

# Thermodynamic Properties of the Generalized Murnaghan Equation of State of Solids

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In the Murnaghan approximation, an isothermal relation between pressure ( $P$ ) and volume ( $V$ ) for solids is derived from the assumption that the isothermal bulk modulus ( $B$ ) is a linear function of  $P$ . This paper presents a thermodynamic analysis of a generalized form of the equation, based on treating all its various parameters [*viz.*,  $V$ ,  $B$ , and  $(\partial B/\partial P)_T$  at  $P=0$ ] as functions of temperature. Extending a previous study, the effect of  $T$  upon  $(\partial B/\partial P)_T$  is accounted for by using a dimensionless parameter introduced by us, which is used in formulating general expressions for the volume dependence of various thermophysical quantities, *viz.*, the thermal expansion coefficient ( $\alpha$ ), the product  $\alpha B$ , and the Grüneisen and Anderson-Grüneisen parameters. Some combinations of these parameters are identified, which show a simple dependence upon  $P$ . The new expressions are used in analyzing current approximations and the behavior of the solid in the low-compression range. In particular, an expression for  $\alpha$  at high  $P$  is reported which generalizes the Anderson equation and previous results by us.

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**KEY WORDS:** Anderson-Grüneisen; bulk modulus; equation of state; expansivity; high pressure; Murnaghan equation.

## 1. INTRODUCTION

The equation of state (EOS) of solids has been the subject of extensive research [1-5]. A considerable amount of work has been devoted to the relation between pressure ( $P$ ) and volume ( $V$ ) at 0 K, which has recently been treated using first-principles calculations [6, 7] and using phenomenological methods [8-13] that rely on regularities in the binding energy for solids [14, 15]. In particular, starting from a scaling of the binding

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energy function, Rose et al. [9] developed a  $P$ - $V$  relation that accounted for the behavior of solids of various types. In addition to the work on the EOS at zero Kelvin, there has been an increasing interest in the treatment of temperature ( $T$ ) effects [16–20] on the isothermal EOS, which may be related to the progress of the experimental methods to study the properties at high temperatures [21–28]. The present paper is concerned with the thermodynamic basis of incorporating temperature effects on a particular isothermal EOS. Motivated by a renewed interest in modeling the  $P$ - $V$ - $T$  surface and the thermal properties of metallic and nonmetallic systems in the low-compression range [29–35], we focus here on the effects of  $T$  upon the so-called Murnaghan EOS.

In the Murnaghan approximation [36] to the isothermal EOS of solids a relation between  $P$  and  $V$  is derived from the assumption that the isothermal bulk modulus varies linearly with  $P$ . Since the approximation neglects the variation of  $(\partial B/\partial P)_T$  with  $P$  [11, 12, 37, 38], the use of the Murnaghan EOS has been restricted to the low-compression range, where it has long been considered as a useful tool in the representation, analysis and estimation of  $P$ - $V$  data for solids of various types [38–41]. This is due partly to the fact that  $(\partial B/\partial P)_T$  at zero pressure is often [42, 43] available from compression or ultrasonic measurements or has been estimated (e.g., for various elements [44]). The Murnaghan approximation also shows attractive properties if one wishes to describe the pressure contribution to the Gibbs energy ( $G$ ) of the solid. It has been shown [45] that the equation leads to a closed-form expression for that contribution, which facilitates the modeling of the  $G$  function for the various phases of a substance, the use of that information in thermodynamic databases [46], and the calculation of pressure effects on the phase equilibria [34, 35]. The Murnaghan EOS also leads to a closed-form expression for the volume dependence of the Helmholtz energy of the solid [45].

The possibility of generalizing the isothermal Murnaghan EOS by including temperature effects was early considered by Gilvarry [47] and Birch [48], and a temperature-dependent form has been presented elsewhere [45] which takes into account the variation with temperature of  $V$  and  $B$ . That form was applied in evaluations of the  $G(T, P)$  functions for various metals, which accounted for the experimental information on the thermodynamic properties at zero pressure and the low-pressure part of the  $P$ - $T$  phase diagram [34, 35, 49, 50]. The equation [45] was also employed, as a first approximation, in demonstrating the possibility of treating shock-wave data by purely thermodynamic methods, and without invoking the Mie–Grüneisen EOS [51].

Recently, there have been suggestions [29–31] of alternative ways of including the variation with  $T$  of  $V$  and  $B$  in the Murnaghan EOS while

assuming, as in the initial formulation [45], that  $(\partial B/\partial P)_T$  remains constant at  $P=0$ . This approximation has been justified by the lack of detailed information on the effect of  $T$  upon  $(\partial B/\partial P)_T$ . However, Vinet et al. [18] have shown that a temperature-dependent  $(\partial B/\partial P)_T$  is obtained when the "universal" EOS of Rose et al. [9] is combined with an often applied (cf. Section 3.3) approximation about thermal pressure of solids. The work by Vinet et al. [18] concerns various types of solids, and suggests that in certain cases  $(\partial B/\partial P)_T$  could vary significantly with  $T$  between 0 K and the melting point. Motivated by their results, and with the promising development of the experimental techniques in mind, we have investigated the thermodynamics of a formulation of the Murnaghan EOS where the variation of  $(\partial B/\partial P)_T$  with  $T$  is accounted for.

As a difference from previous analyses of data on specific systems, here we study the general thermodynamic properties of the Murnaghan EOS, because of the practical importance of the equation, and as a convenient first step toward the treatment of the large compression range. Extending recent work on the volume effects upon the thermal properties of high-melting [52] and ferromagnetic [53] elements, and the EOS of solids [54, 55], we focus on the relations between the volume dependence of various properties and the parameters accounting for the effect of  $T$ . The temperature dependence of  $(\partial B/\partial P)_T$  is treated using a new dimensionless parameter introduced by us, and its connections with other currently used quantities (e.g., the Grüneisen and Anderson-Grüneisen parameters) are considered. Moreover, the general relations which are derived here are applied in examining current approximations about the  $P$ - $V$ - $T$  behavior of solids.

The structure of the paper is as follows. In Section 2 we derive the basic relations, which involve  $\alpha$  and  $B$ , and in Section 3 we apply our results in a study of various thermodynamic parameters for solids. Next we examine the volume dependence of  $\alpha$  and obtain an expression which generalizes previous work by Anderson [39] and by us [54]. Finally, we turn to the volume dependence of the Grüneisen parameter. The paper ends with a brief summary in Section 4.

## 2. BASIC THERMODYNAMIC RELATIONS

### 2.1. Isothermal Bulk Modulus

We express the isothermal bulk modulus  $B$

$$B(T, P) = -V \left( \frac{\partial P}{\partial V} \right)_T \quad (1)$$

as a linear function of  $P$ ,

$$B(T, P) = B(T, 0) + nP \quad (2)$$

where  $B(T, 0)$  is the bulk modulus at zero pressure and the pressure-independent parameter  $n$  is a function of temperature. Differentiating Eq. (2) with respect to  $T$  yields

$$\left(\frac{\partial B}{\partial T}\right)_P = \frac{dB(T, 0)}{dT} + \left(\frac{dn}{dT}\right)P \quad (3)$$

which can be written as

$$\left(\frac{\partial B}{\partial T}\right)_P = -\alpha(T, 0) B(T, 0) \left[ \delta(T, 0) - \beta(T, 0) \frac{P}{B(T, 0)} \right] \quad (4)$$

where  $\alpha$  represents the thermal expansion coefficient,

$$\alpha(T, P) = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (5)$$

$\delta$  is the so-called isothermal Anderson–Grüneisen parameter

$$\delta(T, P) = -\frac{1}{\alpha B} \left(\frac{\partial B}{\partial T}\right)_P \quad (6)$$

and  $\beta(T, 0)$  is dimensionless quantity introduced by us,

$$\beta(T, 0) \equiv \frac{1}{\alpha(T, 0)} \left(\frac{dn}{dT}\right) \quad (7)$$

In the remainder of the work we are interested in accounting for the pressure effect upon various properties of the solid in terms of  $\beta$  and other dimensionless parameters such as  $n$  and  $\delta$ .

According to Eq. (4) the effect of temperature upon  $B(T, P)$  depends on the parameters  $\delta(T, 0)$  and  $\beta(T, 0)$ . In the most frequent case  $B(T, 0)$  decreases with increasing temperature and  $\alpha(T, 0)$  is positive, i.e.,  $\delta(T, 0)$  is a positive quantity. Some insight on the behavior of  $\beta(T, 0)$  may be gained from information on the temperature dependence of  $(\partial B/\partial P)_T$ , which is available for various substances. Data on solid Ne, Ar, Kr, and Xe analyzed by Birch [56] shows an increase with  $T$  in the pressure derivative of  $B$  at  $P=0$ , and a similar behavior is shown by NaCl [17, 57], CsI [58], and CaF<sub>2</sub> above 195 K [59], whereas for MgO, the effect of  $T$  upon  $(\partial B/\partial P)_T$  seems to be negligible [60]. Some information on Cu [61]

suggests a decrease of  $n$  with increasing  $T$  below room temperature. Contrasting with that, a thermodynamic study [62] of shock-wave information for Mo, comprising Hugoniot data obtained starting at 293 K [63] and 1673 K [27], based on the method of analysis presented in Ref. 51 and letting  $n$  vary linearly with  $T$  above room temperature, indicates that  $dn/dT > 0$ . In view of these results we do not make any assumption about the sign of  $dn/dT$  and  $\beta(T, 0)$  but treat them as quantities that, in principle, can have either sign.

For the particular case where  $\beta(T, 0) > 0$  and—as usual— $\alpha(T, 0)$  and  $\delta(T, 0)$  are positive, Eq. (4) predicts that the rate of decrease in  $B$  with increasing  $T$  gets smaller at higher pressures and becomes zero at the pressure

$$P^* = \frac{\delta(T, 0)}{\beta(T, 0)} B(T, 0) \quad (8)$$

The consequences of this result on the behavior of the thermal expansivity at high  $P$  are examined in the next section.

## 2.2. Thermal Expansion Coefficient

Integrating Eq. (2) at constant temperature yields

$$\frac{V(T, P)}{V(T, 0)} = \left[ 1 + n \frac{P}{B(T, 0)} \right]^{-1/n} \quad (9)$$

which leads to the following relation for the thermal expansion coefficient  $\alpha$  [Eq. (5)]:

$$\frac{\alpha(T, P)}{\alpha(T, 0)} = \frac{1 + [n - \delta(T, 0)][P/B(T, 0)]}{1 + n[P/B(T, 0)]} + \beta(T, 0) \varphi_1(T, P) \quad (10)$$

where  $\delta$  and  $\beta(T, 0)$  are defined by Eqs. (6) and (7), respectively, and

$$\varphi_1(T, P) \equiv \frac{1}{n^2} \left\{ \ln \left[ 1 + n \frac{P}{B(T, 0)} \right] - \frac{n[P/B(T, 0)]}{1 + n[P/B(T, 0)]} \right\} \quad (11)$$

In the following we examine the predictions of Eq. (10), starting with the behavior at low pressures. In particular, we consider the limiting condition  $P \rightarrow 0$  and approximate Eq. (10) with a series expansion in powers of  $[P/B(T, 0)]$ . We obtain

$$\frac{\alpha(T, P)}{\alpha(T, 0)} \simeq 1 - \delta(T, 0) \left[ \frac{P}{B(T, 0)} \right] + \left[ n\delta(T, 0) + \left( \frac{1}{2} \right) \beta(T, 0) \right] \left[ \frac{P}{B(T, 0)} \right]^2 + \dots \quad (12)$$

The first two terms of Eq. (12) reproduce an equation for the thermal expansivity reported long ago by Birch [64]. The present study shows that the temperature dependence of  $n$ , described by  $\beta(T, 0)$ , is involved in the second-order correction to his approximation. A consideration of the higher-order corrections in Eq. (12), which are given by the general formula

$$\frac{\alpha(T, P)}{\alpha(T, 0)} \simeq 1 - \delta(T, 0) \left[ \frac{P}{B(T, 0)} \right] + \sum_{i=0} (-1)^i \cdot n^i \cdot \left[ n\delta(T, 0) + \left( \frac{i+1}{i+2} \right) \beta(T, 0) \right] \left[ \frac{P}{B(T, 0)} \right]^{i+2} \quad (13)$$

suggests that the importance of  $\beta(T, 0)$  in determining the deviations from the linear behavior at low  $P$  will increase with the ratio  $\beta(T, 0)/n\delta(T, 0)$ .

### 2.3. Behavior of $\alpha(T, P)$ at High Pressures

Whereas the choice of the Murnaghan equation originates in our interest in the thermodynamics of the low-compression range, we extend the analysis of Eq. (10) by examining its mathematical behavior at very large  $P$ , since that leads to additional insight into the properties of the generalized formulation, and the consequences of accounting for the temperature dependence of  $n$ .

Equation (10) describes the effect of pressure on  $\alpha(T, P)/\alpha(T, 0)$  as the sum of two terms. The first term does not involve  $\beta(T, 0)$ , but  $\delta(T, 0)$ . In the usual case  $\delta(T, 0) > 0$ , and that term decreases with increasing pressure from the value 1 at  $P=0$ , down to the value  $[n - \delta(T, 0)]/n = 1 - [\delta(T, 0)/n]$  at extremely high  $P$ . The second term in Eq. (10) is the product of the purely temperature-dependent quantity  $\beta(T, 0)$  times  $\varphi_1$ , which is the function of  $T$  and  $P$  defined by Eq. (11). In Fig. 1 we plot  $\varphi_1(T, P)$  versus  $P/B(T, 0)$ , for various values of  $n$ . Since  $\varphi_1(T, P)$  is positive and increases with  $P/B(T, 0)$ , the second term in Eq. (10) will give a positive contribution to  $\alpha(T, P)/\alpha(T, 0)$  if  $\beta(T, 0) > 0$  and a negative contribution if  $\beta(T, 0) < 0$ . As a consequence, in the case where  $\beta(T, 0) > 0$  and  $\alpha(T, 0) > 0$ , the variation of  $\alpha(T, P)$  with  $P$  will be determined by the competing effects of the two terms in Eq. (10), and there is the possibility of a minimum in the  $\alpha(T, P)$  versus  $P$  function. We examine this possibility further by considering the pressure derivative of  $\alpha$ . The Maxwell relation

$$\left( \frac{\partial \alpha}{\partial P} \right)_T = \frac{1}{B^2} \left( \frac{\partial B}{\partial T} \right)_P \quad (14)$$

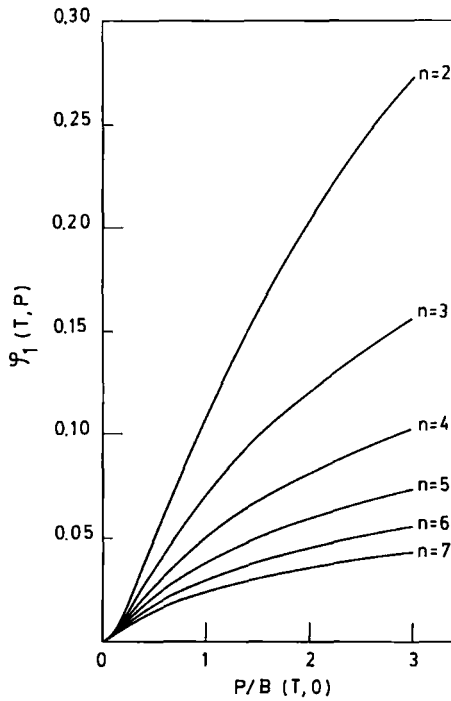


Fig. 1. The quantity  $\varphi_1(T, P)$  defined by Eq. (11) versus the ratio  $P/B(T, 0)$ , for various values of the parameter  $n$ .

implies that the minimum in  $\alpha$  occurs at a pressure such that  $(\partial B/\partial T)_P$  is zero, which corresponds to the critical pressure  $P^*$  introduced in the previous section [Eq. (8)]. By inserting this pressure value in Eq. (10) we evaluate the minimum  $\alpha(T, P)/\alpha(T, 0)$  ratio as

$$\frac{\alpha(T, P^*)}{\alpha(T, 0)} = \frac{n - \delta(T, 0)}{n} + \frac{\beta(T, 0)}{n^2} \ln \left[ 1 + n \frac{\delta(T, 0)}{\beta(T, 0)} \right] \quad (15)$$

The first term in Eq. (15) is the limiting  $\alpha(T, P)/\alpha(T, 0)$  ratio given by the Murnaghan approximation for  $P \rightarrow \infty$  when  $n$  is independent of  $T$  [54]. That ratio is negative if  $n < \delta(T, 0)$ . In spite of that, Eq. (15) predicts that

$$\frac{\alpha(T, P^*)}{\alpha(T, 0)} \geq 0 \quad (16)$$

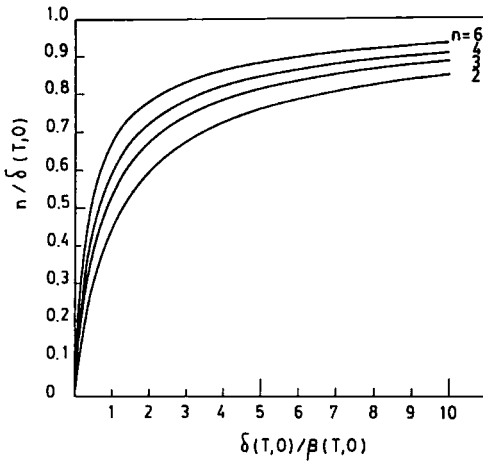


Fig. 2. The ratio  $n/\delta(T,0)$  which satisfies Eq. (17) with the equality sign versus the ratio  $\delta(T,0)/\beta(T,0)$ , for various values of the parameter  $n$ .

if the ratio  $n/\delta(T,0)$ , being less than unity, is large enough to satisfy the condition

$$\frac{n}{\delta(T,0)} \geq 1 - \left( \ln \left[ 1 + n \frac{\delta(T,0)}{\beta(T,0)} \right] \right) / n \frac{\delta(T,0)}{\beta(T,0)} \tag{17}$$

Values of the  $n/\delta(T,0)$  ratio satisfying Eq. (17) with the equality sign are plotted in Fig. 2 versus  $\delta(T,0)/\beta(T,0)$  for various values of  $n$ . Taking, for instance,  $\delta(T,0)/\beta(T,0) = 1$  and  $n = 4$ , we have from Fig. 2 that  $\alpha(T, P^*)/\alpha(T, 0) = 0$  if  $n/\delta(T,0) \simeq 0.6$ . Larger values of  $n/\delta(T,0)$  and the same  $\delta(T,0)/\beta(T,0)$  will make  $\alpha(T, P^*)/\alpha(T, 0) > 0$ , which in the usual case  $\alpha(T, 0) > 0$  implies that  $\alpha(T, P)$  will be positive at all pressures. According to Fig. 2, the smallest  $n/\delta(T,0)$  ratios leading to  $\alpha(T, P^*) > 0$  for other values of  $n$  decrease rapidly with the relation  $\delta(T,0)/\beta(T,0)$ , in particular, if  $\delta(T,0)/\beta(T,0) < 3$ . In Section 3.5 we show that the condition  $\delta(T,0)/\beta(T,0) = 1/n$  leads to a particularly simple expression for the volume dependence of the thermodynamic Grüneisen parameter in the Murnaghan approximation. Using Eq. (17) we predict for that case  $\alpha(T, P^*)/\alpha(T, 0) > 0$  if  $n/\delta(T,0) > 1 - \ln 2 \simeq 0.31$ .

### 3. ANALYSIS OF THERMODYNAMIC PARAMETERS FOR SOLIDS

#### 3.1. Pressure Effects on the Quantity $\alpha B$

The properties of the product  $\alpha B$  are of interest in analyzing the temperature dependence of the so-called thermal pressure of solids. That



dependence is usually described by means of the quantity  $(\partial P/\partial T)_V$ , which is related to the product  $\alpha B$  by the identity

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha B \quad (18)$$

Here we derive a relation describing the effect of  $P$  upon  $\alpha B$ . By combining Eqs. (2) and (10), we obtain

$$\frac{\alpha(T, P) B(T, P)}{\alpha(T, 0) B(T, 0)} = 1 + [n - \delta(T, 0)] \frac{P}{B(T, 0)} + \beta(T, 0) \varphi_2(T, P) \quad (19)$$

where

$$\varphi_2(T, P) \equiv \left[ 1 + n \frac{P}{B(T, 0)} \right] \varphi_1(T, P) \quad (20)$$

and  $\varphi_1(T, P)$  is defined by Eq. (11). In Fig. 3 we plot  $\varphi_2$  versus  $P/B(T, 0)$ , for various values of  $n$ . Equation (19) describes the pressure dependence of  $\alpha B$  as the sum of two contributions. The first contribution is proportional to  $P$ , and is positive if  $n > \delta(T, 0)$  and negative if  $n < \delta(T, 0)$ . The second contribution is the product of the quantity  $\varphi_2$ , which is positive and

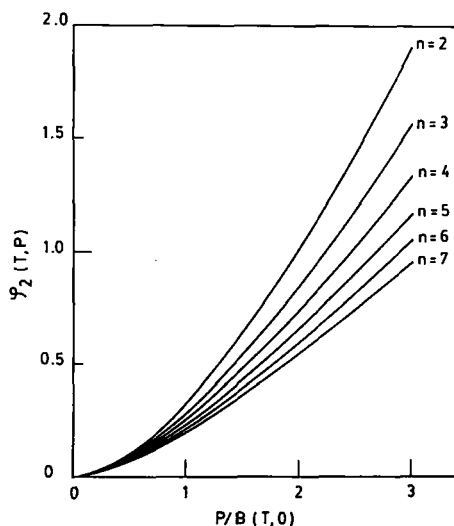


Fig. 3. The quantity  $\varphi_2(T, P)$  defined by Eq. (20) versus the ratio  $P/B(T, 0)$ , for various values of the parameter  $n$ .

increases with  $P$  (Fig. 3), times the parameter  $\beta(T, 0)$ , which measures the temperature dependence of  $n$  [Eq. (7)] and can have either sign (Section 2.1).

The role of  $\beta(T, 0)$  in determining the pressure effects on the properties of the solid may be further illustrated by the predictions of Eq. (19) when  $P \rightarrow 0$ . Keeping the leading terms of an expansion of  $\varphi_2(T, P)$  in powers of  $P/B(T, 0)$ , we write

$$\frac{\alpha(T, P) B(T, P)}{\alpha(T, 0) B(T, 0)} \approx 1 + [n - \delta(T, 0)] \left[ \frac{P}{B(T, 0)} \right] + \left( \frac{1}{2} \right) \beta(T, 0) \left[ \frac{P}{B(T, 0)} \right]^2 + \dots \quad (21)$$

The first two terms in Eq. (21) reproduce the results of Ref. 45 for the Murnaghan approximation when  $n$  is independent of  $T$ . The present treatment predicts that the temperature dependence of  $n$  will be reflected in a deviation from the linear relation between  $\alpha B$  and  $[P/B(T, 0)]$  when  $P \rightarrow 0$ . In particular,  $\beta(T, 0)$  is directly related to the coefficient of the second-order correction that linear variation, whereas the higher-order terms are also dependent upon the values of  $n$ . This is illustrated by the higher-order terms of the expansion of Eq. (19) in powers of  $P/B(T, 0)$  which are given by the general formula

$$\frac{\alpha(T, P) B(T, P)}{\alpha(T, 0) B(T, 0)} \approx 1 + [n - \delta(T, 0)] \left[ \frac{P}{B(T, 0)} \right] + \beta(T, 0) \sum_{i=0} \frac{(-1)^i \cdot n^i}{(i+1)(i+2)} \left[ \frac{P}{B(T, 0)} \right]^{i+2} \quad (22)$$

The pressure dependence of  $\alpha B$ , as given by Eq. (19), is discussed further in Section 3.3.

### 3.2. Pressure Effects on the Anderson–Grüneisen Parameter

The isothermal Anderson–Grüneisen parameter  $\delta$ , which is defined by Eq. (6), and the related parameter  $\delta_s$ , which is obtained in a similar way from the isentropic bulk modulus  $B_s$ , are useful quantities in studying properties related to the anharmonic behavior of solids, and have been the subject of considerable interest [39, 54, 65–76]. In the present study we have focused on the relations between  $\delta$  and three thermodynamic properties, *viz.*, the thermal expansion coefficient  $\alpha$ , the product  $\alpha B$ , and the

thermodynamic Grüneisen parameter. We start by deriving a relation for the pressure dependence of  $\delta$ . Using Eqs. (4) and (19) we obtain

$$\frac{\delta(T, P)}{\delta(T, 0)} = \frac{1 - [\beta(T, 0)/\delta(T, 0)][P/B(T, 0)]}{1 + [n - \delta(T, 0)][P/B(T, 0)] + \beta(T, 0)\varphi_2(T, P)} \quad (23)$$

In connection with the modeling of the thermal expansivity at high pressure (Section 3.4), it is sometimes [39] assumed that  $\delta$  is independent of  $P$ . Equation (23) shows that such approximation will hold exactly at all pressures if the parameters of the Murnaghan equation satisfy the conditions

$$\beta(T, 0) = 0 \quad (24)$$

and

$$n = \delta \quad (25)$$

Equation (24) implies that the pressure-independent parameter  $n$  is also independent of  $T$ , i.e., that  $n$  is a constant. It follows from Eqs. (24) and (25) that in the Murnaghan approximation the condition that  $\delta$  is independent of  $P$  at all temperatures implies that  $\delta$  is a constant, identical to  $n$ , the pressure derivative of  $B$  [54, 77]. If  $n - \delta(T, 0) > 0$  and  $\beta(T, 0) > 0$ , the approximation  $\delta(T, P) = \delta(T, 0)$  with  $\delta(T, 0) > 0$  leads to a larger  $\delta(T, P)$  than given by the Murnaghan equation and leads to a smaller  $\delta(T, P)$  if  $n - \delta(T, 0) < 0$  and  $\beta(T, 0) < 0$ .

The properties of the  $\delta(T, P)/\delta(T, 0)$  ratio when  $\beta(T, 0) = 0$  and  $n \neq \delta$  have been discussed elsewhere [54], and it remains to examine the case where  $n$  varies with  $T$  in such a way that the relation  $n = \delta(T, 0)$  applies. That case is discussed in the following in connection with the behavior of the solid when  $P \rightarrow 0$ . An expansion of Eq. (23) in powers of  $P/B(T, 0)$  yields

$$\begin{aligned} \frac{\delta(T, P)}{\delta(T, 0)} \simeq & 1 - \left[ n - \delta(T, 0) + \frac{\beta(T, 0)}{\delta(T, 0)} \right] \left[ \frac{P}{B(T, 0)} \right] \\ & + \left\{ [n - \delta(T, 0)] \left[ n - \delta(T, 0) + \frac{\beta(T, 0)}{\delta(T, 0)} \right] - \frac{\beta(T, 0)}{2} \right\} \left[ \frac{P}{B(T, 0)} \right]^2 \\ & - \left[ [n - \delta(T, 0)] \left\{ [n - \delta(T, 0)] \right. \right. \\ & \times \left. \left. \left[ n - \delta(T, 0) + \frac{\beta(T, 0)}{\delta(T, 0)} \right] - \beta(T, 0) \right\} \right. \\ & \left. - \beta(T, 0) \left[ \frac{n}{6} + \left( \frac{1}{2} \right) \frac{\beta(T, 0)}{\delta(T, 0)} \right] \right] \left[ \frac{P}{B(T, 0)} \right]^3 + \dots \quad (26) \end{aligned}$$

As a difference from  $\alpha(T, P)/\alpha(T, 0)$  [Eq. (12)] and  $\alpha(T, P) B(T, P)/\alpha(T, 0) B(T, 0)$  [Eq. (21)], the effect of pressure on  $\delta(T, P)/\delta(T, 0)$  depends upon  $\beta(T, 0)$  already in the linear approximation. If  $n = \delta(T, 0)$  (and  $\beta(T, 0) \neq 0$ ), Eq. (26) reduces to

$$\frac{\delta(T, P)}{\delta(T, 0)} \approx 1 - \left[ \frac{\beta(T, 0)}{\delta(T, 0)} \right] \left[ \frac{P}{B(T, 0)} \right] - \left( \frac{1}{2} \right) \beta(T, 0) \left[ \frac{P}{B(T, 0)} \right]^2 + \beta(T, 0) \left[ \frac{n}{6} + \left( \frac{1}{2} \right) \frac{\beta(T, 0)}{\delta(T, 0)} \right] \left[ \frac{P}{B(T, 0)} \right]^3 + \dots \quad (27)$$

i.e., the effect of  $P$  upon  $\delta(T, P)$  is predicted to depend, to the second order in  $P/B(T, 0)$ , on the parameters  $\beta(T, 0)$  and  $\delta(T, 0)$ , only. For the usual case  $\delta(T, 0) > 0$ , Eq. (27) predicts that at sufficiently low pressures,  $\delta(T, P)$  will decrease with  $P/B(T, 0)$  if  $\beta(T, 0) > 0$  but increase with  $P/B(T, 0)$  if  $\beta(T, 0) < 0$ .

### 3.3. Relations Between $\alpha B$ and $\delta$

A general relation between  $\alpha B$  and  $\delta$  can be obtained by derivating the product  $\alpha B$  with respect to  $P$  and taking into account Eqs. (6) and (14). We find

$$\left[ \frac{\partial(\alpha B)}{\partial P} \right]_T = \alpha(T, P) \left\{ \left( \frac{\partial B}{\partial P} \right)_T - \delta(T, P) \right\} \quad (28)$$

Extrapolations of  $P$ - $V$ - $T$  data have often [78-80] been based on the observation that for various types of solids (i.e., rare-gas solids [81], NaCl [17, 82], LiF, NaF, KF, and CsCl [83, 84], MgO [85, 86], various minerals [79, 80] the alkali metals [87, 88], and Cu [61]), the volume dependence of the product  $\alpha B$  at constant  $T$  seems to be very small, i.e.,

$$\left[ \frac{\partial(\alpha B)}{\partial V} \right]_T = \frac{-B}{V} \left[ \frac{\partial(\alpha B)}{\partial P} \right]_T \approx 0 \quad (29)$$

Equation (28) [with  $\alpha(T, P) \neq 0$ ] indicates that Eq. (29) is fulfilled exactly when

$$\left( \frac{\partial B}{\partial P} \right)_T = \delta(T, P) \quad (30)$$

i.e., the functions of  $T$  and  $P$   $(\partial B/\partial P)_T$  and  $\delta(T, P)$  are the same. In the Murnaghan approximation  $(\partial B/\partial P)_T$  is independent of  $P$ , and Eq. (30)

requires  $\delta$  to be independent of  $P$ . That will be the case if Eqs. (24) and (25) apply. If those equations do not apply, the approximation  $\alpha(T, P) B(T, P) = \alpha(T, 0) B(T, 0)$  overestimates  $\alpha(T, P) B(T, P)$  compared with the Murnaghan equation if  $n\delta(T, 0)$  and  $\beta(T, 0)$  are negative and underestimates  $\alpha(T, P) B(T, P)$  if  $n\delta(T, 0)$  and  $\beta(T, 0)$  are positive. If  $n\delta(T, 0)$  and  $\beta(T, 0)$  have different signs there is the possibility of a partial cancellation between the last two terms on the right-hand side of Eq. (19).

By combining Eqs. (19) and (23) we obtain

$$\frac{\alpha(T, P) B(T, P) \delta(T, P)}{\alpha(T, 0) B(T, 0) \delta(T, 0)} = 1 - \left[ \frac{\beta(T, 0)}{\delta(T, 0)} \right] \frac{P}{B(T, 0)} \quad (31)$$

Equation (31) summarizes our results about the effects of pressure upon the quantities  $\alpha$ ,  $B$ , and  $\delta$  of a solid that obeys the temperature-dependent Murnaghan equation of state. It shows that the product  $\alpha B \delta$  varies linearly with pressure, decreasing with increasing  $P$  if the ratio  $\beta(T, 0)/\delta(T, 0)$  is positive and increasing with  $P$  if the ratio is negative. When  $n$  is independent of temperature and  $\alpha(T, 0) \neq 0$ , we have from Eq. (7)  $\beta(T, 0) = 0$ , and Eq. (31) takes the form

$$\alpha(T, P) B(T, P) \delta(T, P) = k(T) \quad (32)$$

where  $k(T)$  is only a function of temperature.

#### 3.4. Relations Between $\alpha$ , $\delta$ , and $V$

The analysis of the thermal expansivity at high pressures has sometimes [39, 48, 77] been made in terms of a relation between  $\alpha$  and  $V$ . A relation of that kind can be obtained from the present results by starting from Eq. (31) and eliminating the ratio  $B(T, P)/B(T, 0)$  by means of Eqs. (2) and (9). We obtain

$$\frac{\alpha(T, P) \delta(T, P)}{V^n(T, P)} = \frac{\alpha(T, 0) \delta(T, 0)}{V^n(T, 0)} \left\{ 1 - \left[ \frac{\beta(T, 0)}{\delta(T, 0)} \right] \frac{P}{B(T, 0)} \right\} \quad (33)$$

Equation (33) is proposed here as the most general relation between  $\alpha$  and  $V$  that follows from the Murnaghan approximation. If the  $n$  parameter is independent of  $T$  and  $\alpha(T, 0) \neq 0$ , we have from Eq. (7)  $\beta(T, 0) = 0$ , and Eq. (33) reduces to

$$\frac{\alpha(T, P) \delta(T, P)}{V^n(T, P)} = \frac{\alpha(T, 0) \delta(T, 0)}{V^n(T, 0)} \quad (34)$$

which has previously been reported by us [54]. If the Anderson–Grüneisen parameter is independent of pressure, Eqs. (24) and (25) hold, and Eq. (33) leads to

$$\frac{\alpha(T, P)}{V^n(T, P)} = \frac{\alpha(T, 0)}{V^n(T, 0)} \quad (35)$$

Equation (35) (with  $\delta$  instead of  $n$ ) reproduces Anderson's [39] formula for expansivity at high pressures.

### 3.5. Volume Dependence of the Grüneisen Parameter

The thermodynamic Grüneisen parameter  $\gamma_G$  is defined as

$$\gamma_G(T, P) = \frac{\alpha B V}{C_V} \quad (36)$$

where  $C_V$  is the heat capacity at constant volume. The properties of  $\gamma_G$  are of great interest in discussions of the EOS of solids (e.g., Refs. 52 and 89). In particular, the volume dependence of  $\gamma_G$  is often considered in connection with the treatment of shock-wave data (cf. Ref. 55 and references therein).

In the present section we examine the relation between  $\gamma_G$  and  $V$  given by the temperature-dependent Murnaghan approximation. By combining Eqs. (31) and (36) we obtain

$$\begin{aligned} & \frac{\gamma_G(T, P) C_V(T, P) \delta(T, P)}{V(T, P)} \\ &= \frac{\gamma_G(T, 0) C_V(T, 0) \delta(T, 0)}{V(T, 0)} \left\{ 1 - \left[ \frac{\beta(T, 0)}{\delta(T, 0)} \right] \frac{P}{B(T, 0)} \right\} \end{aligned} \quad (37)$$

Eliminating  $P/B(T, 0)$  by means of Eq. (9) yields

$$\begin{aligned} & \frac{\gamma_G(T, P) C_V(T, P) \delta(T, P)}{\gamma_G(T, 0) C_V(T, 0) \delta(T, 0)} \\ &= \frac{V(T, P)}{V(T, 0)} \left[ 1 - \frac{\beta(T, 0)}{n\delta(T, 0)} \left\{ \left[ \frac{V(T, P)}{V(T, 0)} \right]^{-n} - 1 \right\} \right] \end{aligned} \quad (38)$$

which gives the volume dependence of the product  $\gamma_G C_V \delta$ . If the  $n$  parameter is independent of  $T$  and  $\alpha(T, 0) \neq 0$ , we have from Eq. (7)  $\beta(T, 0) = 0$ , and Eq. (38) becomes

$$\frac{\gamma_G(T, P) C_V(T, P) \delta(T, P)}{\gamma_G(T, 0) C_V(T, 0) \delta(T, 0)} = \frac{V(T, P)}{V(T, 0)} \quad (39)$$

i.e., the product  $\gamma_G C_V \delta$  is predicted as proportional to  $V$ . When  $n$  depends on  $T$ , Eq. (39) describes only the limiting behavior for  $V(T, P)/V(T, 0) \approx 1$ , but at larger compressions the predictions of Eq. (39) will overestimate the product  $\gamma_G(T, P) C_V(T, P) \delta(T, P)$  if  $\beta(T, 0)/\delta(T, 0) > 0$  and will underestimate the product if  $\beta(T, 0)/\delta(T, 0) < 0$ .

In the particular case where

$$\frac{\beta(T, 0)}{\delta(T, 0)} = n \quad (40)$$

the volume dependence of  $\gamma_G$  [Eq. (38)] takes a rather simple form, *viz.*,

$$\frac{\gamma_G(T, P) C_V(T, P) \delta(T, P)}{\gamma_G(T, 0) C_V(T, 0) \delta(T, 0)} = \frac{V(T, P)}{V(T, 0)} \left\{ 2 - \left[ \frac{V(T, P)}{V(T, 0)} \right]^{-n} \right\} \quad (41)$$

Finally, if the Anderson-Grüneisen parameter is independent of  $P$ , Eqs. (24) and (25) hold, and Eq. (37) takes the form

$$\left[ \frac{\gamma_G(T, P)}{V(T, P)} \right] C_V(T, P) = g(T) \quad (42)$$

where  $g(T)$  is a function only of  $T$ . At a fixed temperature,  $C_V$  and the ratio  $(\gamma_G/V)$  are predicted to vary with pressure in such a way that their product remains constant.

#### 4. SUMMARY AND CONCLUDING REMARKS

The Murnaghan approximation is a useful tool in the treatment of pressure effects on the properties of solids in the low-compression range. In the present work we have studied the thermodynamic properties of the most general form of the Murnaghan equation, where all its parameters are temperature dependent. We have obtained relations describing the pressure dependence of the thermal expansivity, the product  $\alpha B$ , and other thermodynamic quantities. Our results show that in the Murnaghan approximation certain combinations of thermodynamic parameters, *viz.*,  $\alpha B \delta$ ,  $\alpha \delta / V^n$ , and  $\gamma_G C_V \delta / V$ , vary in a rather simple way with pressure, and we report relations describing that variation in terms of properties corresponding to  $P = 0$ . The present work also illustrates the use of the Anderson-Grüneisen parameter in treating pressure effects upon quantities like  $\alpha$ ,  $\alpha B$ , and  $\gamma_G$ , which are related to the anharmonic behavior of solids.

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