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Estimating enthalpy and bulk modulus from thermal expansion data — a case study with α-Al_2O_3 and SiC

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Abstract

A simple thermodynamic framework has been formulated for calculating elastic properties from a knowledge of thermal expansivity and specific heat or vice versa. This approach rests on the validity of two plausible assumptions. In the first, by assuming the ratio (λ) of thermal expansivity (α_V) to isobaric specific heat (C_P) to be temperature independent, certain approximate expressions connecting rather explicitly the temperature dependence of volume and enthalpy with that of bulk modulus have been derived. In the second step, where this ratio happens to be mildly temperature dependent, a different functional relationship between thermal and elastic quantities has been established by invoking the temperature independence of Anderson-Gruneisen (δ_S) parameter. The application potential of these relations in estimating the thermophysical data for the missing quantities from known ones has been investigated against α-Al_2O_3 and SiC by estimating their bulk moduli from respective thermal expansion and enthalpy data. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

It is often the case that most of the problems in materials engineering can be treated effectively if, accurate knowledge of materials properties is readily available. However, in practice, the scenario is such that the existing experimental data on thermal and elastic properties for many materials, except for a few standard ones, are often incomplete. Even in those cases where critically assessed data exists, very little seems to have been done with respect to ensuring their internal consistency.[1] In this regard an important aspect concerning the latter issue is the judicious use of appropriate thermodynamic formalism(s) that would serve to link in a consistent manner the available information on various physical properties. This point is of considerable importance in such systems, where the existing information is somewhat inhomogeneous. That is, the availability of extensive information on one or few physical quantities is accompanied by only scarce data for the other related physical properties. Therefore, the task of estimating the missing quantities from the known ones becomes crucial and this must be sought on proper theoretical basis. It is in this context, we present in this paper, a simple thermodynamic framework that addresses the possibility of a well-defined interrelationship between volume thermal expansivity (α_V), enthalpy (H) and compressibility (κ_T) of a simple condensed system.

In essence, we explore the thermodynamic consequences of two plausible hypotheses widely prevalent in thermal physics. In the first, by taking the ratio (λ) of volume thermal expansivity (α_V) to isobaric specific heat (C_P) to be temperature independent, we derive using established thermodynamic principles, simple exponential relations connecting rather explicitly the enthalpy (H) and adiabatic bulk modulus (B_S) with volume ratio (V_T/V_O). Secondly, in cases where this ratio (λ) happens to be temperature dependent, a different functional relationship based on the constancy of the adiabatic Anderson–Gruneisen parameter (δ_S) with temperature has been established for estimating enthalpy from thermal expansion data. It must be stated that the present formalism is valid only at temperatures exceeding the

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Debye characteristic temperature (θ_D). Although, the proposed method is based on the temperature insensitivity of certain carefully chosen thermophysical parameters, it is simple to implement, and further can be used in discrete temperature ranges within which the above mentioned assumptions are expected to be obeyed effectively. In the following section the necessary theoretical framework is dealt with briefly.

2. Development of basic thermodynamic relations

2.1. Relationship between thermal expansion and enthalpy

Let us begin with the definition of the thermal Gruneisen parameter (γ_G).[2]

$$\gamma_G = \alpha_V B_S V / C_P, \tag{1}$$

where α_V is the coefficient of volume thermal expansion, V is the (molar) volume, B_S is the adiabatic bulk modulus and C_p is the isobaric (molar) specific heat.

Upon rearranging Eq. (1) we get

$$\gamma_G/(B_S V) = \alpha_V/C_P. \tag{2}$$

Deferring a detailed inquiry to a latter point in this paper, it is first assumed as a trial measure that the ratio of thermal expansivity (α_V) to isobaric specific heat(C_P) is a temperature independent constant (λ). That is,

$$\alpha_V/C_P = \lambda, \tag{3}$$

Further, by substituting the definition of $\alpha_V = V^{-1}(\partial V/\partial T)_P$ in Eq. (3) we obtain

$$1/V(\partial V/\partial T)_P = C_P \cdot \lambda. \tag{4}$$

Separating the variables we may rewrite Eq. (4) as,

$$\int dV/V = \lambda \int C_P \, dT. \tag{5}$$

Recalling $\lambda \int C_P \, dT = \lambda \int dH$, we perform the integration between the limits set by $T = \{T_o, T\}$ and $V = \{V_o, V_T\}$, to obtain the following relation connecting $\eta = V_T/V_o$ the volume ratio, and $\Delta H = H_T\text{-}H_o$, the corresponding enthalpy difference.

$$\ln (V_T/V_o) = ln\ (\eta) = \lambda \, \Delta H. \tag{6}$$

or,

$$V_T = V_o \exp(\lambda \, \Delta H). \tag{7}$$

In Eqs. (6) and (7) V_0 is the reference volume at the reference temperature T_0. Since $V \propto a^3$ where a being the lattice parameter and further $V \propto 1/\rho$, ρ being the density, Eq. (7) can be rewritten in the following useful forms.

$$a_T = a_o \exp[(\lambda/3) \, \Delta H]. \tag{8}$$

$$\rho_T = \rho_o \exp(-\lambda \, \Delta H). \tag{9}$$

Eqs. (6)–(9) can be used to estimate isobaric volume thermal expansion from the corresponding data on enthalpy or vice versa by just requiring the value of α_V/C_P at one reference temperature (T_o).

It is quite likely that for many solids the assumption that thermal expansivity varies linearly with specific heat is not strictly obeyed over an extended temperature range. But, as illustrated in Fig. 1, the linear variation of α_V over C_P is only marginally affected even at very high temperatures for most of the normal solids. It is clear from this figure, that for temperatures not too close to the melting point, where higher order anharmonicity effects and the defect contributions become important, the temperature independence of λ is fairly maintained.

On the other hand, even in cases, where λ exhibits a mild temperature dependence it is still possible to estimate enthalpy from thermal expansion data by taking a slightly different route. This involves invoking directly the temperature invariance of another popular thermophysical parameter namely the adiabatic Anderson–Gruneisen parameter (δ_S). This method is described below.

2.2. Isobaric enthalpy variation with volume via Anderson–Gruneisen parameter

Let us rearrange Eq. (1) in a slightly different manner.

$$\gamma_G \, (C_P/V) = \alpha_V \, B_S. \tag{10}$$

By substituting $C_P = (\partial H/\partial T)_P$ and $\alpha_V = (1/V)\,(\partial V/\partial T)_P$ in Eq. (10), we get

$$(\gamma_G/V)\,(\partial H/\partial T)_P = (1/V)\,(\partial V/\partial T)_P \, B_S. \tag{11}$$

or

$$\gamma_G \int dH = \int B_S \, dV. \tag{12}$$

In deriving Eq. (12), γ_G is assumed to be temperature independent. At this stage to proceed further, we need to express analytically the isobaric volume dependence

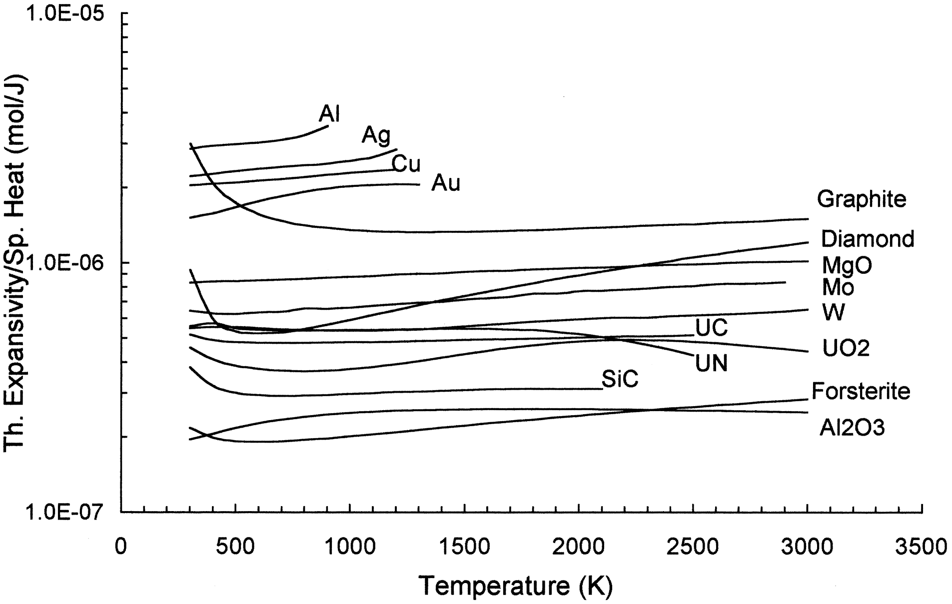

Fig. 1. The apparent temperature independence of the ratio (α_V/C_P) for various solids that differ in their bonding properties is graphically illustrated. The experimental data for α_V and C_P are taken from standard sources and are too numerous to be listed on an individual basis.

of B_S. In this study we shall use a simple functional form proposed by Anderson[3] for expressing the isobaric volume dependence of bulk modulus of many minerals.

$$B_S = B_o\,(\eta)^{-\delta^S}, \tag{13}$$

where $\delta_S \equiv -(\alpha_V B_S)^{-1}\,(\partial B_S/\partial T)_P$, is the adiabatic Anderson–Gruneisen parameter assumed to be temperature independent. Substituting Eq. (13) into Eq. (12) and upon performing integration and subsequent rearrangement of terms, we finally get the following expression

$$H_{T=}H_o\ -\ k\{1-\eta^{(1-\delta S)}\}. \tag{14}$$

where, $k = (B_oV_o)\{\gamma_G\,(1—\delta_S)\}^{-1}$ is again a temperature independent constant. Eq. (14) enables a direct calculation of enthalpy to be made as a function of relative volume (V_T/V_o), once the constant k is known. It should be emphasized that Eq. (14) does not depend on the temperature independence of α_V/C_P; but instead stipulates that γ_G and δ_S must be relatively temperature insensitive. It should also be recalled at this point, that Eq. (14) resembles in spirit and philosophy, another similar approximate thermodynamic relationship of Anderson connecting bulk modulus and enthalpy.[3]

2.3. Estimation of bulk modulus from enthalpy

It is also possible to relate the enthalpy variation with bulk modulus rather more directly by developing further, the original assumption viz. (α_V/C_P) is temperature independent. The procedure is simple and goes as follows.

Starting from Eq. (1), we obtain the following relation

$$\gamma_G\ (\partial H/\partial V)_P = B_S. \tag{15}$$

Differentiating Eq. (7), we can express $(\partial H/\partial V)_P$ in the following manner

$$(\partial H/\partial V)_P = (\lambda V_o)^{-1}\ \exp\{-\lambda \Delta H\}. \tag{16}$$

Substituting for $(\partial H/\partial V)_P$ from Eq. (16) into Eq. (15), we get an appealing approximate relation connecting B_S and ΔH.

$$B_S = \{\gamma_G/(\lambda V_o)\}\ \exp(-\lambda \Delta H). \tag{17}$$

or,

$$\ln(B_S) = \ln\{\gamma_G/(\lambda V_o)\}\ -\ \lambda \Delta H. \tag{18}$$

It should be noted that Eq. (18) assumes the temperature independence of γ_G. Further, it also offers an independent method of obtaining λ from the slope of $\ln(B_S)$ versus ΔH curve. It is interesting to observe that the intercept $\{\gamma_G/(\lambda V_o)\}$ corresponds dimensionally with that of bulk modulus. Therefore it can be used as a scaling factor (B_o) in establishing the functional dependence of B_S with ΔH.

3. Application

The application potential of this model is now investigated by evaluating certain thermophysical properties of two standard ceramics, namely α-Al_2O_3 and 6H-SiC.

3.1. α-Al_2O_3

Befitting to its status as a standard reference material for calibrating thermal property measurements, α-Al_2O_3 possesses a critically assessed thermophysical database.[8–13] It would therefore be interesting to assess the applicability of the present formalism against this reference material. In Table 1, the available experimental data on various thermal and elastic properties are summarised. The experimental C_p, data comes from the recent recommendations of Archer.[10] The data on thermal expansion is taken from the assessment of White and Roberts.[11] The availability of reliable experimental data on bulk modulus is restricted to only about 1800 K.[13] In view of this, we plan to estimate the bulk modulus data for temperatures up to 2000 K from experimental thermal expansion and enthalpy data using Eq. (18). The thermal Gruneisen parameter (γ_G) required for this purpose is estimated from the available data, vide Eq. (1). It turned out that γ_G varies only marginally with temperature (Table 1). For the purpose of calculation we use the value corresponding to the temperature of 300 K. In Fig. 2, the temperature dependence of the ratio α_V/C_p is presented. As can be seen from this figure, α_V/C_p may be taken as almost temperature insensitive. In the present work, we use the average value, which is 2.0389×10^{-7} mol/J.

The calculated and the corresponding experimental bulk modulus values[13] are compared in Table 1. It is evident that the calculated values are in reasonable agreement with the experimental ones, demonstrating the general validity of the procedure developed here. However, for temperatures above 650 K, an increasing deviation between the estimated and experimental values is noticed. This is due to the small, yet finite temperature dependence of λ (Fig. 2). A polynomial fit to the estimated B_s with temperature (T) is given below:

$$B_s(\text{GPa}) = 5 \times 10^{-9}(T/K)^3 - 2 \times 10^{-5}(T/K)^2 - 0.0048\,(T/K) + 256.61. \qquad (19)$$

Using this expression for B_S and experimental thermal expansivity data (Table 1), the adiabatic Anderson–Gruneisen parameter (δ_S) is calculated using the following expression[2]

$$(\delta_S) = -\,(1/\alpha_V B_S)\,(\partial B_S/\partial T)_P. \qquad (20)$$

The calculated δ_S is listed in Table 1.

As a measure of ensuring thermodynamic self consistency, we next proceed to estimate enthalpy, or more appropriately the relative enthalpy $\Delta H = H(T) - H(300)$ using the calculated B_S data in Eq.(14). It is instructive to recall that the use of Eq. (14) does not

Table 1
A listing of experimental data on thermal and elastic properties of α-Al_2O_3[d]

T (K)	C_P[a] (J/mol, K)	α_V[c] (10^{-5} K^{-1})	V[c] (10^{-5} m^3)	B_S[b] (exp) (GPa)	δ_S	γ_G	B_S (cal.) GPa
300	79.45	1.6199	2.5605	253.6	3.761	1.32	252.8
400	96.14	1.9907	2.5650	252.6	3.659	1.34	252.4
500	106.15	2.2350	2.5709	250.9	3.754	1.36	251.9
600	112.50	2.3919	2.5767	248.6	3.935	1.36	251.3
700	116.92	2.4977	2.5832	246.6	4.132	1.36	250.7
800	120.15	2.5762	2.5898	244.4	4.320	1.36	250.1
900	122.67	2.6457	2.5964	242.4	4.467	1.36	249.5
1000	124.70	2.7119	2.6037	240.0	4.579	1.36	248.9
1100	126.43	2.7839	2.6103	237.8	4.630	1.37	248.2
1200	127.95	2.8558	2.6177	235.2	4.645	1.37	247.6
1300	129.35	2.9304	2.6251	232.6	4.614	1.38	246.9
1400	130.67	2.9988	2.6333	230.0	4.553	1.39	246.3
1500	131.91	3.0611	2.6415	228.1	4.447	1.39	245.6
1600	133.09	3.1173	2.6497	225.9	4.317	1.40	245.0
1700	134.23	3.1614	2.6580	224.0	4.159	1.40	244.3
1800	135.33	3.2084	2.6670	221.8	3.963	1.40	243.6
1900	136.40	3.2670					242.9
2000	136.92	3.3579					242.3

[a] The heat capacity C_P is taken from the assessment of Archer.[10]

[b] The adiabatic bulk modulus (B_S), is from Anderson's work.[3,13]

[c] Molar volume (V) and coefficient of volume thermal expansion (α_V) are from White and Roberts.[11]

[d] The experimental data for bulk modulus[13] is available only up to 1800 K. Gruneisen (γ_G) and Anderson–Gruneisen (δ_S) parameters are calculated in the present study.

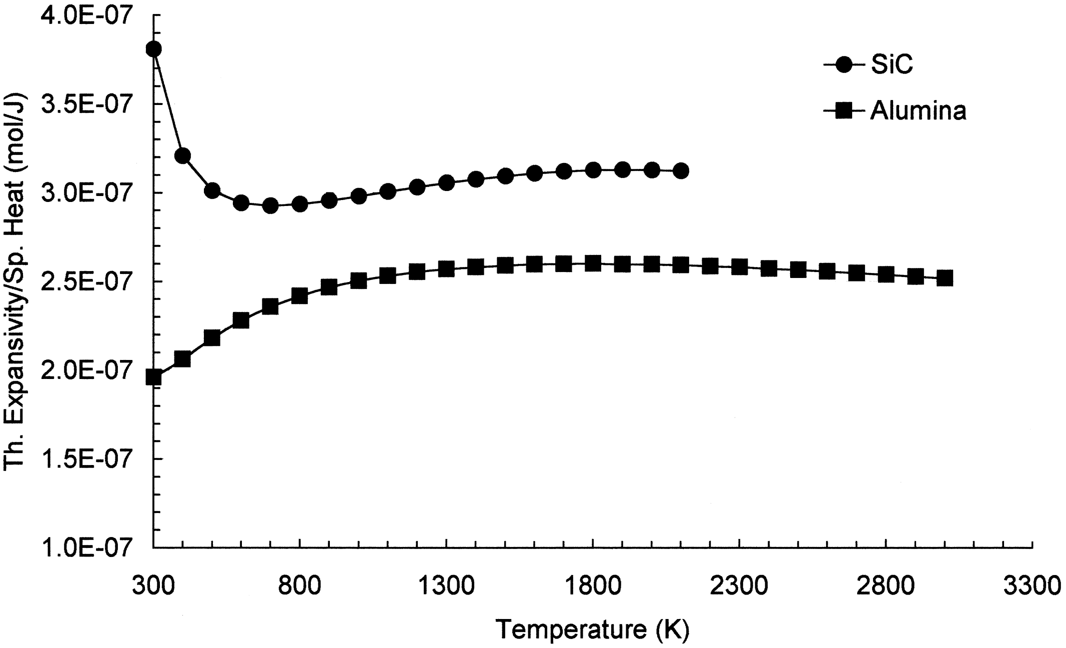

Fig. 2. The temperature dependence of α_V/C_P for α-Al_2O_3 and 6H-SiC is graphically displayed. Note that in the intermediate to fairly high temperature regime, this ratio may be considered as effectively temperature invariant.

stipulate the strict temperature dependence of λ. The enthalpy values thus estimated are compared with its experimental counterpart in Fig. 3. As is evident from this figure, the deviation between these two enthalpy sets is indeed small for temperatures exceeding 500 K. The large deviation observed in the initial 300–500 K region stems from lower than the average value of the Anderson–Gruneisen parameter found in this temperature domain.

3.2. 6H-SiC

The thermophysical property scenario for 6H-SiC has been recently reviewed by Munro.[14] In the present study the thermal expansion data are taken from the X-ray diffraction study of Li and Bradt,[15] and the heat capacity data from the work of Krillin et al.[16] The single crystal elastic properties appear to have been comparatively less investigated. In view of this situation we follow in the present study the recommended polycrystal estimates of Munro.[14] The experimental data on thermal and elastic properties of SiC are surveyed in Table 2. The strategy adopted for SiC is quite similar to that of α-Al_2O_3. As shown in Fig. 2, the ratio α_V/C_P is again fairly temperature independent for temperatures exceeding 500 K. The thermal Gruneisen parameter is also temperature independent, as evident from Table 2. For SiC, we intend to estimate adiabatic bulk modulus (B_S), for which there is a paucity of reliable experimental data,[14] using Eq. (18). The calculation is performed by choosing the following values for the input parameters:

$$\lambda = 3 \times 10^{-7}\text{mol/J};\ \gamma_G = 0.72;\ \text{and}\ V_O = 1.25074 \times 10^{-5}\ \text{m}^3.$$

The results of the calculation are listed in Table 2. As mentioned before, the absence of reliable single crystal elastic property data makes a true comparison of estimated results rather difficult; nevertheless, as can be seen from Table 2, the calculated B_S values compare reasonably well with the experimental isothermal B_S values. We are not aware, to the best of our knowledge, any other estimate of single crystal B_S data for SiC. Judging by the experience of Al_2O_3, it is hoped that the present estimates are reliable ones to the extent permitted by the uncertainties in the input high temperature enthalpy and thermal expansivity data.

4. Discussion

Following the pioneering lead provided by Gruneisen,[4] there have been many studies in the past concerned with probing the interrelationship between various thermophysical quantities.[5,6] In a sense it can be said that the field of classical thermodynamics of solids is a fully matured one, in that, the basic features of the equation of state for condensed phases have been well laid out. However, in actual practice one often needs certain simple enabling interrelationships rather than elaborate recipes for quickly arriving at an estimate for missing thermophysical quantities. In this perspective, it is imperative that the use of any approximate method

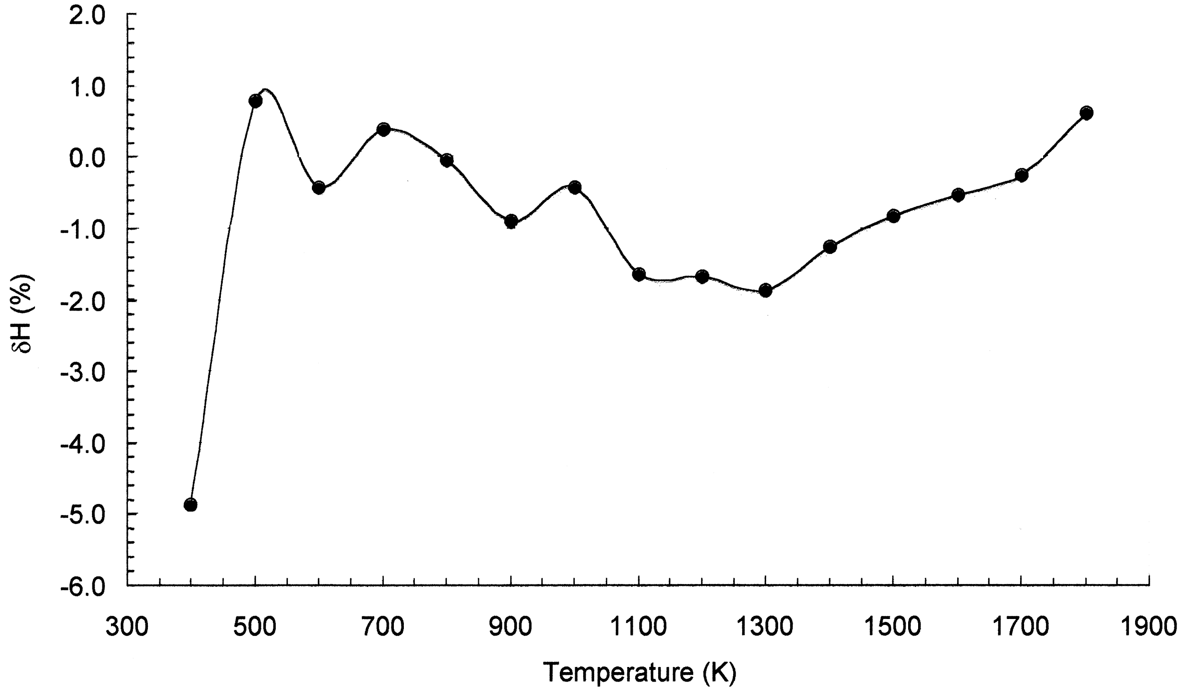

Fig. 3. The calculated enthalpy is compared with the experimental data in the form of percentage error (δH) for α- Al_2O_3. δH is defined as $(H_{cal}-H_{exp})\times 100/H_{cal}$. Note that the agreement between these two sets of values is reasonably good, despite the uncertainty in the assessed experimental data and the small temperature dependence of the Anderson–Gruneisen parameter (δ_S) in the 300–500 K region.

Table 2
A listing of experimental data on thermal and elastic properties of (6H)-SiC[a]

T(K)	C_P(J/mol,K)	α_V(10^{-5}K^{-1})	V(10^{-5} m3)	B_S (exp)(GPa)	γ_G	B_S (cal.)(GPa)
300	27.0565	1.03002	1.24802	203.09	0.9649	
400	34.1524	1.09493	1.24934	201.8	0.8083	
500	38.4147	1.15631	1.25074	200.52	0.7549	191.9
600	41.2732	1.21419	1.25221	199.24	0.7340	191.7
700	43.3481	1.26856	1.25376	197.97	0.7264	191.4
800	44.9503	1.31941	1.25538	196.69	0.7248	191.2
900	46.2477	1.36675	1.25705	195.42	0.7260	190.9
1000	47.3349	1.41058	1.25879	194.15	0.7283	190.6
1100	48.2673	1.4509	1.26058	192.88	0.7309	190.4
1200	49.0788	1.4877	1.26241	191.61	0.7332	190.1
1300	49.7912	1.52099	1.26429	190.35	0.7351	189.8
1400	50.4197	1.55078	1.26621	189.08	0.7364	189.5
1500	50.9759	1.57704	1.26816	187.82	0.7369	189.2
1600	51.4685	1.5998	1.27014	186.56	0.7366	188.9
1700	51.9053	1.61905	1.27214	185.31	0.7353	188.6
1800	52.2926	1.63478	1.27417	184.05	0.7331	188.3

[a] The specific heat is taken from Krillin et al.[16] and thermal expansion is from Li and Bradt[15]. The bulk modulus for polycrystalline SiC is from the assessment of Munro.[14]

must necessarily preserve the overall thermodynamic consistency among various quantities estimated during the course of a critical assessment.[1]

Viewed in this context, the present framework is based on a few proven assumptions. It is a well-appreciated fact in literature that both specific heat and thermal expansion are two diverse, yet related manifestations of the vibrational response of a material.[2] Further at temperatures that are not too low they vary quasi linearly as well. This latter point emerges from a linear chain model, if terms other than the leading one are ignored in representing the anharmonic contributions.[7] Further, as evident from Fig. 1, the available experimental data for many solids with different bonding characters also lends considerable support to the assumption that the ratio of thermal expansivity to heat capacity is fairly temperature insensitive. It must be mentioned that the present treatment does not derive from the use of either Debye or Einstein like approximations that are commonly employed in thermal property estimations. In this sense, the present study is purely thermodynamic in nature and has the advantage of serving as a useful means of ensuring the thermodynamic consistency of a composite thermophysical property database.

5. Conclusions

In conclusion, we may add that not withstanding the limitations of the key assumptions invoked in the present scheme, it is possible to obtain a simple and thermodynamically consistent framework for interrelating thermal and elastic properties. It is hoped that this procedure will be of considerable use in obtaining reliable estimates of quantities for which the experimental information is lacking, from known thermophysical data. Besides, it can also serve as a useful aid for obtaining thermodynamically consistent extrapolations of the limited data into the experimentally unexplored temperature regime. It is this crucial point that makes our thermodynamically self-consistent recipe eminently suited to the task of assessment cum estimation of thermal properties in a holistic fashion.

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