Anderson-Grüneisen parameter δ of some hexagonal metals and MgO from third-order elastic-constant data

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A simple procedure is described to calculate the Anderson-Grüneisen parameter δ from the third-order elastic constants of a crystal and is used to evaluate the same for nine hexagonal metals and for the cubic magnesium oxide (MgO). In all the crystals, with the exception of beryllium, the relation $\delta = 2\gamma$ is very nearly satisfied. The relevance of these calculations to the anharmonicity in these crystals is discussed. Anderson's theory has been used to explain the temperature dependence of the bulk modulus of the hexagonal metals magnesium, zinc, cadmium, and beryllium and the results are compared with experimental values.

I. INTRODUCTION

Wachtman[1] *et al.* suggested that an equation of the form

$$y = y_0 - b_1 T e^{-T_0/T} \tag{1.1}$$

represents the variation of Young's modulus with temperature, for several oxides. y and y_0 are the Young's moduli at any temperature T, and absolute zero temperature, respectively; b_1 and T_0 are two empirical parameters characteristic of the solid. Anderson[2] gave physical interpretation to these constants occurring in the Wachtman equation by considering the corresponding equation for the adiabatic bulk modulus B_S, viz.,

$$B_S = B_{00} - bTe^{-T_0/T} . \tag{1.2}$$

Anderson[2] showed that the constant b is given by

$$b = \frac{3R\gamma\delta}{V_0} . \tag{1.3}$$

Here γ is the Grüneisen parameter given by

$$\gamma = \alpha V B_S / C_p . \tag{1.4}$$

V_0 is the specific volume per atom at absolute zero and δ is an important physical constant (analogous to the Grüneisen constant) independent of temperature and is given by

$$\delta = -\frac{1}{\alpha}\left(\frac{\partial \ln B_S}{\partial T}\right)_p . \tag{1.5}$$

Following Chang,[3] we shall call δ the Anderson-Grüneisen parameter. Here α is the coefficient of thermal volume expansion, R is the gas constant, and B_{00} is the bulk modulus at absolute zero and one atmosphere. C_p is the specific heat at constant pressure. The constant δ was first introduced by Grüneisen,[4] and Eq. (1.5) was derived by him for the case of the Born potential (or the Mie potential)

$$\Phi = -A/V^{m/3} + B/V^{n/3} . \tag{1.6}$$

From theoretical considerations Anderson[2] derived a relationship which gives the temperature dependence of the bulk modulus as a function of the specific heat and atomic volume,

$$\frac{dB_S}{dT} = -\delta\gamma\frac{C_p}{V} , \tag{1.7}$$

where V is the atomic volume. Using the Mie-Grüneisen equation-of-state and the Born potential, Anderson[2] showed that

$$\delta = \tfrac{1}{3}(m+n) + 2 - \gamma . \tag{1.8}$$

Chang,[3] entirely from thermodynamical considerations, the Grüneisen equation of state of solids, and assuming that the ratio C_v/C_p is independent of temperature, showed that δ is related to the pressure dependence of the bulk modulus as

$$\delta = \frac{dB_T}{dp} - 1 \simeq \frac{dB_S}{dp} - 1 , \tag{1.9}$$

where B_T is the isothermal bulk modulus. Assuming the Dugdale and MacDonald[5] relationship between γ and the change of compressibility of a solid with volume, Chang[3] also showed that

$$\delta = 2\gamma . \tag{1.10}$$

Once the value of δ is known it can be used to predict the bulk modulus of a solid as a function of temperature by integrating Eq. (1.7) and writing B_S as

$$B_S = B_{00} - \frac{\delta\gamma}{V_0}\int_0^T C_v\, dT . \tag{1.11}$$

In particular, Eq. (1.11) is useful to predict the data in regions where direct experiment is difficult.

The object of the present paper is to present a simple method for calculating the Anderson-Grüneisen parameter δ of a crystal from its measured third-order elastic-(TOE) constant data, and it is applied to the evaluation of the δ of nine hexagonal metals and also the cubic MgO, the first

solid for which Anderson[2] evaluated δ. Also the temperature dependence of the bulk modulus of magnesium, zinc, cadmium and beryllium is calculated from Anderson's theory using the δ values obtained from their third-order elastic-constants data. Finally a comparison is made between the calculated values of B_S and those obtained from the measured elastic constants of these metals.

II. CALCULATION OF δ FROM TOE CONSTANT DATA

A. hcp solids

We will consider the hcp solids first. Ramji Rao and Srinivasan[6] derived the expressions for the pressure derivatives of the second-order elastic (SOE) constants of a hexagonal crystal in terms of its TOE constants, using Murnaghan's[7] finite strain elasticity theory. Brugger[8] also presented extensive tables of $d(\rho_0 w^2)/dp$ for various crystal systems. The final expressions for the effective elastic constants are given here for convenience:

$$\begin{aligned}
C'_{11} &= C_{11} + \eta(4C_{11} + 2C_{12} + C_{111} + C_{112}) \\
&\quad + \xi(-C_{11} + 2C_{13} + C_{113}), \\
C'_{12} &= C_{12} + \eta(C_{111} + 2C_{112} - C_{222} + 2C_{12}) \\
&\quad + \xi(-C_{12} + C_{123}), \\
C'_{13} &= C_{13} + \eta(C_{113} + C_{123}) + \xi(C_{13} + C_{133}), \\
C'_{33} &= C_{33} + \eta(4C_{13} - 2C_{33} + 2C_{133}) \\
&\quad + \xi(5C_{33} + C_{333}) .
\end{aligned} \tag{2.1}$$

TABLE I. References for the SOE and TOE constants data (at room temperature).

Crystal	References for SOE and TOE data.
Mg	Slutsky and Garland (Ref. 12)
	Naimon (Ref. 13)
	Srinivasan and Ramji Rao (Ref. 14)
Be	Silversmith and Averbach (Ref. 15)
	Srinivasan and Ramji Rao (Ref. 14)
Zn	Alers and Neighbours (Ref. 16)
	Swartz and Elbaum (Ref. 17)
	Srinivasan and Ramji Rao (Ref. 14)
Cd	Garland and Silverman (Ref. 18)
	Menon and Ramji Rao (Ref. 19)
Zr	Fisher, Manghnani, and Sokolowski (Ref. 20)
	Menon and Ramji Rao (Ref. 21)
Ti	Fisher and Renken (Ref. 22)
	Ramji Rao and Menon (Ref. 23)
Gd	Fisher, Manghnani, and Kikuta (Ref. 24)
	Ramji Rao and Menon (Ref. 25)
Dy	Fisher, Manghnani, and Kikuta (Ref. 24)
	Ramji Rao and Menon (Ref. 26)
Er	Fisher, Manghnani, and Kikuta (Ref. 24)
	Ramji Rao and Menon (Ref. 27)
MgO	Bogardus (Ref. 10)

Here η is the Lagrangian strain in the basal plane and ξ is the longitudinal strain along the hexagonal axis. In terms of the hydrostatic pressure p, η and ξ are given by

$$\eta = \frac{(C_{13} - C_{33})p}{(C_{11} + C_{12})C_{33} - 2C_{13}^2}$$

and (2.2)

$$\xi = \frac{(2C_{13} - C_{11} - C_{12})p}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} .$$

The bulk modulus of the strained hexagonal crystal is given by

$$B' = \tfrac{1}{9}(2C'_{11} + C'_{33} + 2C'_{12} + 4C'_{13}) , \tag{2.3}$$

where the C'_{ij} are given by (2.1).

δ can now be obtained from Eq. (2.3) and is given by the expression

$$\begin{aligned}
\delta &= \frac{dB'}{dp} - 1 = -1 + \frac{C_{13} - C_{33}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} \\
&\quad \times [\tfrac{1}{9}(4C_{111} + 6C_{112} + 4C_{113} + 4C_{123} \\
&\quad + 2C_{133} - 2C_{222} + 8C_{11} + 8C_{12} + 4C_{13} - 2C_{33})] \\
&\quad + \frac{2C_{13} - C_{11} - C_{12}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} \\
&\quad \times [\tfrac{1}{9}(2C_{113} + 2C_{123} + 4C_{133} + C_{333} \\
&\quad + 8C_{13} - 2C_{11} - 2C_{12} + 5C_{33})] .
\end{aligned} \tag{2.4}$$

Using Eq. (2.4) the δ values are calculated for nine hexagonal metals and are given in Table II.

B. Cubic crystals

Birch[9] derived the expressions for the effective elastic constants of a strained cubic crystal under a hydrostatic pressure p using the finite strain theory and these are given (in Bogardus's[10] paper also) here using Brugger's[11] notation:

$$\begin{aligned}
C'_{11} &= C_{11} + \frac{\epsilon}{3}(C_{111} + 2C_{112} + 2C_{11} + 2C_{12}) , \\
C'_{12} &= C_{12} + \frac{\epsilon}{3}(2C_{112} + C_{123} - C_{11} - C_{12}) .
\end{aligned} \tag{2.5}$$

Here $\epsilon = -3p/(C_{11} + 2C_{12})$ is the uniform volume strain under a hydrostatic pressure p. The bulk modulus of the strained cubic crystal is given by

$$B' = \tfrac{1}{3}(C'_{11} + 2C'_{12}) \tag{2.6}$$

and

$$\delta = -1 - \frac{1}{3(C_{11} + 2C_{12})}(C_{111} + 6C_{112} + 2C_{123}) . \tag{2.7}$$

Equation (2.7) is used to calculate the δ of MgO.

TABLE II. Values of δ and γ.

Crystal	δ calculated from Eq. (2.4) for hcp metals and from Eq. (2.7) for MgO	γ experimental values are taken from White (Ref. 28), Gschneidner (Ref. 29), and Anderson (Ref. 2)
Mg	(a) 1.66 [using Naimon's (Ref. 13) TOE values]	1.50 (Ref. 28)
	(b) 2.69 [using theoretical TOE values (Ref. 14)]	
Be	4.08	1.15
Zn	(a) 4.00 [using Swartz and Elbaum's TOE values (Ref. 17)]	2.03
	(b) 4.32 [using theoretical TOE values (Ref. 14)]	
Cd	4.20	2.28
Zr	1.56	0.71
		0.83
Ti	2.21	1.28
		1.18
Gd	1.33	0.52
		0.55
Dy	1.44	0.78
		0.68
Er	2.09	1.01
		0.88
MgO	2.83 (present value)	
	2.86 [Chang (Ref. 3)]	1.53 (Ref. 2)

III. RESULTS AND DISCUSSION

References for the SOE and TOE constant data for the nine hexagonal metals and the cubic MgO are given in Table I, but the detailed values are not given here so as to conserve space. The calculated values of δ and the Grüneisen γ for these ten crystals are presented in Table II.

In magnesium and zinc the δ value is calculated using the experimental TOE constants of Naimon,[13] and Swartz and Elbaum,[17] respectively, and also from the theoretical TOE constants calculated by Srinivasan and Ramji Rao.[14] For the remaining seven hcp metals δ has been calculated from the theoretical TOE constants. In zinc, the values of δ calculated from the experimental and theoretical TOE constants are very nearly the same. In magnesium, the value of δ obtained from the theoretical TOE constants is larger than that obtained from the experimental TOE constants and is nearer to the 2γ value. In all the hcp metals worked out in this paper, except magnesium (with experimental TOE constants) and beryllium, the relation $\delta = 2\gamma$ is nearly satisfied. Perhaps it would be worthwhile to again look into the measured TOE constants of magnesium and reevaluate the TOE constants of beryllium using a larger number of anharmonic parameters (only three were used). Considering the δ values of the heavy rare-earth metals Gd, Dy, and Er, one finds that Gd and Dy are anharmonic to the same degree, while Er appears to be more anharmonic. Zinc and cadmium have high values of δ and thus are the extreme examples of anisotropy among the hcp metals. The δ values of hcp metals (with the exception of Be), whose C/a value is less than the ideal (1.633), are smaller than those whose C/a ratio is greater than 1.633. The experimental SOE constants data of magnesium,[12] zinc,[16] cadmium,[18] and beryllium[30] have been used to evaluate the bulk modulus of these metals at various temperatures and these are compared with the calculated values. Theoretical curves showing the variation of the bulk modulus of these metals with temperature have been obtained from Eq. (1.11). $\int_0^T C_v\,dT$ is the internal energy content of a solid at any temperature relative to that at absolute zero temperature, and

TABLE III. Values of the constants of Mg, Zn, Cd, and Be used in the present calculations.

Metal	Debye Temperature Θ_D	V_0	Density ρ	B_{00} in 10^{11} dyn/cm^2
Mg	330 °K	13.97	1.738	(i) 3.66 (for δ = 2.69) (ii) 3.61 (for δ = 1.66)
Zn	231 °K	9.16	7.133	(i) 8.03 (for δ = 4.32) (ii) 7.99 (for δ = 4.0)
Cd	160 °K	12.99	8.650	6.26
Be	1367 °K	4.88	1.848	11.55

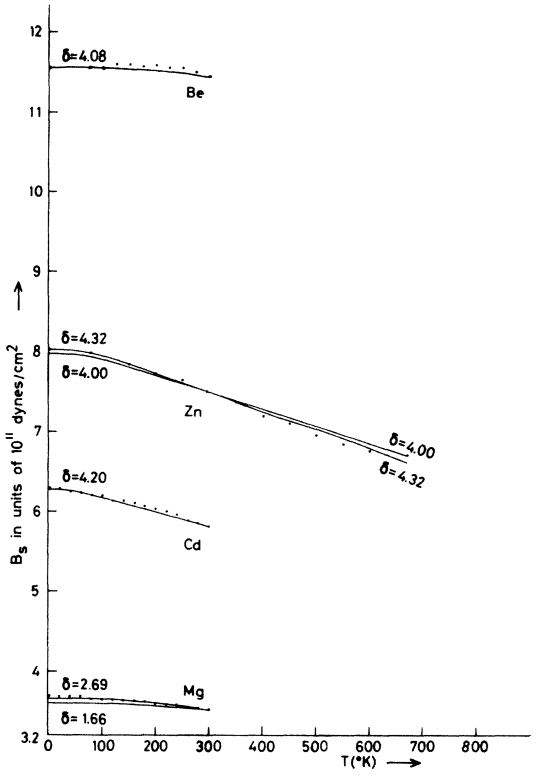

FIG. 1. Variation of the bulk modulus of Mg, Cd, Zn, and Be with temperature. ●, experimental points.

can be tabulated[31] as a function of temperature provided that the characteristic temperature is known. In the present calculations the internal energy content of these metals is obtained by treating them as Debye solids. The values of the parameters V_0, ρ, Θ_D, and B_{00} for the hexagonal metals magnesium, zinc, cadmium, and beryllium are given in Table III. The values of V_0, ρ, and Θ_D correspond to those at room temperature. The variation of the bulk modulus of these metals with temperature is shown in Fig. 1. The agreement is good between the calculated B_S values and those obtained from the measured elastic constants at various temperatures for these four metals. It may be pointed out that Smith and Arbogast[30] mention in their paper that the temperature dependence of C_{12}, and in particular C_{13}, for beryllium is of questionable significance. So the B_S values of beryllium obtained from these elastic constants data are not accurate. The calculated values of B_S for magnesium with $\delta = 2.69$ agree well with the experimental data, while those with $\delta = 1.66$ are lower than the measured values.

In the cubic magnesium oxide the δ value is calculated from the measured SOE and TOE constants by Bogardus[10] and is in good agreement with the value obtained by Chang from the pressure dependence of the bulk modulus. Also in this compound the relation $\delta = 2\gamma$ is only approximately true. Further, Chang showed that the value 2.86 for δ yields values of B_S for MgO that are in good accordance with experimental data. In conclusion, it may be said that we have a simple and unambiguous method for calculating the Anderson-Grüneisen parameter δ of a material from its TOE constants data.

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