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Analysis of thermal expansivity of solids at extreme compression

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Thermodynamics of solids in the limit of infinite pressure formulated by Stacey reveals that the thermal expansivity (alpha) of solids tends to zero at infinite pressure. The earlier models for the volume dependence of thermal expansivity do not satisfy the infinite pressure behaviour of thermal expansivity. The expressions for the volume dependence of the isothermal Anderson- Grüneisen parameter (delta T) considered in the derivation of earlier formulations for alpha (V) have been found to be inadequate. A formulation for the volume dependence of delta T is presented here which is similar to the model due to Burakovsky and Preston for the volume dependence of the Grüneisen parameter. The new formulation for alpha (V) reveals that delta T infinity must be greater than zero for satisfying the thermodynamic result according to which alpha tends to zero at infinite pressure. It is found that our model fits well the experimental data on thermal expansivity alpha (V) for hcp iron corresponding to a wide range of pressures (0–360 GPa).

Key words: *thermal expansivity, Anderson-Grüneisen parameter, thermodynamics, hcp iron*

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1. Introduction

The Anderson-Grüneisen parameter is an important physical quantity for understanding the thermoelastic properties of solids at high pressures and high temperatures [1]. In the present paper we study the volume dependence of the Anderson-Grüneisen parameter and derive an improved formula for thermal expansivity of solids which is found to be consistent with the thermodynamic constraint at extreme compression. The isothermal Anderson-Grüneisen $\delta_{\mathrm{T}}$is defined as [1]

$$\delta_{\mathrm{T}} = -\frac{1}{\alpha K_{\mathrm{T}}}\left(\frac{\partial K_{\mathrm{T}}}{\partial T}\right)_{\mathrm{P}}, \tag{1}$$

where α is the thermal expansivity or volume thermal expansion coefficient

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} \tag{2}$$

and K_{T}, the isothermal bulk modulus

$$K_{\mathrm{T}} = -V\left(\frac{\partial P}{\partial V}\right)_{\mathrm{T}}. \tag{3}$$

Using the thermodynamic identity

$$\left(\frac{\partial \alpha}{\partial P}\right)_{\mathrm{T}} = \frac{1}{K_{\mathrm{T}}^2}\left(\frac{\partial K_{\mathrm{T}}}{\partial T}\right)_{\mathrm{P}} \tag{4}$$

in equation (1) we get

$$\delta_{\mathrm{T}} = \frac{\alpha}{V}\left(\frac{\partial \alpha}{\partial V}\right)_{\mathrm{T}}. \tag{5}$$

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Equation (5) can be integrated to obtain α as a function of volume V, provided we know the dependence of the Anderson-Grüneisen parameter δ_{T} on V. It has been found by Anderson and Isaak [2] that δ_{T} depends on V in the following manner

$$\delta_{\mathrm{T}} = \delta_{\mathrm{T}}^{0}\left(\frac{V}{V_0}\right)^{k}, \tag{6}$$

where $\delta_{\mathrm{T}} = \delta_{\mathrm{T}}^{0}$ at $V = V_0$, the reference state ($P = 0$). k is a dimensionless thermoelastic parameter defined as [2]

$$k = \left(\frac{\partial \ln \delta_{\mathrm{T}}}{\partial \ln V}\right)_{\mathrm{T}}. \tag{7}$$

An alternative form for $\delta_{\mathrm{T}}(V)$ has been considered by Chopelas and Boehler [3] as follows

$$\delta_{\mathrm{T}} = (\delta_{\mathrm{T}}^{0} + 1)\frac{V}{V_0} - 1. \tag{8}$$

Equation (8) is the basis for an equation of state (EOS) formulated by Kumar [4,5] which turns out to be the same as the usual Tait EOS [6]. Equation (6) with $k = 1$ is also used for developing an EOS and for investigating the thermoelastic properties of solids [7–10].

The Chopelas-Boehler formulation (equation 8) when used in equation (5) gives the following relationship [7,8]

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{-1}\exp\left[-\left(\delta_{\mathrm{T}}^{0} + 1\right)\left(1 - \frac{V}{V_0}\right)\right], \tag{9}$$

where $\alpha_0$is the thermal expansivity at $P = 0$. On the other hand, when the Anderson- Isaak formulation (equation 6) is used in equation (5), we get

$$\frac{\alpha}{\alpha_0} = \exp\left\{-\frac{\delta_{\mathrm{T}}^{0}}{k}\left[1 - \left(\frac{V}{V_0}\right)^{k}\right]\right\}. \tag{10}$$

Anderson et al. [8] have made a comparative study of equations (9) and (10). It should be emphasized here that the Chopelas-Boehler relationship (equation 9) and the Anderson-Isaak formulation (equation 10) are not consistent with the infinite pressure behaviour based on thermodynamics. The thermal expansivity α should tend to zero at extreme compression, V approaching zero [11,12]. But equation (9) predicts $\alpha \to \infty$, and equation (10) gives a finite value of α at extreme compression ($V \to 0, P \to \infty$). We therefore present a revised formulation for α(V).

2. Formulation based on the Burakovsky-Preston model

Burakovsky and Preston [13] have recently formulated a model for the volume dependence of the Grüneisen parameter γ based on the following expression

$$\gamma = \gamma_\infty + a\left(\frac{V}{V_0}\right)^{1/3} + b\left(\frac{V}{V_0}\right)^{n}, \tag{11}$$

where γ_∞ is the value of γ at extreme compression $V \to 0$. The value of γ_∞= 1/2 or 2/3 based on the Thomas-Fermi model [13,14]. γ_∞ is treated as a universal constant, i.e., the same for all materials, whereas a, b and $n(> 1)$ are material-dependent parameters. It was found [15] that the Burakovsky-Preston model equation (11) satisfies the thermodynamic constraints $\gamma \to \gamma_\infty$, $q = (\mathrm{d}\ln\gamma/\mathrm{d}\ln V)_{\mathrm{T}} \to 0$, and $\lambda = (\mathrm{d}\ln q/\mathrm{d}\ln V)_{\mathrm{T}} \to \lambda_\infty$, where γ_∞ and λ_∞ are finite positive values.

It is appropriate to consider that the Anderson-Grüneisen parameter δ_{T} follows a volume dependence similar to equation (11). A similarity for the volume dependence of γ and δ_{T} was pointed out earlier by Tallon [16]. We can thus write

$$\delta_{\mathrm{T}} = \delta_{\mathrm{T}_\infty} + c_1\left(\frac{V}{V_0}\right)^{1/3} + c_2\left(\frac{V}{V_0}\right)^{m}, \tag{12}$$

where $\delta_{T\infty}$ represents the value of δ_T at $V \to 0$. In analogy with equation (11), $\delta_{T\infty}$ can be considered as a universal constant and c_1, c_2 and m as constants for a given material. When we use equation (12) in equation (5), and then on integrating we find the following expression for the thermal expansivity α,

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{\delta_{T\infty}} \exp\left\{-3c_1\left[1-\left(\frac{V}{V_0}\right)^{1/3}\right] - \frac{c_2}{m}\left[1-\left(\frac{V}{V_0}\right)^{m}\right]\right\}. \tag{13}$$

On comparing equation (13) with equations (9) and (10) we note that $\delta_{T\infty} = -1$ in the Chopelas-Boehler formulation (equation 9), and $\delta_{T\infty} = 0$ in the Anderson-Isaak formulation. The infinite pressure condition for α based on thermodynamics ($\alpha \to 0$ at $V \to 0$) is satisfied only when $\delta_{T\infty}$ is greater than zero. This is a result similar to that ($\delta_{S\infty} > 0$) obtained by Stacey and Davis [11]. Here δ_S is the adiabatic Anderson-Grüneisen parameter related to the temperature derivative of adiabatic bulk modulus K_S [1]

$$\delta_S = -\frac{1}{\alpha K_S}\left(\frac{\partial K_S}{\partial T}\right)_P . \tag{14}$$

It should be mentioned that K_S and K_T are related by the thermodynamic identity

$$K_S = K_T(1+\gamma\alpha T). \tag{15}$$

Stacey and Davis [11] emphasized that isothermal and adiabatic properties become identical in the limit of infinite pressure. So, when $\delta_{S\infty} > 0$, we should also have $\delta_{T\infty} > 0$.

An independent expression for $\delta_{T\infty}$ can be obtained from the thermodynamic identity [1]

$$\delta_T = K'_T - 1 + q + \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T , \tag{16}$$

which gives at $P \to \infty$

$$\delta_{T\infty} = K'_\infty - 1 + \left[\left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T\right]_\infty . \tag{17}$$

To know more about $\delta_{T\infty}$, we use the following thermodynamic identities [1,12]

$$\left[\frac{\partial \ln(\alpha K_T)}{\partial \ln V}\right]_T = \delta_T - K'_T \tag{18}$$

and

$$\left[\frac{\partial \ln(\alpha K_T)}{\partial \ln V}\right]_S = q - 1. \tag{19}$$

3. Results and discussions

The Grüneisen parameter is related to the thermal and elastic properties of the material by the formula

$$\gamma = \frac{\alpha K_T V}{C_V} = \frac{\alpha K_S V}{C_P} , \tag{20}$$

where C_V and C_P are the specific heats at constant volume and constant pressure, respectively. It follows from equation (20) that α should decrease with a decreasing volume or an increasing pressure since gamma decreases and bulk modulus increases faster than $1/V$. It is desirable to judge the suitability of equation (13) for α (V) which is based on a model for δ_T(V) (equation 12) similar to that (equation 11) formulated by Burakovsky and Preston [13] for γ(V).

We have in all five parameters viz. α_0, $\delta_{T\infty}$, c_1, c_2 and m in equation (13). Equation (12) at $V = V_0$ gives

$$\delta_T^0 = \delta_{T\infty} + c_1 + c_2 . \tag{21}$$

We take $\delta_{T\infty}$= 2/3 based on equation (17) using $K'_{\infty} = 5/3$ derived from the Thomas-Fermi model [13,14], and neglecting the last term in equation (17) for the volume derivative of C_V since it is very small at high pressure and high temperature [1,11]. The value 2/3 for $\delta_{T\infty}$ can also be supported from the identities (18) and (19). Equation (18) can be integrated along an isotherm whereas equation (19) can be integrated along an adiabat. We integrate equation (19) between the limits $V = V_0$ to $V \to 0$ to obtain

$$[\ln(\alpha K_T)]_{V_0}^{0} = \int_{V_0}^{0} (q-1)\frac{\mathrm{d}V}{V}\,. \tag{22}$$

Since $q = (\mathrm{d}\ln\gamma/\mathrm{d}\ln V)_T$ becomes zero at $V \to 0$ [11], it is found from equation (22) that the product αK_T tends to infinity at $P \to \infty$ or $V \to 0$. Equation (18) was used by Anderson [17] and others [18, 19] to discuss the nature of variation of αK_T with volume. According to equation (18), $\alpha K_T \to \infty$ only when $\delta_T - K'_T$ is negative at $P \to \infty$. This reveals that $\delta_{T\infty}$ must be less than K'_{∞}. Thus the value of $\delta_{T\infty}$ should be constrained as follows:

$$0 < \delta_{T\infty} < K'_{\infty}\,. \tag{23}$$

The value of 2/3 for $\delta_{T\infty}$ taken in the present study satisfies the above constraint. $\delta_{T\infty}$ should be considered as a universal constant in the same sense as γ_{∞} and K'_{∞}. The other parameters δ_T^0, α_0, c_1, c_2 and m depend on the material chosen for the study. To judge the suitability of equation (13) for $\alpha(V)$ we use the experimental data for hcp iron which was well studied for a wide range of pressures [20,21]. For hcp iron we take $\delta_T^0 = 5.32$ and $\alpha_0 = 7.83 \cdot 10^{-5}$ K^{-1} from Isaak and Anderson [20]. Using δ_T^0= 5.32 and $\delta_{T\infty} = 2/3$ in equation (21) we have

$$c_1 + c_2 = 4.65. \tag{24}$$

The parameters c_1, c_2 and m are now fitted to experimental data [20,21] for hcp iron in the pressure range 0–360 GPa given in table 1. The fitted parameters are found to have the values c_1= 3.60, $c_2 = 1.05$, and $m = 1.5$. With the help of these parameters, values of $\alpha(V)$ are determined using equation (13) and then compared with the experimental values reported by Isaak and Anderson [20] in figure 1. We find that our model fits the experimental data well particularly in view of the fact that the experimental data become increasingly imprecise as pressure increases due to non-hydrostaticity, comparably low quality of pressure standards, recrystallization etc.

Table 1. Experimental data for the thermal expansivity α (P, V) in 10^{-5}K^{-1} for hcp iron [20,21].

V/V_0	P (GPa)	α (10^{-5} K^{-1})
1.0000	0	7.83
0.8767	30.0	3.88
0.8470	41.8	3.42
0.8172	56.2	2.94
0.7875	74.0	2.47
0.7578	95.9	2.02
0.7281	123.1	1.61
0.6984	156.8	1.27
0.6686	199.0	1.00
0.6389	252.1	0.82
0.6092	319.3	0.71
0.6048	330.0	0.70
0.5944	359.5	0.68

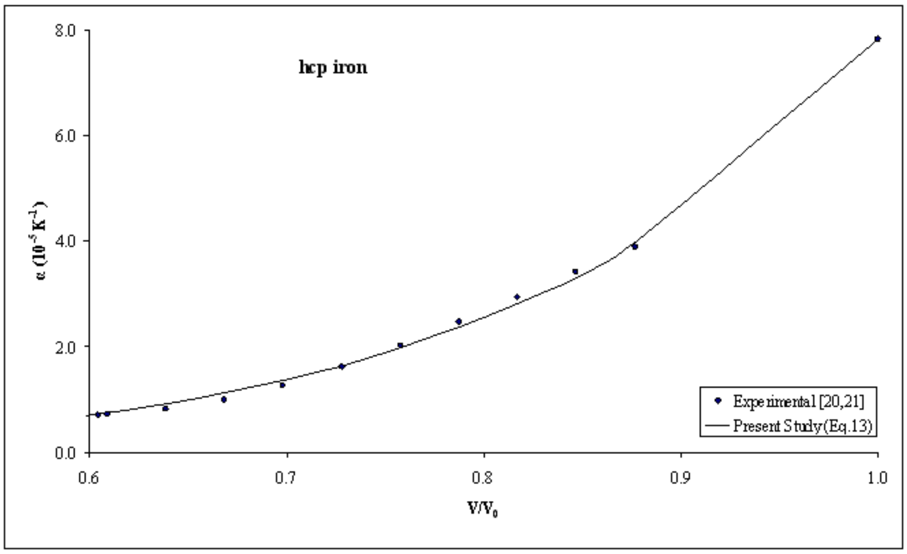

Figure 1. Thermal expansivity $\alpha(V)$ for hcp iron, continuous curve calculated in the present study (equation 13), and experimental data [20,21].

4. Conclusions

It was emphasized by Tallon [16] that the volume dependence of δ_{T}should be similar to that of γ. The volume dependence of δ_T is required for investigating the variation of thermal expansivity α with volume V. We have presented a formulation for $\alpha(V)$ (equation 13) using a model for $\delta_T(V)$ (equation 12) which is similar to the model for $\gamma(V)$ (equation 11) originally due to Burakovsky and Preston [13]. In both the models (equation (11) and equation (12)) the first term on the right is a universal constant (γ_∞ or $\delta_{\mathrm{T}\infty}$), and the remaining two terms depend on the volume representing the concave up and concave down behaviour [13]. The experimental data for thermal expansivity of hcp iron [20,21] for a wide pressure range up to 360 GPa have been fitted well with the help of equation (13) using the reasonable values of parameters, $m > 1$ and $c_1/c_2 = 3.4$, in agreement with the original model due to Burakovsky and Preston [13].

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Аналіз термічного розширення твердих тіл при екстремальному стисненні

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Згідно умови, сформульованої Стейсі для термодинаміки твердих тіл в границі нескінченого тиску, їх термічне розширення прямує до нуля при нескінченому тиску. Попередні моделі для опису залежності термічного розширення від об'єму не задовільняють цій умові. Вирази для залежності ізотермічного параметра Андерсона-Грюнайзена від об'єму, отримані в попередніх формулюваннях, виявилися невідповідними. Нами представлено об'ємну залежність параметра Андерсона-Грюнайзена, яка є подібною до отриманої раніше для однієї з моделей. Отримані нами результати демонструють, що параметр Андерсона-Грюнайзена при нескінченому тиску мусить бути більшим ніж нуль для того, щоб задовільнити термодинамічну умову, згідно якої термічне розширення прямує до нуля при нескінченому тиску. Знайдено, що наша модель узгоджується добре з експериментальними даними, що стосуються об'ємної залежності для заліза з гексагональною щільною упаковкою в широкій області тисків (0–360 GPa).

Ключові слова: *термічне розширення, параметр Андерсона-Грюнайзена, термодинаміка*

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