$$\begin{aligned} h_P^f &= h_0^f + \left. \frac{\partial h_P^f}{\partial P} \right|_{P=0} P + \frac{1}{2} \left. \frac{\partial^2 h_P^f}{\partial P^2} \right|_{P=0} P^2 + O(P^3) \\ &= h_0^f + P \nu_0^f \left[(1 - \alpha_0^f T) \left(1 - \frac{1}{2} \frac{P}{K_0^f} \right) + \frac{1}{2} \frac{\alpha_0^f \delta_0^f T}{K_0^f} P \right] + O(P^3), \end{aligned} \quad (27)$$

where in Eqs. (26) and (27), ν_0^f is the formation volume of the thermal defects, α_0^f is the thermal expansion of thermal defects, K_0^f is the isothermal bulk modulus of defects, and δ_0^f is the isothermal Anderson–Grüneisen parameter of defects. The subscript 0 indicates the pressure is zero or atmospheric pressure. According to the cB Ω model, ν_p^f/Ω_p changes little with pressure and temperature [80], therefore as an approximation, we have assumed that ν_p^f/Ω_p is a constant. After omitting the higher order terms in Eqs. (26) and (27), the thermal defect contribution to thermal expansion becomes:

$$\begin{aligned}\Delta\alpha(T,P) &= \frac{\nu_0^f}{\Omega_0} \frac{h_0^f}{k} \left[1 + \frac{P\nu_0^f}{h_0^f} f_h(T,P) \right] \exp\left(\frac{-g_0^f}{kT}\right) \exp\left[-\frac{P\nu_0^f}{kT} f_g(T,P)\right] \frac{1}{T^2} \\ &= \Delta\alpha(0,T) \left[1 + \frac{P\nu_0^f}{h_0^f} f_h(T,P) \right] \exp\left[-\frac{P\nu_0^f}{kT} f_g(T,P)\right],\end{aligned}\quad (28)$$

where $\Delta\alpha(0,T)$ is the defect contribution to the thermal expansion at zero pressure, Ω_0 is the volume per atom at zero pressure:

$$f_h(T,P) = (1 - \alpha_0^f T) \left(1 - \frac{1}{2} \frac{P}{K_0^f} \right) + \frac{1}{2} \frac{\alpha_0^f \delta_0^f T}{K_0^f} P, \quad (29a)$$

and:

$$f_g(T,P) = 1 - \frac{1}{2} \frac{P}{K_0^f}. \quad (29b)$$

$\Delta\alpha(0,T)$ is represented by:

$$\Delta\alpha(0,T) = \frac{\nu_0^f h_0^f}{\Omega_0} \exp\left(-\frac{g_0^f}{kT}\right) \frac{1}{kT^2}, \quad (30)$$

where the subscript 0 in the formation parameters indicates the zero pressure condition. Since $g_0^f = h_0^f - Ts_0^f$, we have:

$$\Delta\alpha(0,T) \approx \frac{\nu_0^f h_0^f}{\Omega_0} \exp\left(\frac{s_0^f}{kT}\right) \exp\left(-\frac{h_0^f}{kT}\right) \frac{1}{kT^2}. \quad (31)$$

If ν_0^f/Ω_0 , s_0^f and h_0^f are constants, or slowly varying functions of temperature, Eq. (30) is applicable for fitting the thermal expansion difference between the real and the perfect crystal for each specific material. This assumption is approximately correct when the temperature is not very low, and also when it is slightly below the melting point of the crystal [80]. Eq. (30) can be simplified as [82]:

$$\Delta\alpha(0,T) = A \exp\left(\frac{-B}{T}\right) \frac{1}{T^2}, \quad (32)$$

and the resulting lattice parameter difference between the real and perfect crystal becomes:

$$\Delta L = L_q \left[A_1 \exp\left\{ \frac{A}{B} \exp\left(\frac{-B}{T}\right) \right\} - 1 \right], \quad (33)$$

where L_q is the lattice parameter of the perfect crystal and A_1 , A , and B are fitting parameters. The formation enthalpy of a thermal defect at zero pressure can then be obtained as:

$$h_0^f = Nk_B B. \quad (34)$$

When the thermal expansion is treated to consist of independent contributions from a perfect crystal and its thermal defects, the thermodynamic contribution of thermal defects is added to Eq. (15) [82]. Thermal expansion at atmospheric pressure is then represented as:

$$\alpha_{V,0} = \sum_{i=1}^n 3X_i \frac{\left(\frac{\theta_i}{T}\right)^2 \exp\left(\frac{\theta_i}{T}\right)}{\left[\exp\left(\frac{\theta_i}{T}\right) - 1\right]^2} + \sum_{i=1}^m 3A_i \exp\left(\frac{-B_i}{T}\right) \frac{1}{T^2}, \quad (35a)$$

and:

$$\ln\left(\frac{V}{V_0}\right) = \left[\sum_{i=1}^n \frac{3X_i \theta_i}{\exp\left(\frac{\theta_i}{T}\right) - 1} + \sum_{i=1}^m 3 \frac{A_i}{B_i} \exp\left(\frac{-B_i}{T}\right) \right] T, \quad (35b)$$

where in Eq. (35) the first term represents the contribution of the perfect crystal, and the second term is the contribution of m kinds of thermal defects. The anharmonic effects are included as a pseudo defect. We have applied this approach to alkali halides and other ionic compounds and have obtained their defect formation enthalpies [82,83]. The methods have also been extended to calculate the high pressure defect contributions to the thermal expansion of NaCl [81] and MgO [84].

1.6. Equations of state (EOS) and high temperature/pressure dependence of thermal expansion

Equations of state describe the relationship of volume, pressure and temperature of materials. Anderson et al. [73] have reviewed equations of state of solids for geophysics and ceramic science. Most EOS are based on either finite strain expansions of the free energy or empirical interatomic potentials. As described by Birch [85], one can assume an equation of state of the form:

$$P = K_T^0(T) F(V_0/V), \quad (36)$$

where $F(V_0/V)$ is any function of the ratio V_0/V . Most of the equations of state for solids fall into this category. By differentiating Eq. (36) with respect to T at constant V , a relationship for the thermal expansion at high and room pressure is obtained:

$$\frac{\alpha_V}{\alpha_{V,0}} = 1 - \frac{\delta_T^0}{K_T} P, \quad (37)$$

where α_V and $\alpha_{V,0}$ are the thermal expansion at high and room pressure, respectively, δ_T^0 is the isothermal Anderson–Grüneisen parameter at room pressure, and K_T is the isothermal bulk modulus at pressure P . If information is available for the high pressure bulk modulus, we can apply Eq. (37) to predict the high pressure thermal expansion. Unfortunately, like the thermal expansion, bulk moduli measurements at high pressures are scarce. Taylor expansions of the bulk moduli have been used to estimate high pressure values for various materials. Upon assuming $\alpha_V K_T$ is independent of pressure [85], Eq. (37) becomes:

$$\alpha_V = \frac{\alpha_{V,0}}{\left(1 + \frac{\delta_T^0}{K_T^0} P\right)}. \quad (38)$$

This can also be represented as:

$$\alpha_V = \frac{\alpha_{V,0}}{\left(1 + \frac{1}{\alpha_{V,0}} \frac{\partial \beta_T^0}{\partial T} P\right)}, \quad (39)$$

where β_T^0 is the compressibility at room pressure. When accurate atmospheric pressure/low temperature data for the thermal expansion and the compressibility are available the thermal expansion at high pressure can be predicted with Eq. (38) or Eq. (39). We have shown for NaCl [81] and MgO [84] that, directly applying Eq. (38) or Eq. (39) to NaCl and MgO yields a thermal expansion which decreases with temperature at high pressure. As discussed earlier, high temperature thermal expansion can be expressed as the sum of contributions from a perfect crystal and its thermal defects. This is important at high pressures because defect contributions follow different rules than those of the perfect crystal. The number of existing defects at any pressure strictly depends upon the magnitude of each defect's formation energy and the temperature. At temperatures below the high temperature cutoff frequency, ν_m , all lattice modes of the solid are excited and the semiempirical quasi-harmonic model (QHM) calculation of Eq. (15) or Eq. (16) is in excellent agreement with experiment. In this temperature regime, we can directly apply Eq. (38) or Eq. (39) to predict high pressure thermal expansion. In real crystals, above the temperature where ν_m is excited, complex interactions between defect and normal modes contribute to the increased anharmonicity of the lattice. Because both the atmospheric pressure thermal expansion $\alpha_{V,0}$ and the compressibility β_T^0 include defect contributions, we have taken an indirect approach for the prediction of the high pressure thermal expansion at high temperatures. As we have shown elsewhere, the thermal expansion at high temperatures and pressures can be represented by [81,84]:

$$\alpha_V(T,P) = \frac{\alpha_V^0}{\left(1 + \frac{1}{\alpha_V^0} \frac{\partial \beta_T^{0,QH}}{\partial T} P\right)} + \Delta\alpha(T,P), \quad (40)$$

where α_V^0 is the contribution of the perfect crystal at atmospheric pressure. This is approximately represented by Eq. (15) where $\beta_T^{0,QH}$ is the compressibility of a perfect crystal and $\Delta\alpha(T,P)$ is the contribution of the thermal defects at high temperature/pressure given by Eq. (28). As previously demonstrated for MgO [84] and NaCl [81], the thermal defect contributions to the thermal expansion are small and can be neglected at high pressures. Therefore, high pressure thermal expansion can be directly calculated from Eq. (39). At low pressures, the defect contributions included in Eq. (40) must be considered.

1.7. Thermophysical property interrelationships

For materials with a higher temperature dependence of $K_T V$, an $\alpha_V K_T V$ model has been proposed to be more appropriate [69]. Eqs. (14a) and (14b) must be rearranged as follows:

$$\alpha_V K_T V = \sum_{i=1}^n 3X_i'' E(h\nu_i/kT), \quad (41)$$

where $X'' = \gamma_i \rho_i$ includes the effects of the mode Grüneisen parameter and the density of states. This parameter, represents the partial temperature derivative of the work done by the thermal pressure. For face centered cubic materials, including NaCl [69], Cu [86], MgO, ZnS, and KCl [43], this function approaches a limit at high temperatures that resembles a specific heat curve. Since thermophysical properties are available at low and intermediate temperatures for many materials, Eq. (41), after

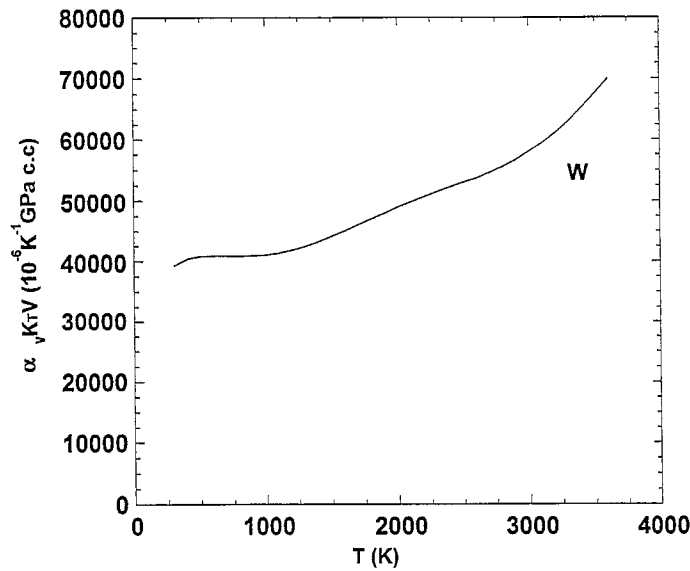


Fig. 6. The temperature dependence of $\alpha_v K_T V$ data for W.

assuming a linear bulk modulus K_T at high temperatures, enables the estimation of a temperature dependent lower limit of the thermal expansion.

This approach, however, is not applicable to BCC refractory metals due to the strong defect contributions at high temperatures. We have shown elsewhere that bulk moduli of W and Ta do not follow a linear temperature dependence relationship at high temperatures [87]. Fig. 6 illustrates the temperature dependence of $\alpha_v K_T V$ for W. From the figure, it is evident that this parameter dramatically increases at high temperatures.

Thermal expansion, bulk modulus, and specific heat are interrelated through the Grüneisen relationship Eq. (3). As shown previously, defects in BCC refractory metals have large effects on these properties at high temperatures. Similar effects on other physical properties, such as the high temperature self-diffusion coefficients, should also be evident. Based on an empirical $cB\Omega$ model, Varotsos and Alexopoulos [80] related self-diffusion with other bulk thermodynamic properties. They calculated self-diffusion coefficients for several BCC metals: Na, Li, K, W, and Nb [88,89]. Falter and Zierau [90] extended the $cB\Omega$ model to tungsten and estimated its bulk moduli at high temperatures from self-diffusion data.

It is well known that diffusion coefficients follow the equation:

$$D = D_0 \exp(-g_{\text{act}}/kT), \quad (42)$$

where g_{act} is the Gibbs activation free energy. Since $g_{\text{act}} = h_{\text{act}} - s_{\text{act}}T$, Eq. (42) can be expressed as:

$$D = D_0 \exp(s_{\text{act}}/k) \exp(-h_{\text{act}}/kT), \quad (43)$$

where s_{act} and h_{act} are the activation entropy and enthalpy, respectively. According to the empirical $cB\Omega$ model [91], the activation free energy is:

$$g_{\text{act}} = c_{\text{act}} K_T \Omega, \quad (44)$$

where c_{act} is a constant independent of the temperature and pressure, K_T is the isothermal bulk modulus and Ω is the mean volume per atom. Substituting Eq. (44) in Eq. (42) relates the diffusion coefficient to the bulk modulus as:

$$D = D_0 \exp(-c_{\text{act}} K_T \Omega / kT). \quad (45)$$

Following Eq. (45), the bulk modulus K_T at any temperature can be expressed in terms of the diffusion coefficient as:

$$K_T = -K_T^0 \exp\left(-\int_0^T \alpha_V dT\right) \ln\left(\frac{D}{D_0}\right) \frac{kT}{h_{\text{act}}}, \quad (46)$$

in addition:

$$K_S = K_T \left(1 - K_T \frac{\alpha_V^2 V T}{C_p}\right)^{-1}. \quad (47)$$

Here, α_V is the coefficient of thermal expansion, C_p the specific heat, K_T^0 the linear extrapolation of K_T to zero temperature, and V the molar volume. When data for the thermal expansion and the specific heat are available, the bulk modulus at any temperature can be estimated from Eqs. (46) and (47). Falter and Zierau [90] applied this method to K and W. They found strong correlations between thermoelastic and diffusion behavior and were able to calculate the bulk modulus of W from diffusion, thermal expansion, and specific heat data. With our defect mode thermal expansion model and the specific heat data for W at high temperatures, we have recalculated the high temperature bulk moduli for tungsten and compared the results with previous work [87]. There, diffusion data over a limited temperature range are also utilized to calculate the bulk moduli of tantalum. Its thermoelastic and diffusional behavior are closely related. Utilizing available thermoelastic data, the relationships allow the calculation of tantalum self-diffusion coefficients over a broad temperature range. Fig. 7 compares calculated W bulk moduli with the earlier experimental data and Falter and Zierau's [90] calculations. Our bulk moduli results [87] are slightly higher than the earlier calculations at high temperature and indicate a nonlinear reduction of the bulk modulus with increasing temperature. Such an increase is consistent with the defect effects on the thermal expansion.

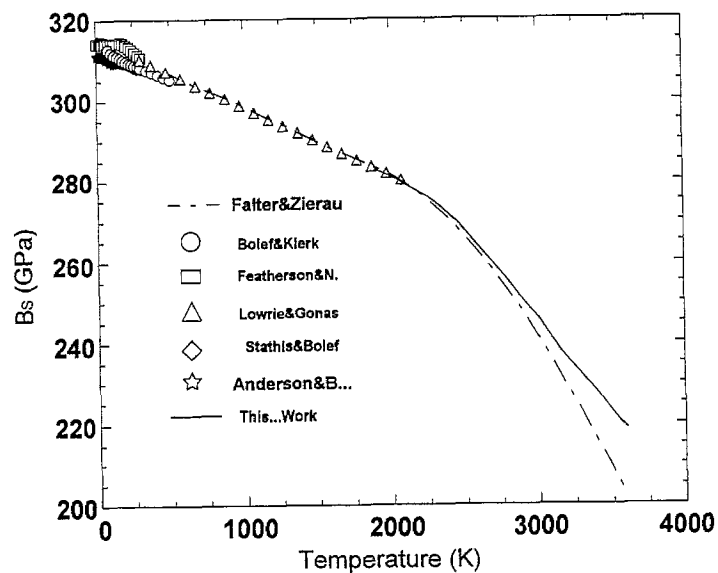


Fig. 7. The adiabatic bulk modulus of W (from Wang and Reeber [87]).

1.8. Thermal expansion of the refractory BCC metals

As the refractory BCC metals have many applications, their thermophysical properties have been the subject of numerous theoretical and experimental investigations. Extensive data on their thermal expansion has been published (e.g., Touloukian et al.'s [23] review includes thirty-three sets of data for V, thirty-six for Nb, seventy-seven for Mo, forty-one for Ta, and sixty-nine for W prior to 1973). Recommended values and polynomial expressions for thermal expansion are provided. Since then, additional measurements on the BCC refractory metals, especially at high temperatures, have become available. However, a critical evaluation of available data from cryogenic to their melting temperatures is needed. Attempts to evaluate this data have been carried out by many investigators [92–95]. With the single exception of Fokin and Chekhovskoi [95], who utilized a defect term with a polynomial, the others simply provided empirical expressions and evaluated data to temperatures significantly below the melting point. In this review, available data for V, Nb, Mo, Ta, and W are analyzed within the constraints of our simple vibrational model and semiempirical equation of state [82].

Three Einstein frequencies for Eq. (15) are sufficient to represent the low to moderate temperature thermal expansions of the BCC refractory metals. The crystal expansion of a defect free pseudo-quasi harmonic crystal can be empirically fitted to experimental data from cryogenic to intermediate temperatures. Fitting parameters X_i , θ_i ($i = 1, 2, \dots, n$) for this 'perfect crystal' are determined by least squares. It is assumed that the difference between the high temperature experimental data and the model extrapolation can be represented by the anharmonic and thermal defect contributions. These, illustrated in the second term of Eq. (35a) or Eq. (35b), are represented by the two empirical parameters A_i and B_i . The first, a pseudo-defect mode, is assumed to represent the high temperature anharmonic effects. The second is assumed to account for the thermal defects introduced at high temperatures. The resulting expressions neglect any small electronic contributions. Eqs. (35a) and (35b) provide a quantitative analytical relationship for calculating the coefficients of thermal expansion of these BCC metals from approximately 20°K to their melting points. The thermodynamic parameters obtained for the thermal defects are compared with other independent studies.

2. Results

2.1. Lattice parameters

To compare the measurements of different investigators, all lattice parameter data have been normalized to 298°K. Table 1 lists the lattice parameters for BCC refractory metals corrected to 298°K and normalized to a Cu $K\alpha_1$ X-ray wavelength of 1.540597 Å, except for Mo which is normalized to Cu $K\beta_1 = 1.39217$ Å. Room temperature lattice parameter references are provided in Table 1 ([96–100]).

Table 1
Lattice parameters of BCC metals at 298°K

Metal	Lattice parameter (Å)	Reference
V	3.02428	[96]
Nb	3.30059	[97]
Ta	3.30280	[98]
Mo	3.14700	[99]
W	3.16540	[100]

Table 2
Thermal expansion model parameters for V, Nb, Mo, Ta, W

Metal	V	Nb	Ta	Mo	W
θ_1 (K)	45.0	70.0	11.25	55.0	15.0
θ_2 (K)	235.0	226.25	151.25	271.25	213.75
θ_3 (K)	827.5	1386.25	675.00	621.25	598.75
X_1 (10^{-7} K^{-1})	1.891	6.592	0.592	0.711	0.368
X_2 (10^{-7} K^{-1})	76.118	66.877	60.086	47.180	39.609
X_3 (10^{-7} K^{-1})	25.999	7.911	10.212	10.318	8.312
A_1 (10^2 K)	5.345	2.277	3.451	1.488	4.410
A_2 (10^4 K)	2.487	19.611	22.281	4.499	30.372
B_1 (K)	6351.935	6757.070	8430.905	5628.810	8647.856
B_2 (K)	17,290.259	23,698.432	28,373.724	18,893.399	30,495.713

2.2. Thermal expansions

The extensive data for all of the BCC metals are referenced in Appendix A. Touloukian et al. [23] in 1973 have tabulated many references, some recommended values and have given polynomial expressions over extended temperature ranges for all metals reviewed. Additional data prior to 1973 and later data are included here. All of the available information is reviewed and the self-consistent sets of data are fitted within the constraints of Eqs. (35a) and (35b). Model parameters for all of the refractory metals are summarized in Table 2.

2.2.1. Vanadium

Other results for vanadium, in addition to the thirty-three cited by Touloukian et al. [23], are included [101–107]. A subtle phase transition at about 200–230 K is reported [108]. Polycrystalline dilatometry data approximate the bulk thermal expansion in this temperature range. Fig. 8a depicts the thermal expansion. Self-consistent data [107,109–112] were fitted within the constraint of Eq. (35a) and the result obtained is plotted as a solid line in Fig. 8a with the majority of the larger data set (data at temperatures lower than 800°K from Brodskiy and Neymark [113] are also utilized in the fitting). Fig. 8b illustrates the difference between experimental results and the perfect crystal model from Eq. (15). The solid line approximates the total contributions of the pseudo-anharmonic and thermal defect modes.

The thermal expansion of vanadium approximately doubles between room temperature and its melting point. The temperature dependence of lattice parameters is given in Fig. 8c.

2.2.2. Niobium

Touloukian et al. [23] reviewed thirty-six sets of thermal expansion measurements for niobium and provided recommended values and polynomial expressions from 100 to 2300°K. Experimental results of other investigators [40,101,105,114–120] are included in this review.

For niobium, no phase transitions complicate the thermal expansion except at cryogenic temperatures where a superconducting phase occurs [109]. Fig. 9a illustrates the thermal expansion of Nb. Self-consistent data [40,103,109,115,116,118–126] are fitted within the constraint of Eq. (35a) to provide the recommended thermal expansion. This solid curve is compared with the majority of the larger data set. Fig. 9b illustrates the difference between experimental results and the perfect crystal as represented by the defect free model. Fig. 9c provides the lattice parameter dependency on temperature.

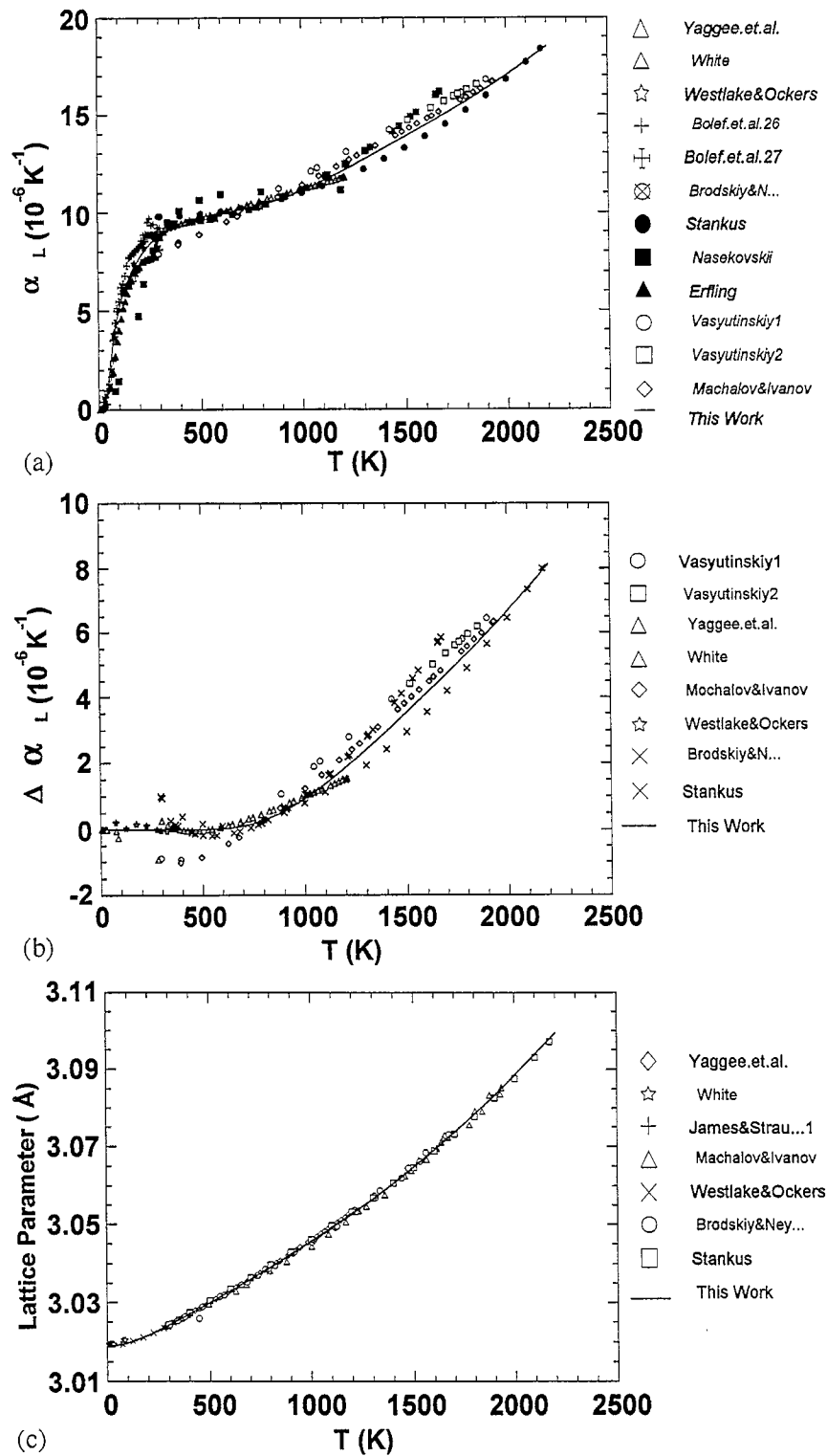


Fig. 8. Thermal expansion of vanadium. (a) The coefficient of linear thermal expansion. (b) Difference of thermal expansion between selected experimental data and the perfect crystal. (c) Selected lattice parameter data and our fitting result.

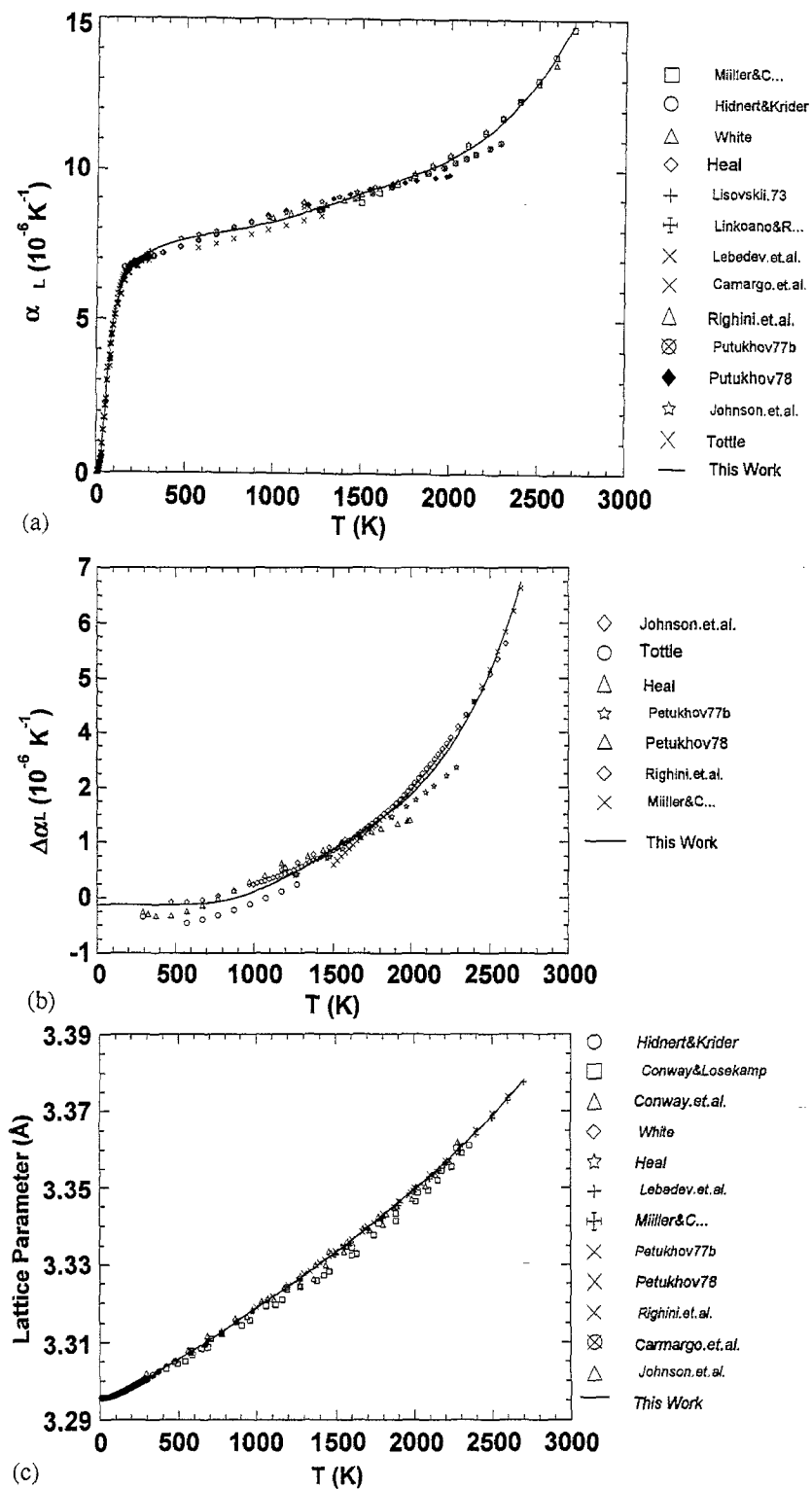


Fig. 9. Thermal expansion of niobium. (a) The coefficient of linear thermal expansion. (b) Difference of thermal expansion between selected experimental data and the perfect crystal. (c) Selected lattice parameter data and our fitting result.

Similar to vanadium, the coefficient of thermal expansion of Nb also increases approximately twofold from room temperature to the melting point. Pseudo-anharmonic and thermal defect modes are also utilized for fitting the excess thermal expansion.

2.2.3. Molybdenum

Touloukian et al. [23] reviewed seventy-seven sets of thermal expansion data for molybdenum, providing recommended values to 2800°K and polynomial expressions from 293 to 2800°K. Slack and Bartram [92] and Fokin and Chekhovskoi [95] have also reviewed the thermal expansion of Mo. Most early references are found in those three reviews. Data exist from other authors [40,105,127–129]. The self-consistent data [40,125,130–138] are fitted within the constraint of Eq. (35a).

Fig. 10a compares selected data for the coefficient of thermal expansion with the calculated results represented by a solid line. Fig. 10b illustrates the differences between experimental data and the ‘perfect crystal’ model. Fig. 10c provides selected data for the lattice parameter temperature dependency and calculated results.

The thermal expansion of Mo increases about threefold, nearly 50% more than V or Nb, from room temperature to its melting point. A pseudo-anharmonic and thermal defect mode are also applied for fitting the excess expansion contribution as illustrated in Fig. 10b.

2.2.4. Tantalum

Touloukian et al. [23] reviewed forty-one sets of thermal expansion data for tantalum and have provided recommended values and polynomial expressions from 293 to 3200°K. Other data have also been published [40,105,110,139–143]. The self-consistent data [40,109,132,133,142–145] are fitted within the constraint of Eq. (35a).

Fig. 11a compares selected data for the coefficient of thermal expansion with result from Eq. (35a) shown by a solid curve. Fig. 11b illustrates differences between selected data and the ‘perfect crystal’ model. Two additional modes similar to other BCC metals were utilized in the fitting. For Ta, the thermal expansion from room temperature to the melting point increases approximately twofold. Fig. 11c compares selected sets of lattice parameter data as a function of temperature with our model.

2.2.5. Tungsten

Sixty-nine sets of data for the coefficients of thermal expansion of tungsten were reviewed by Touloukian et al. [23]. The thermal expansion of W has also been reviewed by Slack and Bartram [92] and White and Roberts [93]. Most references are found in these three reviews with the exception of the following works [26,40,44,102,105,128,139,141,146–155]. The self-consistent data sets [36,40,134,155–161] are fitted within the constraint of Eq. (35a).

Fig. 12a compares selected data with model calculations (solid line) from Eq. (35a) for the thermal expansion of tungsten. Fig. 12b illustrates the difference between the experimental data and the perfect crystal or defect-free model. The fitting parameters for the two additional Einstein modes required are displayed in Table 2. The thermal expansion for W increases about threefold from room temperature to the melting point. Fig. 12c compares selected experimental lattice parameters as a function of temperature for W with our recommended values.

2.3. Defect formation enthalpies and their contributions to thermal expansion

Figs. 8b, 9b, 10b, 11b and 12b illustrate differences between the experimental data and the ‘perfect’ crystal model for these metals. The respective enthalpies of the pseudo-anharmonic and the thermal defect modes obtained here are compared with the results of other investigators in Table 3.

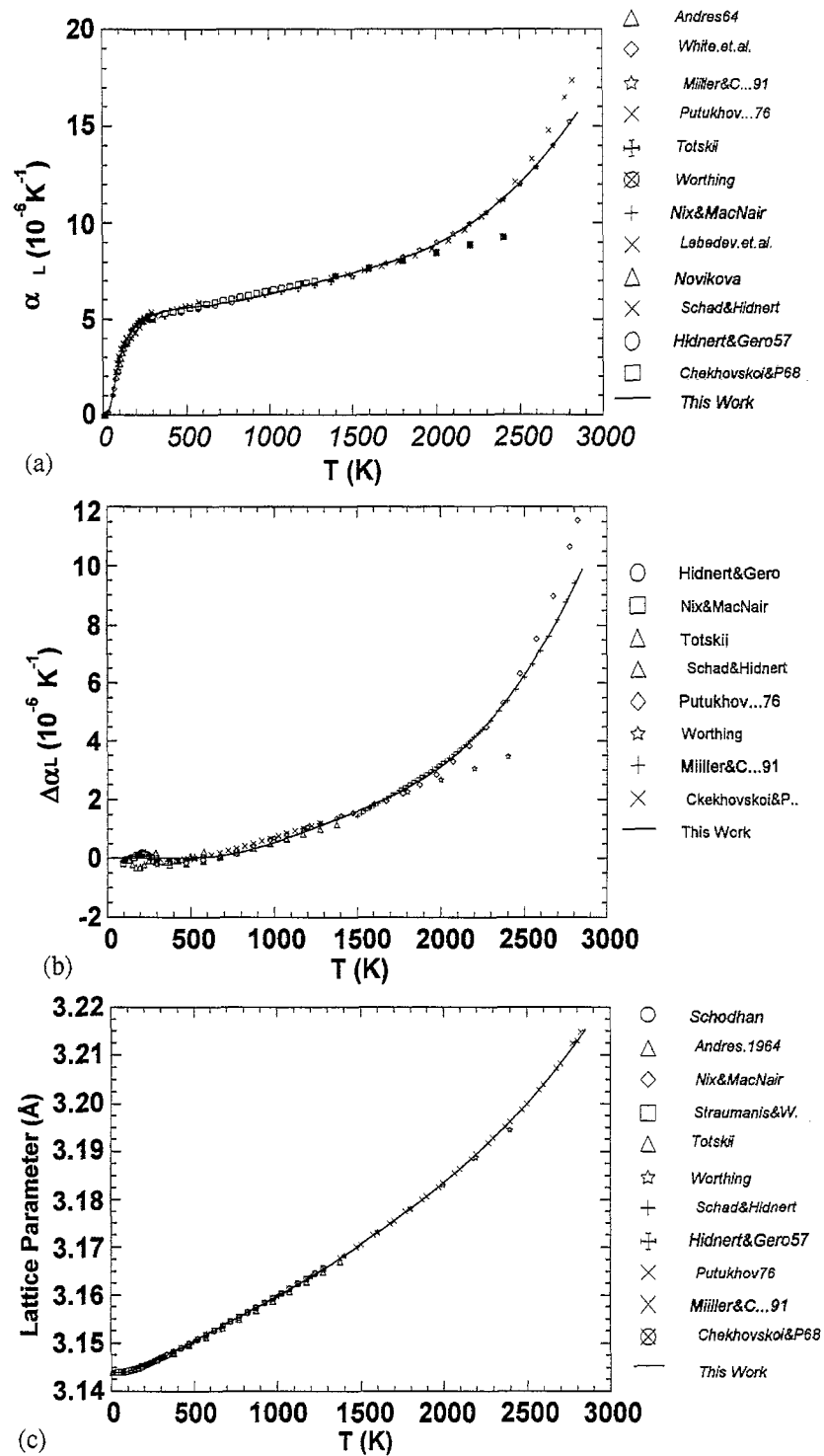


Fig. 10. Thermal expansion of molybdenum. (a) The coefficient of linear thermal expansion. (b) Difference of thermal expansion between selected experimental data and the perfect crystal. (c) Selected lattice parameter data and our fitting result.

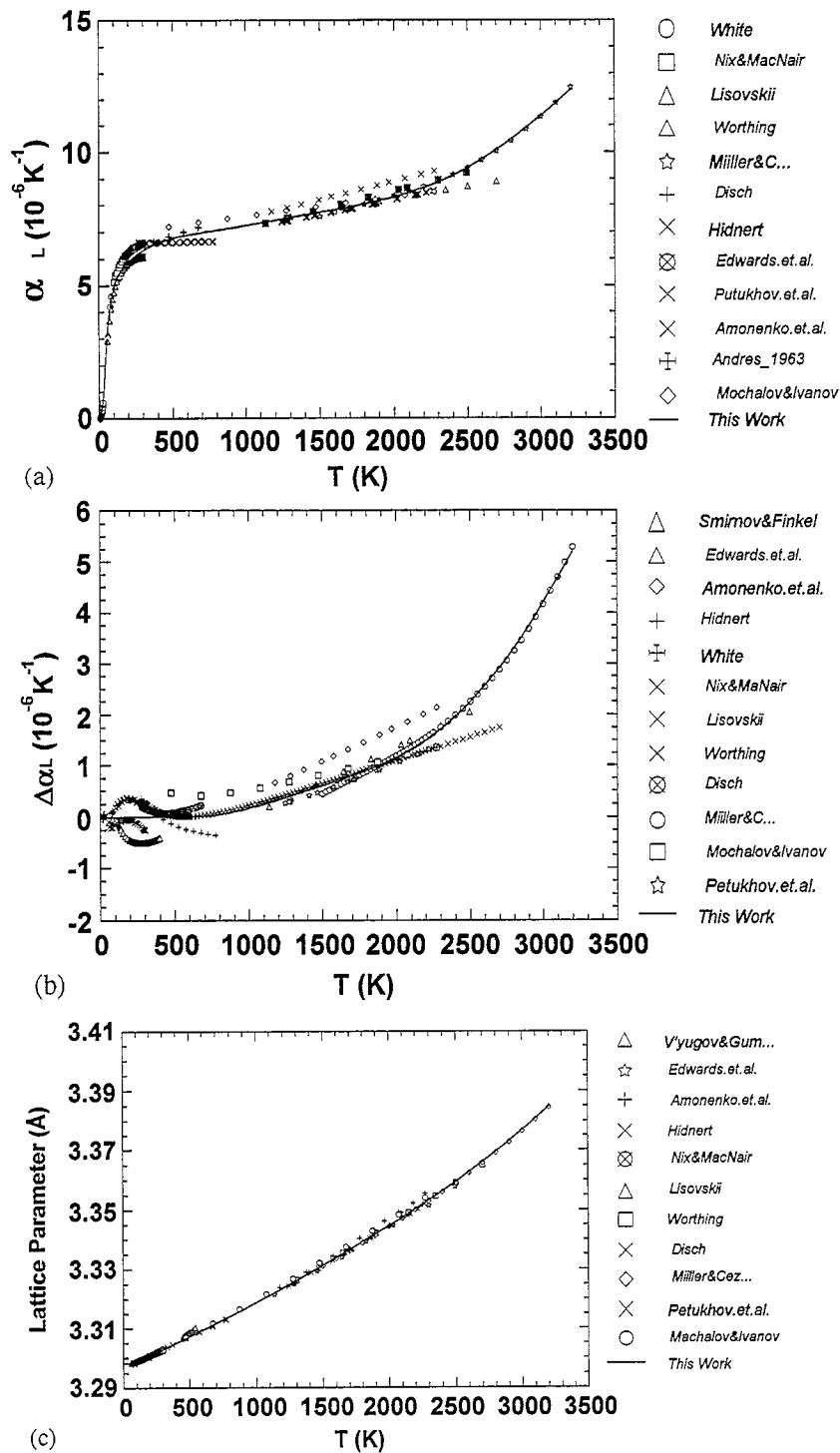


Fig. 11. Thermal expansion of tantalum. (a) The coefficient of linear thermal expansion. (b) Difference of thermal expansion between selected experimental data and the perfect crystal. (c) Selected lattice parameter data and our fitting result.

Our estimates of the thermal defect modes are in reasonable agreement with the results of other workers utilizing different methods. It is evident that the enthalpies for the first mode are very small. Because

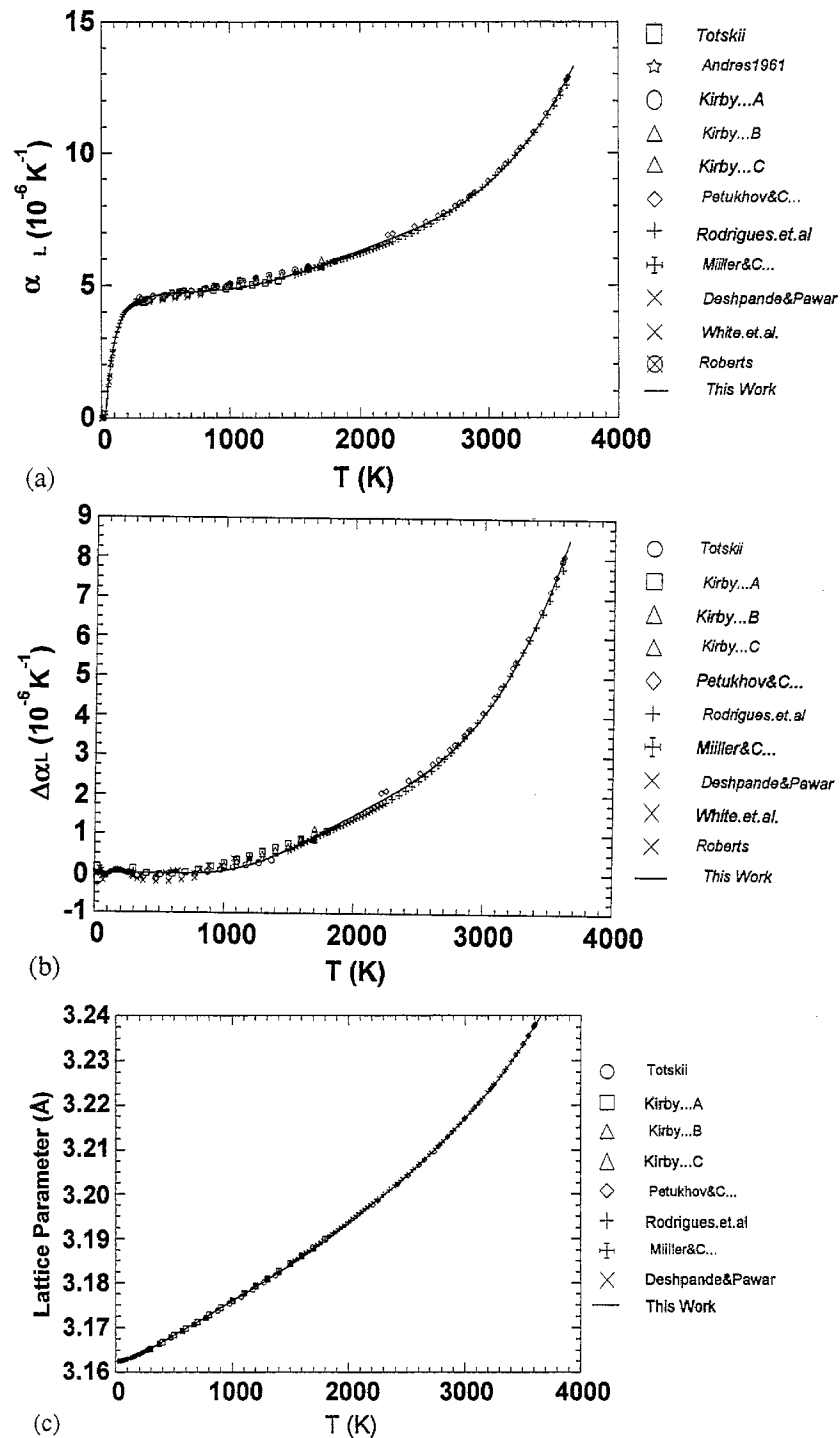


Fig. 12. Thermal expansion of tungsten. (a) The coefficient of linear thermal expansion. (b) Difference of thermal expansion between selected experimental data and the perfect crystal. (c) Selected lattice parameter data and our fitting result.

of the former, the first mode is attributed to anharmonic contributions and the second one to thermal defects. The formation enthalpies for the second mode are slightly smaller than those from other investigations, with the exception of Nb. This is interesting considering that the defect mode lattice

Table 3
Comparison of formation enthalpies (unit in eV)

	Maier et al. [2]	Kraftmakher and Strelkov [165]	This work	
			Mode 1	Mode 2
V	2.1 ± 0.2		0.55	1.49
Nb	2.6 ± 0.3	2.04	0.58	2.04
Ta	2.8 ± 0.6	2.90	0.73	2.44
Mo	3.0 ± 0.2	2.24	0.48	1.63
W	4.0 ± 0.3	3.15	0.74	2.63

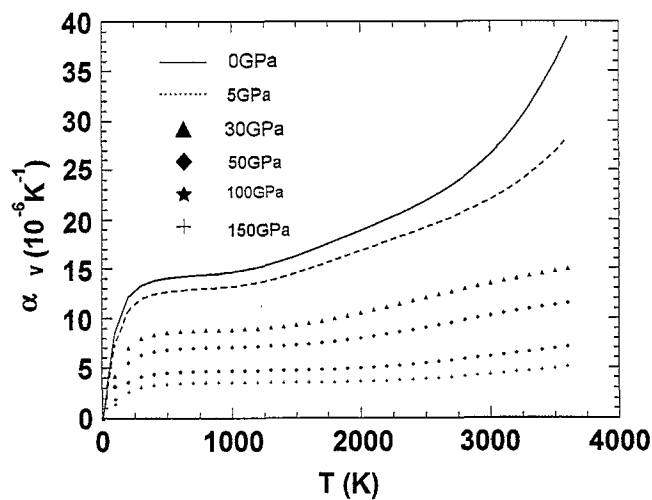


Fig. 13. Thermal expansion of tungsten at high temperatures/pressures.

vibration model is such a simple one. Other factors, such as the temperature dependence of the defect formation parameters, possible defect ordering, and the general uncertainty of the formation entropy values will be discussed later.

2.4. High pressure thermal expansion of tungsten

The high pressure thermal expansion of BCC refractory materials can be theoretically calculated if the thermodynamic properties at atmospheric pressure are known [87,162]. The high pressure thermal expansions of MgO [84] and NaCl [81] have previously been calculated. The same approach is used for tungsten. A defect formation volume of 55% is applied in the calculation for tungsten. This is constrained by its effect on the temperature dependence of the compressibility for a 'perfect crystal'. Larger values, such as 60%, result in an unrealistic increase in the compressibility with temperature. Fig. 13 shows the temperature/pressure dependence of thermal expansion for tungsten. The defect contribution is less than 1% at 30 GPa and 3600°K. At higher pressures, this contribution can be neglected. This general approach should be valid for calculating the high pressure thermal expansion of all BCC metals.

3. Discussion and conclusions

Thermal expansions at selected high temperatures for these five BCC refractory metals are listed in Table 4. To compare the interrelationships among these metals, it is desirable to normalize their

Table 4
The thermal expansion of BCC refractory metals at selected temperatures

T (K)	V		Nb		Ta		Mo		W	
	α_L	a (Å)	α_L	a (Å)	α_L	a (Å)	α_L	a (Å)	α_L	a (Å)
50	1.73	3.01925	2.08	3.29570	3.01	3.29811	0.68	3.14396	1.07	3.16261
100	5.13	3.01980	5.07	3.29632	5.10	3.29882	2.79	3.14425	2.86	3.16294
150	6.74	3.02071	6.21	3.29727	5.82	3.29973	3.98	3.14479	3.64	3.16346
200	7.72	3.02181	6.71	3.29834	6.22	3.30072	4.62	3.14547	4.05	3.16408
250	8.38	3.02303	7.00	3.29947	6.46	3.30177	4.98	3.14623	4.29	3.16474
300	8.85	3.02433	7.21	3.30064	6.62	3.30285	5.21	3.14703	4.44	3.16543
400	9.43	3.02711	7.49	3.30307	6.81	3.30507	5.46	3.14871	4.60	3.16686
500	9.75	3.03001	7.67	3.30558	6.90	3.30734	5.59	3.15046	4.68	3.16833
600	9.97	3.03300	7.79	3.30813	6.96	3.30963	5.69	3.15224	4.72	3.16982
700	10.17	3.03606	7.89	3.31073	6.99	3.31194	5.79	3.15405	4.75	3.17133
800	10.42	3.03919	8.00	3.31336	7.02	3.31427	5.93	3.15590	4.78	3.17284
900	10.75	3.04240	8.12	3.31603	7.06	3.31660	6.10	3.15780	4.82	3.17436
1000	11.16	3.04574	8.26	3.31875	7.11	3.31896	6.29	3.15976	4.87	3.17590
1100	11.63	3.04921	8.42	3.32152	7.18	3.32133	6.51	3.16178	4.94	3.17746
1200	12.15	3.05283	8.60	3.32435	7.27	3.32373	6.73	3.16387	5.03	3.17904
1300	12.71	3.05663	8.80	3.32724	7.37	3.32616	6.96	3.16604	5.14	3.18066
1400	13.28	3.06060	9.00	3.33020	7.49	3.32864	7.18	3.16828	5.28	3.18232
1500	13.87	3.06476	9.20	3.33323	7.62	3.33115	7.41	3.17059	5.43	3.18402
1600	14.47	3.06910	9.41	3.33634	7.77	3.33372	7.65	3.17297	5.59	3.18578
1700	15.08	3.07364	9.63	3.33951	7.91	3.33633	7.91	3.17544	5.76	3.18758
1800	15.70	3.07838	9.85	3.34277	8.07	3.33900	8.20	3.17800	5.94	3.18945
1900	16.35	3.08331	10.10	3.34610	8.23	3.34172	8.53	3.18066	6.12	3.19137
2000	17.03	3.08846	10.39	3.34953	8.39	3.34450	8.92	3.18344	6.30	3.19335
2100	17.75	3.09383	10.73	3.35307	8.56	3.34733	9.38	3.18635	6.48	3.19539
2200	18.50	3.09945	11.14	3.35674	8.74	3.34950			6.67	3.19749
2300			11.63	3.36056	8.93	3.35319			6.86	3.19965
2400			12.23	3.36457	9.15	3.35622			7.07	3.20188
2500			12.95	3.36880	9.39	3.35934			7.29	3.20418
2600			13.81	3.37331	9.68	3.36254			7.53	3.20656
2700			14.82	3.37814	10.00	3.36585			7.80	3.20901
2800					10.38	3.36928			8.11	3.21157
2900					10.82	3.37285			8.46	3.21423
3000					11.32	3.37658			8.87	3.21702
3100					11.91	3.38050			9.33	3.21994
3200					12.57	3.38464			9.87	3.22303
3300									10.48	3.22631
3400									11.17	3.22980
3500									11.97	3.23353
3600									12.81	3.23753

thermal expansions according to their Debye and melting temperatures. Table 5 lists the characteristic values for these metals. Fig. 14 gives the thermal expansion normalized with their respective Debye temperatures, θ_D [163], and melting points, T_M [164]. Results for V, Nb, Ta, Mo, and W fall into two distinct subgroups relative to their position in columns VB and VIB of the periodic table. The relative thermal expansion values correspond to elemental positions in the periodic table. The thermal expansion increases about twofold for group VB metals and threefold for group VIB metals from the Debye temperature to their respective melting points. At temperatures below the Debye temperature, all are similar. Thermal expansion increases more rapidly for the lighter metals. In contrast, when the thermal expansions are normalized relative to their melting temperatures, Fig. 14b, the relative thermal expansions for group VB metals are higher than and distinct from the group VIB metals. This suggests

Table 5
Characteristic parameters for BCC refractory metals

	V	Nb	Ta	Mo	W
θ_D	399.2	276.6	263.8	474.5	384.4
T_{MP}	2183	2742	3293	2896	3695
α_D	9.42	7.12	6.51	5.56	4.58
α_{MP}	18.37	15.30	13.27	16.23	13.73

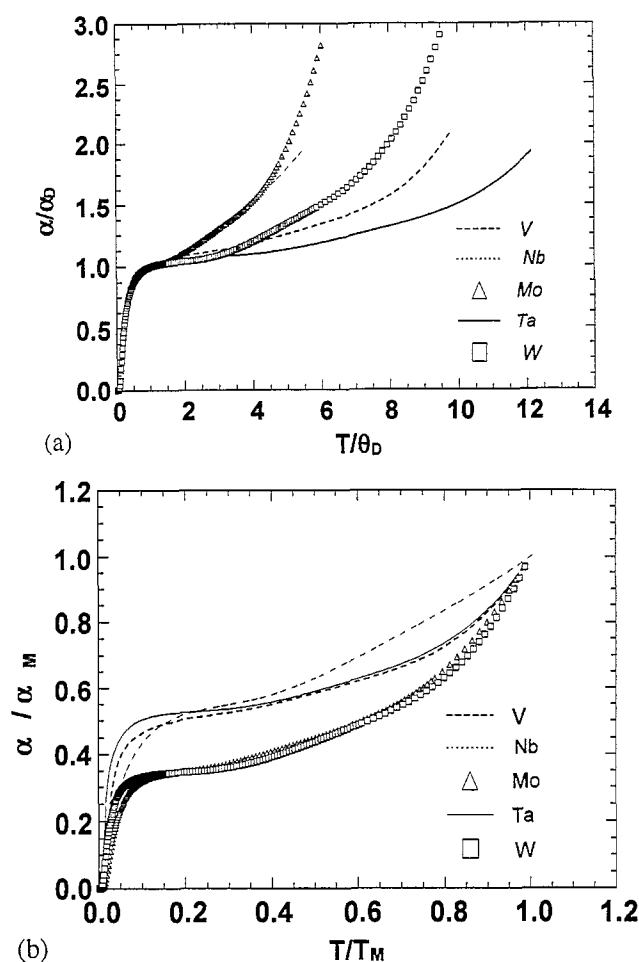


Fig. 14. Normalized thermal expansion according to characteristic temperatures. (a) Relative to Debye temperature. (b) Relative to melting temperature.

that the melting temperature may be a more fundamental thermodynamic scaling parameter than the Debye temperature.

Fig. 15 compares our results with those of previous workers. In Fig. 15a, Touloukian et al. [23] recommended thermal expansions calculated from their polynomial expressions are compared. Differences are all less than 10% for temperatures less than 1500°K. However, for Ta, the relative difference reaches 90% at the highest temperature. This is partly because their review was, unfortunately, based on earlier measurements where the purity of the samples and the sample annealing procedures affected the experiments. Our review included much later measurements [40]. Fig. 15b

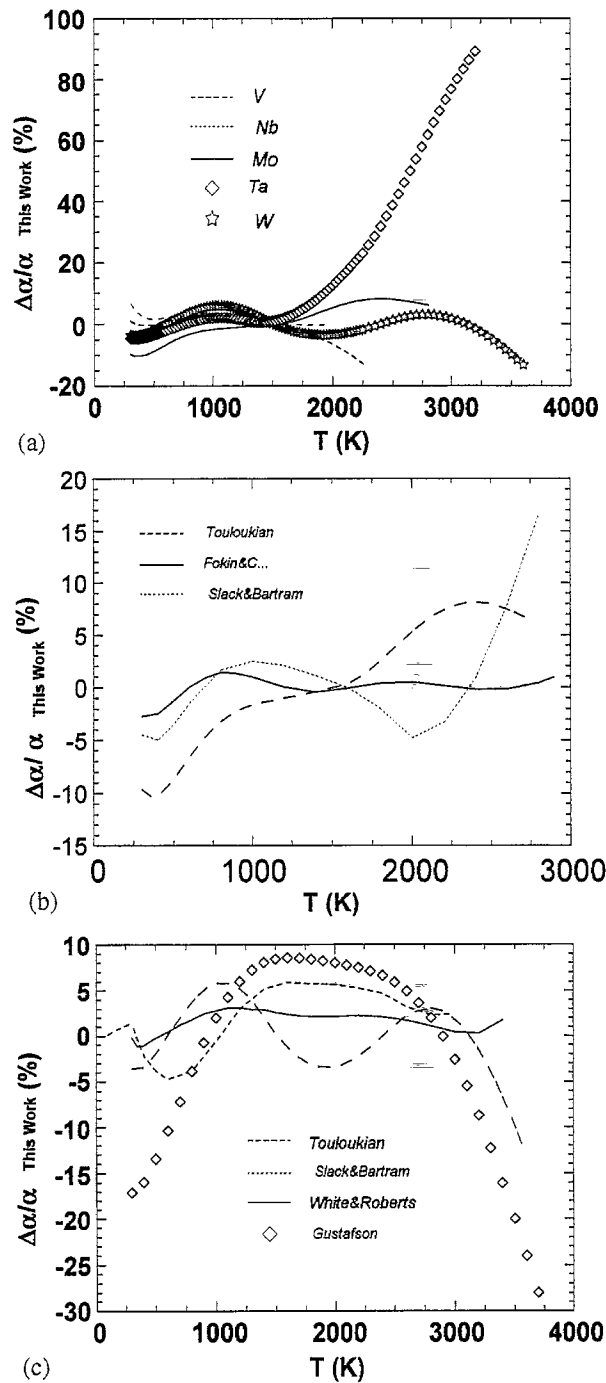


Fig. 15. (a) Comparison with the estimates of Touloukian et al [23]. (b) Comparison with previous work for Mo. (c) Comparison with previous results for W.

illustrates previous evaluations for Mo [23,92,95]. The difference between our results and Touloukian et al.'s [23] reaches a maximum deviation of only 10%. Slack and Bartram [92] had larger deviations, about 17% at their highest temperature. Fokin and Chekhovskoi's [95] evaluation is within 3% of our estimate. They utilized similar data but a slightly different analytical approach. Fig. 15c compares our results with previous reviews for W [23,92–94]. White and Roberts' [93] values are within 3% of

ours to their highest temperature of 3400°K. The largest difference between Slack and Bartram's review and our results is only 6% with their highest temperature limited to 3000°K. Touloukian et al.'s evaluation is 12% lower than ours at 3600°K. The trend of the polynomial representations is illustrated in Fig. 15c. Gustafson's [94] results are about 28% lower than our work at the highest temperature.

The contribution of defects to the thermophysical properties is still a controversial issue. Different conclusions are sometimes obtained from similar experiments [165,166]. It is seen from Eq. (31) that thermal expansion is dependent not only on formation enthalpy, but also on the formation entropy and the ratio between the formation volume of the defect and the mean atomic volume per atom of the crystal. Formation parameters obtained by earlier investigators are usually different from each other for they often used different approaches. The ratio between the formation volume of a defect and the mean atomic volume per atom of the crystal remains uncertain. A value of 60% of the mean atomic volume per atom has been assumed reasonable for most metals [3,165].

Positron annihilation provides much smaller estimates of the formation entropies, but yields higher formation enthalpies than the specific heat method for the BCC refractory metals [2,165]. It has been suggested that positron annihilation tends to provide higher formation enthalpies and lower entropies for the FCC metals [167]. According to the latest differential dilatometry experiments [5], the measured formation entropies are three times higher than the early published measurements [168] for the FCC metals. If this is assumed to be the case for the BCC metals, vacancy contributions will provide greater contributions to their thermal expansions. Varotsos [169] has proposed a thermodynamic method for estimating the upper and lower limits for the formation entropy. Kraftmakher [3] applied that approach to calculate the formation entropies for metals. His results are higher than the earlier positron annihilation estimates. The improved values of the thermodynamic parameters in this study provide new upper and lower limits at 90% of the respective melting points.

Table 6 lists our results for the formation entropy with estimates from earlier investigations [2,165]. These values were recalculated with a formation volume of 55% for comparison with our results. It is seen that Maier et al.'s [2] estimates of the formation entropies are either close to or smaller than our lower limits. Estimates of the formation entropies by Kraftmakher and Strelkov [165] are higher than our upper limits. Disregarding divacancies, these estimates are close to the upper limits except for Mo. As an example of the relative differences of the estimates, Fig. 16 illustrates the defect contributions to the thermal expansion for W calculated from the formation parameters in Table 6. The defect contributions are negligible when calculated with Maier et al.'s parameters. Their formation entropies are low and the corresponding formation enthalpies are high. Kraftmakher and Strelkov's [165] formation entropies are too high and provide a significant defect contribution to the thermal expansion. Fig. 16 illustrates that the defect contributions to thermal expansion can be very sensitive to the defect formation parameters.

In summary, data for V, Nb, Ta, Mo and W have been critically reviewed in terms of a model that includes the contributions from a pseudo-quasi harmonic perfect crystal, the crystal anharmonicity,

Table 6
The Formation entropies of BCC refractory metals

	Maier et al. [2]	Kraftmakher and Strelkov [165]	Upper limit (0.9 T_M)	Lower limit (0.9 T_M)	This work
V	2.0		2.9	1.5	2.06
Nb	2.0	4.15	3.4	1.7	3.81
Ta	2.0	5.45	3.6	1.8	3.76
Mo	2.0	5.7	4.3	2.2	2.56
W	2.0	6.5	4.2	2.1	3.99

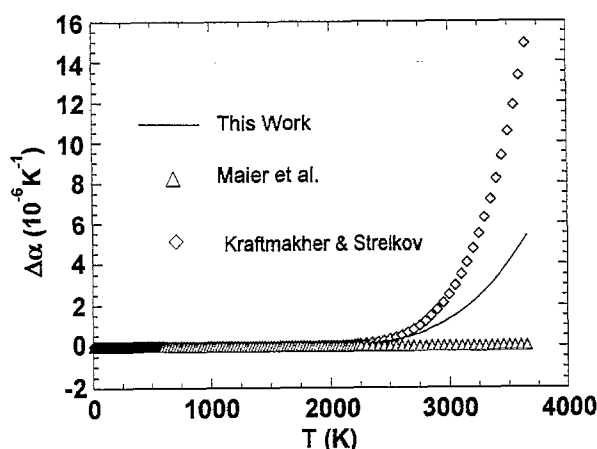


Fig. 16. The thermal defect contributions to thermal expansion calculated from different formation parameters.

and the crystal's thermal defects. Quantitative expressions are provided for the coefficient of thermal expansion for these BCC metals from near 20°K to their melting temperatures. Contributions of thermal defects are discussed. Vacancy formation enthalpies and entropies are estimated. These contributions, which are very sensitive to the magnitude of the defect formation parameters, are compared with earlier thermodynamic predictions and previous work from positron annihilation, thermal expansion, and specific heat measurements.

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Appendix A

References of thermal expansion data for V, Nb, Ta, Mo, and W

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