Preprint

THE MURNAGHAN EQUATION OF STATE AND HIGH-PRESSURE COMPRESSION CURVE FOR ANISOTROPIC NON-CUBIC CRYSTALS

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ABSTRACT -- The two parameters of the Murnaghan equation of state can be determined accurately by ultrasonic measurements on either single-crystals or polycrystalline aggregates. However, for anisotropic non-cubic crystals, the values determined ultrasonically on aggregates are different from the corresponding values calculated either from the single-crystal second-order elastic constants and their first pressure derivatives or from the singlecrystal third-order elastic constants. For moderately anisotropic solids, like cadmium (hexagonal) and corundum (trigonal), the bulk modulus of singlecrystal materials is always smaller than that of the corresponding aggregates of zero-porosity. On the other hand, the pressure derivative of the bulk modulus of single-crystal material is larger than the corresponding quantity determined on pore-free polycrystalline aggregates. A consequence of these differences is that the two parameters in the Murnaghan equation derived from

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the single-crystal acoustic data based on the uniformstress-model may not give the accurate pressure-volume relation for aggregate materials made of crystals whose elastic anisotropy is large.

The Murnaghan form of an equation of state is useful not only in solid state physics but also in studies of shockwaves, problems of underground nuclear detection, and a host of other disciplines. The equation was derived from Murnaghan's "integrated linear theory of finite strain"[1], and it has been observed earlier [2-4] that this macroscopic equation of state is superior to other equations obtained thus far from quantum mechanics or lattice theory.

The Murnaghan equation of state can be written in a form
[1]

$$p = \frac{B_0}{B_0} (y^{B_0} - 1)$$
 (1)

where $y = (V_0/V) = (\rho/\rho_0)$ and

$$B_{O} \equiv \{-V_{O}\left(\frac{\partial p}{\partial V}\right)_{T}\}_{p = 0}$$
(2)

$$B_{O}' = \left\{ \left(\frac{\partial B^{T}}{\partial p} \right)_{T} \right\}_{T} = 0$$
(3)

and

Experimentally, the Murnaghan parameters B_{O} and B_{O} ' can be determined accurately from ultrasonic measurements made either on single-crystals or on pore-free polycrystalline aggregates [5, 6]. It is expected theoretically that, for solids of isotropic and cubic symmetries, the Murnaghan parameters determined on single-crystals are exactly the same as that measured on the corresponding pore-free polycrystalline aggregates. However, for solids of lower symmetry, the bulk modulus calculated from the single-crystal secondorder elastic constants differs from the corresponding modulus measured on pore-free polycrystalline aggregates; the difference between the two values is proportional to the elastic anisotropy of the crystal. The question thus arises as to the relation between the Murnaghan parameters determined on polycrystalline materials and those obtained from singlecrystals. Our purpose in this communication is to suggest the appropriate Murnaghan parameters for anisotropic noncubic solids and to examine the extent to which the usual application of linear elasticity theory is still useful for predicting the pressure-volume relation of strongly anisotropic crystals.

THE MURNAGHAN PARAMETERS

In the usual application of linear elasticity theory, the bulk modulus of a crystal is defined as [7]

$$B_{1} = -V \cdot \frac{dp}{dV} = f_{1}(1/s_{\mu\nu}) \quad (4)$$

$$\sigma_{ij}(S_{ijkl}, \tilde{R}) = \bar{\sigma}$$

where $s_{\mu\nu}$ are the single-crystal second-order elastic compliances in the usual matrix notation, σ_{ij} are the stress tensors, \tilde{R} is the rotation matrix, and f_1 is a functional constant dependent upon the crystal symmetry. Note that B_1 , a scalar, is some linear combination of the elements of the second-order elasticity tensor. The Murnaghan parameters are thus given by [see, for example, Ref. 5]

$$B_{0} = \{ B_{1}^{T} \}_{p=0}$$
 (5)

and

$$B_{0}' = \{ (B_{1}^{T})' \}_{p=0}$$
 (6)

where the prime refers to isothermal pressure derivative and the superscript T denotes the isothermal value.

It has been shown experimentally [8] that the bulk modulus of polycrystalline aggregates cannot be given by Eq. (4). In light of the Voigt-Reuss-Hill (VRH) approximation [6], the bulk modulus of <u>pore-free</u> polycrystalline aggregates is given by

$$B^* = \frac{1}{2} (B_1 + B_2)$$
(7)

where B_1 is given by Eq. (4) and

$$B_{2} = -V \cdot \frac{dp}{dV} = f_{2} (c_{\mu\nu})$$

$$\varepsilon_{ij}(C_{ijkl}, \tilde{R}) = \bar{\varepsilon}$$
(8)

where $c_{\mu\nu}$ are the single-crystal second-order elastic stiffnesses, ϵ_{ij} are the strain tensors, and f_2 is a functional constant which depends on the crystal symmetry. Hence, the appropriate Murnaghan parameters for the polycrystalline materials are

$$B_{O}^{*} = \{B^{*T}\}_{p=0}$$
(9)

and

$$B_{o}^{*'=} \{ (B^{*'})' \}_{p=0}$$
(10)

where, as before, the prime refers to the isothermal pressure derivative.

Note that B_1 and B_2 are the well-known Reuss and Voigt limits, respectively; for crystals of general symmetry, rigorous expressions for B_1 and B_2 are as follows [9]:

$$1/B_1 = s_{11} + s_{22} + s_{33} + 2 (s_{12} + s_{23} + s_{13})$$
(11)

$$B_{2} = \frac{1}{9} [(c_{11} + c_{22} + c_{33}) + 2 (c_{12} + c_{23} + c_{13})] (12)$$

As the crystal symmetry increases, these expressions reduce to simpler forms; for hexagonal, tetragonal, and trigonal crystals, they become simply:

$$1/B_1 = \frac{1}{D} [c_{11} + c_{12} + 2c_{33} - 4c_{13}]$$
(13)

and

and

$$B_2 = \frac{1}{9} \left[2c_{11} + 2c_{12} + c_{33} + 4c_{13} \right]$$
(14)

where
$$D = C_{33} (C_{11} + C_{12}) - 2C_{13}^2$$

Taking the first pressure derivative and arranging the result [6], we find

$$B_{1}' = (B_{1}/D)^{2} (c_{11} + c_{12} + 2c_{33} - 4c_{13}) D'$$

$$- (B_{1}^{2}/D) (c_{11}' + c_{12}' + 2c_{33}' - 4c_{13}')$$
(15)
$$B_{2}' = \frac{1}{9} [2c_{11}' + 2c_{12}' + c_{33}' + 4c_{13}']$$
(16)

where
$$D' = (c_{11} + c_{12}) c_{33}' + c_{33} (c_{11}' + c_{12}') - 4c_{13} c_{13}'$$
.
It may be noted that the $c_{\mu\nu}$ are typically adiabatic values determined from ultrasonic measurements and the primes refer to their isothermal pressure derivatives.

6

(16)

COMPARISON WITH EXPERIMENTAL DATA ON COMPRESSION

Single-crystal acoustic data (i.e., the second-order elastic constants and their isothermal pressure derivatives) have been determined for three hexagonal crystals -- Mg [10], Cd [11], and CdS [12] and also for two trigonal crystals -a-quartz [13] and corundum [14]. From these data, the adiabatic bulk modulus and its isothermal pressure derivative were calculated. Table 1 lists the initial density and volume of each crystal, adiabatic bulk modulus and its isothermal pressure derivatives evaluated at different boundary conditions, and percent elastic anisotropy in compression. These values of the isothermal pressure derivative of the adiabatic bulk modulus were then converted into (a) the isothermal pressure derivative of the isothermal bulk modulus and (b) the adiabatic pressure derivative of the adiabatic bulk modulus, according to the procedure presented earlier [6]. The results are summarized in Table 2.

Note that, for <u>small</u> elastic anisotropy, as in the cases of Mg and CdS, $\{B_1^T\}_{p=0}$ and $\{B^{*T}\}_{p=0}$ are practically the same; their pressure derivatives are identical. The consequence of this equality is that, for these materials, the compression curves as calculated from the ultrasonic data on single-crystals are expected to be identical with those of the corresponding pore-free polycrystalline materials. An illustration of this can be made for Mg as follows: The ultrasonic equation of state (following Murnaghan [1]) for singlecrystal magnesium is

$$\frac{V}{V_{O}} = [1 + 1.2126 \times 10^{-2} \text{p}]^{-0.2398}, \qquad (17a)$$

whereas the corresponding equation for polycrystalline magnesium is

$$\frac{V}{V_{O}} = [1 + 1.2122 \times 10^{-2} p]^{-0.2398}.$$
 (17b)

In both equations, p is expressed in kilobars. At a typical pressure, say $p = B_0^T/2$, these equations result in $(V/V_0) = 0.763$; this value compares favorably with 0.760, a value found from a smoothed curve based on the experimental data [15-18] on compression.

Fig. 1 is an illustration of the compression of CdS. The line shown is the result of the Murnaghan equation of state with the parameters given in Table 2. The experimental points are the results of isothermal compression measured by Lewis, Perez-Albuerne, and Drickamer [19]. The discontinuity in the compression curve at 20 to 30 kb, observed also in other physical properties [19-26], was attributed to a change from CdS-I(Wurtzite) to CdS-II(Rocksalt) structure. The mechanism of this transformation is not fully understood, but the transformation is generally recognized as first-order. As seen in Fig. 1, the transformation results in about 19% decrease in volume, a change that is in accordance with the earlier calculations [25] of 17% (along the c-axis) and 18% (along the a-axis).

Cadmium exhibits a fairly large elastic anisotropy, 9%. The Murnaghan parameters for single-crystal cadmium are $B_o =$ 4.581 x 10^{11} dyn/cm² and $B_o' = 6.28$, whereas for polycrystalline materials these parameters are 5.012 x 10^{11} dyn/cm² and 6.14. The difference in the bulk modulus is about 10% and that in the pressure derivative is about 2%. Fig. 2 illustrates effects of these differences on the compression curve. The data points entered in the figure are isothermal compression measurements of Bridgman [27], McWhan [28], and Perez-Albuerne et al [17, 29]. The shock-wave compression data of Rice et al [18] and McQueen and Marsh [30] are also entered. Anderson [5] presented a similar diagram up to about 500 kb. The compression curves drawn from the Murnaghan equation of state fit the experimental compression points very well to about 1.4 mb, contradicting the result of Anderson (Figs. 6 and 7 of Ref. 5).

Fig. 3 shows the compression of SiO_2 . The lines drawn in the figure are the results of the Murnaghan equation of state using the acoustic parameters given in Table 2. α -quartz possesses low elastic anisotropy in compression (see Table 1), and for this reason the compression curve drawn from the singlecrystal acoustic parameters is very similar to that drawn from the computed polycrystalline parameters. Compared with these

compression curves are the experimental data on isothermal compression [31, 32] as well as on shock-wave compression [33, 34]. Up to about 150 kb, the compression curves drawn from the Murnaghan equation are in reasonably good agreement with the experimental data. Above 150 kb, the shock-wave compression points [33, 34] deviate sharply from the compression curves of α -quartz, and this deviation is associated with phase transformations of α -quartz to denser polymorphs.

The compression of both single-crystal and polycrystalline corundum is illustrated in Fig. 4 (see also Refs. 5 and 38). The experimental compression points include those of Bridgman [35] and Hart et al [36] measured on single-crystals. Also included are the shock-wave data [37] on both singlecrystal and polycrystalline materials. The lines in the figure represent the Murnaghan equation of state calculated from the acoustic parameters: one derived from the single-crystal acoustic data [14] and the other from the polycrystalline acoustic data [38]. It is apparent that the Murnaghan parameters evaluated from both single-crystal and polycrystalline acoustic data yield a good description of the pressure-volume relation for the experimental compression points including the shock-wave data.

DISCUSSION AND CONCLUDING REMARKS

The Murnaghan parameters for anisotropic non-cubic crystals derived from the single-crystal acoustic data based on the usual application of elasticity theory are different from the corresponding parameters determined on polycrystalline aggregates, even though free of pores. Thus, the compression curve predicted by the Murnaghan equation of state using the single-crystal acoustic parameters is also different from that derived from the polycrystalline materials. This difference, illustrated with hexagonal cadmium, trigonal α -quartz, and trigonal corundum, is small for crystals of relatively low anisotropy but, for highly anisotropic crystals, the difference appears to be significant.

Consider Fig. 5, a plot of the difference between the single-crystal bulk modulus and polycrystalline bulk modulus against percent elastic anisotropy in compression for all the hexagonal crystals of which the single-crystal elastic constants are accurately known. It is apparent from this figure that, as the elastic anisotropy becomes large, the difference in the bulk moduli also becomes large. Similarly, one expects the same trend of the difference for the pressure derivative of the bulk modulus (see Table 1).

In conclusion, the two parameters in the Murnaghan equation of state defined by Eqs. (5) and (6) seem still useful for the description of the pressure-volume relation of a non-cubic crystal. This implies the success of the uniformstress-model (Reuss scheme) for the description of the isotropic properties of anisotropic crystals. If, however, the crystal has a large elastic anisotropy such that the anisotropy causes a heterogeneous stress distribution, the use of Eqs. (9) and (10) as the two parameters in the Murnaghan equation is recommended for aggregate materials made of such an anisotropic crystal.

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Material	Density (gm/cm ³)	Volume (cm ³ /mol	BS 1 (x	B ^S 2 (10 ⁻¹¹)	B*S lyn/cm ²)	$\frac{dB_1^s}{dp}$	$\frac{dB_2^s}{dp}$	$\frac{dB^{*S}}{dp}$	% Elastic Anisotropy
Mg (59Sl) ^(a)	1.738	13.993	3.555	3.557	3.556	4.06	4.06	4.06	0.01
Cd (62Cl)	8.648	12.998	4.858	5.774	5.316	6.66	6.30	6.48	8.72
CdS (67C1)	4.870	29.667	6.176	6.177	6.177	4.12	4.12	4.12	0.01
α-Quartz(65Ml)	2.649	22.684	3.741	3.790	3.766	6.33	6.51	6.42	0.65
α-Al ₂ 0 ₃ (67Gl)	3.986	25.580	25.441	25.472	25.457	4.28	4.26	4.27	0.11

Table 1. Adiabatic bulk modulus and its isothermal pressure derivative of 3 hexagonal and 2 trigonal crystals. All values are at $T = \sqrt{300}$ °K.

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 67C1: J. A. Corll, Phys. Rev. <u>157</u>, 623 (1967).
 67G1: J. H. Gieske, Personal Communications (1967).

Material	^γ G(thermal)	$\frac{\mathrm{T\gamma}_{\mathrm{G}}}{\mathrm{B}^{\mathrm{S}}}(\frac{\mathrm{\partial}\mathrm{B}^{\mathrm{S}}}{\mathrm{\partial}\mathrm{T}})_{\mathrm{P}}$	(^{{B} 1 [}] p= x 10 ⁻¹¹	$0 {B*} \\ p=0.$		$\{\frac{dB_{1}}{dp}\}_{p=0}$	dB* { <u>dp</u> } p=0
Mg	1.55 ^(a)	0.13	BS	3.555	3.555	()B _s /9b) 4.30	4.30
			B^{T}	3.439	3.440	(9B _T /9b) _T 4.17	4.17
Cd	2.20 ^(a)	0.13	BS	4.858	5.316	(9B _a /9b) _s 6.41	6.27
	·		BT	4.581	5.012	(9B _T /9b) _T 6.28	6.14
CdS	1.09 ^(b)	?	B ^S	6.176	6.177	(9B2/9b) ?	?
			B^{T}	6.154	6.155	(98 _T \9b) _T 4.15	4.15
α-Quartz	0.75 ^(C)	0.04	BS	3.741	3.766	(9B ₂ /9b) _s 6.38	6.47
			B^{T}	3.714	3.738	(9B _L \9b) _T 6.34	6.43
a-Al ₂ 0 ₃	1.34 ^(d)	0.03	B ^S	25.441	25.457	(9B ₂ \9b) 4.35	4.34
			Β ^T	25.281	25.296	(∂B ^T /∂p) _T 4.32	4.31

Table 2,	The	Murnaghan	parameters	evaluated	at	different	boundary	conditions.
	All	values are	e at $T = \sqrt{3}$	00 °K.				

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FIGURE CAPTIONS:

Fig. 1. Compression of CdS.

Fig. 2. Compression of Cd.

Fig. 3. Compression of SiO₂.

Fig. 4. Compression of α -Al₂O₃.

Fig. 5. Illustration of the difference between the single-crystal bulk modulus and polycrystalline bulk modulus as a func-

tion of elastic anisotropy (The micas are monoclinic crystals, but they are included in the figure because original authors reporting $c_{\mu\nu}$ treated these materials as though they are hexagonal crystals).



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