

Iterative Procedure to Estimate the Values of Elastic Constants of a Cubic Solid at High Pressures from the Sound Wave Velocity Measurements

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In order to estimate accurately the values of the elastic constants of a solid at high pressure and at an arbitrary temperature T from the ultrasonic measurements of the velocities of elastic waves propagated in solids as a function of pressure at the temperature T , it is necessary to know *a priori* the compressibility of the solid as a function of pressure at the temperature T . However, this latter information is not always available. Hence, one has to make some kind of approximation to estimate the values of the elastic constants of solids at high pressure. The procedure developed here is more consistent than previous procedures. It requires *a priori* knowledge of the following values: the thermal expansion coefficient, its temperature derivative, the specific heat at constant pressure of a solid at one atmosphere, and the travel-time measurements of the elastic waves propagated through the solid as a function of pressure at a temperature T or at more than one temperature.

INTRODUCTION

An investigator attempting to determine the variation of elastic constants of solids with pressure by ultrasonic measurements on new (or even well known) materials may find that the needed compressibility measurements are either unavailable or if available are unreliable. Cook's method enables one to obtain an estimate of the values of the elastic constants of a solid at high pressure without *a priori* knowledge of the compressibility of the substance.¹ In developing the estimating procedure Cook assumed that the parameter $\Delta(P)$ [c.f. General Notation and Analysis Section, Eq. (5)], remained constant with pressure. The value of $\Delta(P)$ at any pressure P is given by its magnitude at one atmosphere. Ruoff² extended the results of Cook in the case of cubic solids by presenting an estimating procedure which permitted the parameter $\Delta(P)$ to vary with pressure. This was done by expressing $\Delta(P)$ in a power series expansion given by (1):

$$\Delta(P) = \Delta(P=1) + P[\partial\Delta(P)/\partial P]_{P=1} + \frac{1}{2}P^2[\partial^2\Delta(P)/\partial P^2]_{P=1} + \dots, \quad (1)$$

where the quantities on the right-hand side of (1) are evaluated at 1 atm.

Even so the lack of relevant data in the case of most materials limits one to the first derivative of $\Delta(P)$. This is easily seen by differentiating $\Delta(P)$ with respect to pressure P . The present work develops an iterative procedure to estimate the values of the elastic constants of cubic solids at high pressure which differs from the one developed by Ruoff with respect to the assumptions regarding (i) the pressure derivative of the thermal volume expansion coefficient at a temperature T , (ii) the temperature derivative of the volume thermal expansion coefficient at a pressure P , and (iii) the estimation procedure for $\Delta(P)$. It is shown here that no assumptions regarding (i) and (ii) are necessary in order to estimate the elastic constants of cubic solids at

higher pressures provided the ultrasonic measurements are made as a function of pressure at more than one temperature. This enables one to compute a more realistic estimate of elastic constants of cubic solids as a function of pressure.

The size, density, and elastic constants of a material specimen change with the application of pressure. The concomitant changes are observed in the value of the resonant or null frequencies of a standing wave and also in the measurement of travel-time for a pulse between flat parallel faces of the specimen. The analysis presented in this paper refers to frequency measurements but is equally valid for the travel-time measurements of an elastic wave propagated in a medium.

GENERAL NOTATION AND ANALYSIS

By a solid we always refer to a cubic solid. Even though the quantities dealt with here refer to a pressure P and a temperature T , for simplicity the relevant suffix for the temperature is dropped from the general notation.

$\rho(P)$	the density of the material at pressure P
$\beta(P)$	volume-expansion coefficient of the material at pressure P
$C_P(P)$	specific heat at constant-pressure of the material at pressure P
$B^S(P)$	adiabatic bulk modulus of the material at pressure P
$B^T(P)$	isothermal bulk modulus of the material at pressure P
$\chi^T(P)$	isothermal compressibility of the material at pressure P
$L(J, P)$	the thickness of the specimen used in the measurement of the J th velocity mode at pressure P
$\lambda(P)$	$= L(J, P_1)/L(J, P)$; $P_1 < P$; $P=1=1$ atm or 1 bar, only in the case of cubic material

$V(J, P)$	the J th velocity mode in the material at pressure P
$\tau(J, P)$	the travel-time for the J th velocity mode at pressure P
$F(I, J, P)$	the I th null frequency observed for the J th velocity mode in the material at pressure P
$N(I, J, P)$	the number of $\frac{1}{2}$ wavelengths in the specimen corresponding to $F(I, J, P)$
$\tau(I, J, P)$	the travel time in the specimen corresponding to $F(I, J, P)$
$IMP(J, P)$	mechanical impedance of quartz transducer for J th velocity mode at pressure P
$K(I, J, P)$	$IMP(J, P)/(\text{mechanical impedance of the material corresponding to } \tau(I, J, P))$
$V(1, P)$	longitudinal velocity in the (100) direction at pressure P
$V(2, P)$	shear velocity in the (100) direction at pressure P
$V(3, P)$	longitudinal velocity in the (110) direction at pressure P

We need only know any three independent velocity modes in order to obtain the three elastic constants of a solid. In this paper the resonant frequencies measured as a function of pressure for the longitudinal modes of propagation in the (100) and (110) directions and the shear mode of propagation in the (100) direction have been used.³

We also assume the following:

- (i) The temperature dependence of the volume, or the linear expansion coefficient at a temperature T and one atmosphere is known;
- (ii) the specific heat at temperature T and one atmosphere is known; and
- (iii) $[\partial\beta(P)/\partial T]_P \approx [\partial\beta(P_1)/\partial T]_{P_1}$, where $P \geq P_1$, holds.⁴

Then the procedure outlined below can be used to estimate the elastic constants of solids at higher pressures, without reference to *a priori* knowledge of the compressibility of the substance.

The relation between the adiabatic bulk modulus and $V^2(J, P)$, ($J=1, 3$), in a cubic solid may be written as $B^S(P) = \frac{1}{3}\rho(P)[4V^2(3, P) - 4V^2(2, P) - V^2(1, P)]$. (2)

Relation (1), expressed in terms of $L(J, P_1)$, $\tau(J, P)$, $\lambda(P)$, and $\rho(P_1)$, is given as relation (3):

$$B^S(P) = \frac{1}{3}\rho(P_1)\lambda(P)[4L^2(3, P_1)/\tau^2(3, P) - 4L^2(2, P_1)/\tau^2(2, P) - L^2(1, P_1)/\tau^2(1, P)], \quad (3)$$

where $\rho(P) = \lambda^3(P)\rho(P_1)$. By the definition of isothermal bulk modulus we obtain

$$B^T(P) = -\text{Vol.}(P)[\partial P/\partial \text{Vol.}(P)]_T = \rho(P)[\partial P/\partial \rho(P)]_T = \frac{1}{3}\lambda(P)[\partial P/\partial \lambda(P)]_T. \quad (4)$$

And if

$$\Delta(P) = \beta^2(P)B^S(P)T/\rho(P)C_P(P) \quad (5)$$

where temperature T is in Kelvin, then

$$B^T(P) = B^S(P)/[1 + \Delta(P)]. \quad (6)$$

Using Williams and Lamb's⁵ method of ultrasonic wave velocity measurements as modified by Colvin,⁶ transit time for the various wave propagations is obtained from the following relations:

$$N(I, J, P) = \text{Integer}\{[F(I, J, P)/\Delta F(I, J, P)] - 0.5 - K(I, J, P)\}, \quad (7)$$

$$\tau(I, J, P) = [N(I, J, P) + 0.5]/2F(I, J, P) - [K(I, J, P)/2]\{[1/F(R, J, P)] - [1/F(I, J, P)]\}. \quad (8)$$

In the above expressions $K(I, J, P)$ may be written as

$$K(I, J, P) = IMP(J, P)/\rho(P)V(J, P) = IMP(J, P)\tau(J, P)/\rho(P_1)\lambda^2(P)L(J, P_1) \quad (9)$$

where $IMP(J, P)$ is the mechanical impedance of the transducer for the J th velocity mode at pressure P .

It is evident from relation (8) that if the measurements are made near $F(R, J, P)$ any error in the estimation of $\tau(I, J, P)$ due to inaccurate knowledge of $K(I, J, P)$ becomes negligible.

By integrating relation (4) we obtain

$$\lambda(P) = \lambda(P_1) \exp[(P - P_1)/3B^T(P)]. \quad (10)$$

Two things should be noted regarding the derivation of (10) from (4): (i) In the definition of isothermal bulk modulus at a pressure P , one could obtain its value by either decreasing or increasing the pressure slightly; and (ii) when integrating (4) it must be remembered that it is implied in the definition of $B^T(P)$ that it remains constant over the range of integration P_1 to P . In expression (10) it is implied that the isothermal bulk modulus of a substance at pressure P has been obtained by decreasing the pressure from P to P_1 . The expression for $\lambda(P)$ as derived above differs from that obtained by following either Cook's or Ruoff's procedures. The expression for $\lambda(P)$ that will be obtained by following Cook's or Ruoff's procedure may be given by

$$\lambda(P) = 1 + [\rho(P_1)L^2(1)]^{-1} \int_1^P [1 + \Delta(P)] \times \{[4/\tau^2(3, P)] - [4/\tau^2(2, P)] - [1/\tau^2(1, P)]\}^{-1} dP, \quad (11)$$

where $L(J, 1) = L(1)$, and $[1 + \Delta(P)]$ is a constant in Cook's method and equals $[1 + \Delta(1)]$ but is a variable in Ruoff's method.

This expression (11) for $\lambda(P)$ is arrived at by expressing $B^T(P)$ in terms of $\rho(1)$, $L(1)$, $\tau(J, P)$, and $\Delta(P)$ with the help of Eqs. (3) and (6), and integrating (4). Hence, $\lambda(P)$ in (11) can be determined if the value of $\Delta(P)$ can be estimated. Ruoff² estimates the values of $\Delta(P)$ from the relation (1) by means of thermodynamics relations. For example, to evaluate $[\partial\Delta(P)/\partial P]_T$, we would rewrite $B^S(P)$ as

$$B^S(P) = \rho(P) [L^2(P)/\tau^2(P)]. \quad (12)$$

Then $\Delta(P)$ in (5) may be written as

$$\Delta(P) = \beta^2(P) TL^2(P)/[\tau^2(P) C_P(P)], \quad (13)$$

and the logarithm derivative of $\Delta(P)$ yields

$$\begin{aligned} \frac{1}{\Delta(P)} \left(\frac{\partial \Delta(P)}{\partial P} \right)_T &= \frac{2}{\beta(P)} \left(\frac{\partial \beta(P)}{\partial P} \right)_T + \frac{2}{L(P)} \left(\frac{\partial L(P)}{\partial P} \right)_T \\ &\quad - \frac{2}{\tau(P)} \left(\frac{\partial \tau(P)}{\partial P} \right)_T - \frac{1}{C_P(P)} \left(\frac{\partial C_P(P)}{\partial P} \right)_T. \end{aligned} \quad (14)$$

From thermodynamics, we know that

$$[\partial\beta(P)/\partial P]_T = -[\partial\chi^T(P)/\partial T]_P \quad (15)$$

and

$$\left(\frac{\partial C_P(P)}{\partial P} \right)_T = -\frac{T}{\rho(P)} \left\{ \left(\frac{\partial \beta(P)}{\partial T} \right)_P + \beta^2(P) \right\}. \quad (16)$$

Hence, in the limit as $P \rightarrow 1$, the expression (14) reduces to

$$\begin{aligned} \frac{1}{\Delta(1)} \left(\frac{\partial \Delta(P)}{\partial P} \right)_{T, P \rightarrow 1} &= -\frac{2}{\beta(1)} \left(\frac{\partial \chi^T(P)}{\partial T} \right)_{P \rightarrow 1} - \frac{2}{\tau(1)} \left(\frac{\partial \tau(P)}{\partial P} \right)_{T, P \rightarrow 1} + \frac{T}{\rho(1) C_P(1)} \\ &\quad \times \left[\left(\frac{\partial \beta(P)}{\partial T} \right)_{P \rightarrow 1} + \beta^2(1) \right]. \end{aligned} \quad (17)$$

Thus the magnitude of the first derivative of $\Delta(P)$ in the limit as $P \rightarrow 1$ may be determined if the $[\partial\chi^T(P)/\partial T]_{P=1}$, $[\partial\beta(P)/\partial T]_{P=1}$, $\beta(1)$, and $C_P(1)$ are known and the value of $\Delta(P)$ may be approximated at a pressure P by

$$\Delta(P) = \Delta(1) + P[\partial\Delta(P)/\partial P]_{P \rightarrow 1, T}. \quad (18)$$

Similarly the higher derivatives of $\Delta(P)$ may be evaluated if the relevant thermodynamic data are available.

The expression for $\lambda(P)$ in the new method, i.e., relation (10) described in this paper, is seen to differ from the earlier two works for two reasons. In their works, (i) $\lambda(P)$ is defined as $L(J, 1)/L(J, P)$, and (ii) $\Delta(P)$ is estimated by a different procedure.

The quantities measured or known are $\rho(1)$, $L(J, 1)$, $F(I, J, P)$ or $\tau(J, P)$, P and T . For quartz transducers, $IMP(J, P)$ and $F(R, J, P)$ can be obtained safely to 4000 bars and from room temperature to 90°K from the work of McSkimin and Andreatch.⁷ This information is not required if the ultrasonic measurements are of the travel times. $\beta(P)$ is usually known only as a function of temperature at 1 atm. However, the variation in the elastic constants with temperature at pressure P provides one with the temperature derivative of the isothermal compressibility. And from relation (15) one may obtain $\beta(P)$ at temperature T if $\beta(P)$ is known at one atmosphere and temperature T . In a normal substance where $P_1 \leq P$,

$$[\partial\chi^T(P)/\partial T]_P \leq [\partial\chi(P_1)/\partial T]_{P_1} \quad (19)$$

holds. So, to assume that

$$-[\partial\beta(P)/\partial P]_T \approx [\partial\chi^T(P_1)/\partial T]_{P_1=1} \quad (20)$$

ensures that the value of $\Delta(P)$ obtained from (5) is underestimated. If ultrasonic measurements are made as a function of pressure at more than one temperature, a better estimate of $[\partial\chi^T(P)/\partial T]_P$ may be obtained by simply incorporating $[\partial\chi^T(P)/\partial T]_P$ as an additional parameter to be iterated according to the scheme presented in Fig. 2. Where such information is unavailable (19) or (20) may be used. Similarly the computation of $C_P(P)$ from relation (16) by assuming

$$[\partial\beta(P)/\partial T]_T \approx [\partial\beta(P_1)/\partial T]_{P_1=1} \quad (21)$$

implies that the resulting values of $C_P(P)$ from relation (16) will also be underestimated. However, the resultant error in the estimated value of $\Delta(P)$ due to the intrinsic underestimation of $\beta(P)$ and $C_P(P)$ is likely to be small, up to 3-4 kbar for most materials. Thus everything in expression (5) except $B^S(P)$ and $\rho(P)$ are either known or may be approximated with reasonable accuracy.

The iterative procedure described below is that presented in Fig. 1, because we feel that the understanding of the procedure given in Fig. 2 will be facilitated by an understanding of the simpler procedure. Thus the iterative procedure described assumes that relations (20) and (21) hold.

At $P=1$ atm, all the quantities involved are known; no iteration is required to estimate the required elastic constants of solids.

At the next higher pressure all the fundamental quantities in the relations (3), (5), (6), (7), (8), (9), and (10), except $\lambda(P)$ and $K(I, J, P)$, are known. The procedure developed here involves a two stage iteration,

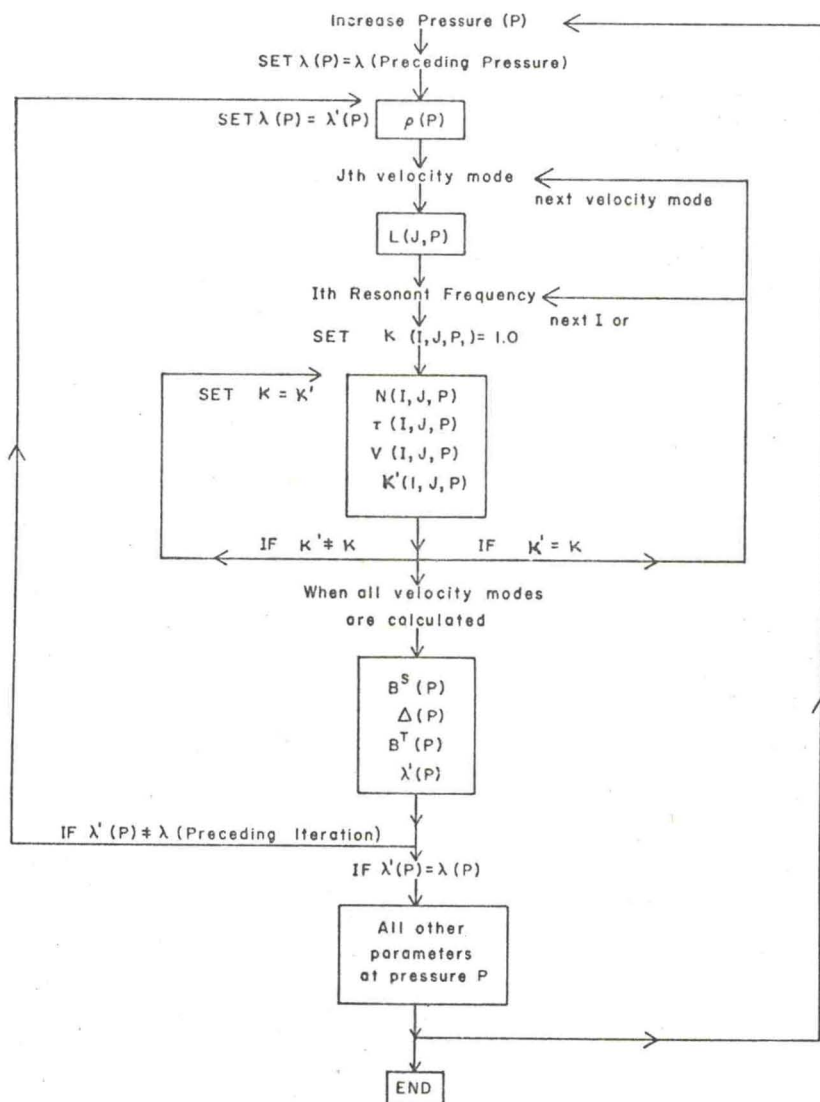


FIG. 1. A flow chart of the iterative procedure to estimate the variation in the elastic constant of a cubic solid with pressure when the elastic wave velocities are obtained from the measurement of the resonant frequencies of a standing wave as a function of pressure at a temperature.

one at the level of pressure and the other on the I th null frequency of the J th mode. We set $\lambda(P) = \lambda$ (Preceding Pressure) and $K(I, J, P) = 1$ and estimate $N(I, J, P)$ and $\tau(I, J, P)$ and $K(I, J, P)$. If the value of $K(I, J, P)$ thus obtained agrees with the previously assigned value we compute $N(I, J, P)$ for the $(I+1)$ th frequency. If this value of $K(I, J, P)$ does not agree with the previously assigned value these values of $N(I, J, P)$ and $\tau(I, J, P)$ are corrected by setting $K(I, J, P)$ equal to the value obtained last, and iterating all over again. This is repeated till two consecutive estimates of $K(I, J, P)$ are the same. A similar computation is performed for all the velocity modes. By interpolation, from these $\tau(I, J, P)$'s one obtains values corresponding to $F(R, J, P)$, each of which is called $\tau(J, P)$. These $\tau(J, P)$'s in turn are used to obtain $V(J, P)$ which together with $\rho(P)$ yield an estimate of $B^S(P)$, $\Delta(P)$, $B^T(P)$, and finally $\lambda'(P)$. If the value of $\lambda'(P)$ thus obtained agrees with the previously assigned value,

TABLE I. The pressure derivative of the adiabatic and isothermal bulk moduli of NaCl and KCl as obtained by Bartels and Schuele (B and S), as obtained in the present work (D) from the data of Bartels and Schuele.

	Bulk modulus	
	B and S	D
NaCl		
295°K		
Adiabatic	5.27	5.33
Isothermal	5.35	5.38
195°K		
Adiabatic	5.13	5.18
Isothermal	5.20	5.23
KCl		
295°K		
Adiabatic	5.34	5.36
Isothermal	5.41	5.44
195°K		
Adiabatic	5.34	5.36
Isothermal	5.41	5.43

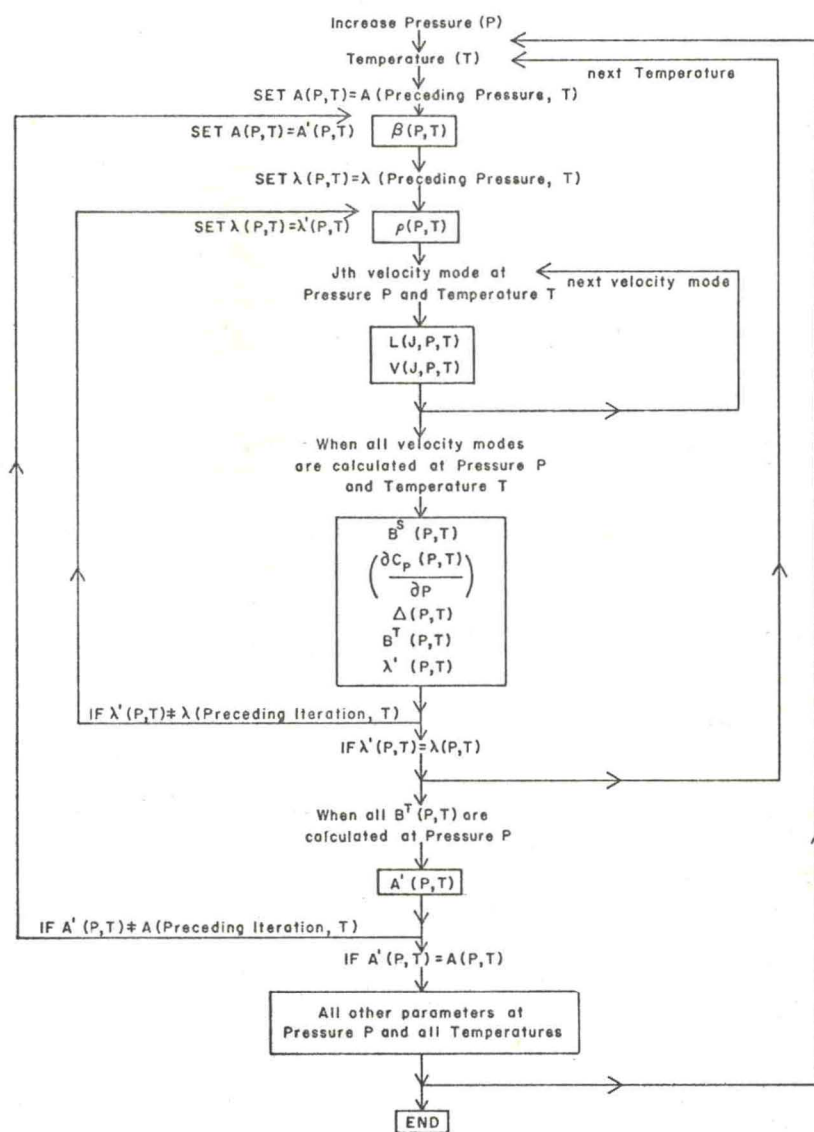


FIG. 2. A flow chart of the iterative procedure to estimate the variation in the elastic constants of a cubic solid with pressure when the travel-time measurements are made as a function of pressure at more than one temperature. $A(P, T) = [\partial \chi(P, T) / \partial T]_P$.

the estimates of $B^S(P)$ and $B^T(P)$ are correct. If this value of $\lambda(P)$ does not agree with the previously assigned value these $B^S(P)$ and $B^T(P)$ are corrected by means of setting $\lambda(P)$ equal to the value of $\lambda(P)$ obtained last and iterating all over again. This is repeated till two consecutive estimates of $\lambda(P)$ are the same. Once this is known all other elastic constant parameters may be obtained. This iterative procedure is sketched diagrammatically in Fig. 1.

Table I displays the estimates of the pressure derivatives of the adiabatic and isothermal bulk moduli of NaCl and KCl at 295° and 195°K obtained from the above mentioned iterative procedure. The required travel time data as a function of pressure for this computation were reconstructed from the pressure derivatives of the travel-time for the various elastic wave velocities given in the paper of Bartels and Schuele.⁸

All other ancillary data used were also taken from Ref. 8. It may be seen that the estimates of the pressure derivatives of the bulk moduli of NaCl and KCl as obtained in the present work for pressures ranging up to 1.7 kbar differ slightly from those obtained by Bartels and Schuele. However, such differences may become significant at higher pressures. It should be noted further that the iterative procedure outlined in the present work may be easily applied to determine the variation in the elastic constants of an isotropic solid.

Figure 2 is the schematic representation of the iteration procedure when the travel-time measurements are made as a function of pressure at more than one temperature.

We are in the process of developing a variant of this iterative procedure designed to estimate the elastic constants of a noncubic solid as a function of pressure.

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² A. L. Ruoff, Intra-Laboratory Rep. No. 8, Thurston High Pressure Laboratory, Cornell University, Ithaca, N. Y., 1968.

³ Changes in the choice of independent velocity modes merely change the expression for the adiabatic bulk modulus in expression (2).

⁴ Assumption (iii) need not be made if ultrasonic measurements are made as a function of pressure at more than one temperature.

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Microdeformation of Solids

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Small-scale indentation experiments performed on nonmetallic specimens are reported. These experiments are very similar to others performed by one of us (N.G.) on metal specimens and reported in a previous issue of this journal. Again, it is believed that the theoretical strength of the perfect lattice is being observed.

In a previous paper¹ Gane and Bowden have reported the results of very small-scale indentation tests performed on electropolished single-crystal specimens of several fcc metals. These experiments were performed inside a scanning electron microscope, and used fine single-crystal titanium carbide tips, similar to field-ion microscope tips, as indenters. These tips were prepared by a two-layer ac electropolishing technique, developed originally by Ralph.² The results of these experiments were notable because (a) no deformation occurred until a critical load on the indenter was reached, and (b) this critical load was often very high, so that the shear stress corresponding to the onset of deformation approached the estimated theoretical shear strength.^{3,4}

The purpose of the present communication is to report that similar results have been obtained from an analogous series of experiments performed on single crystals of two nonmetallic materials, germanium and magnesium oxide. {100} surfaces of magnesium oxide crystals and {111} surfaces of germanium crystals were prepared by chemical polishing and etching,³ and the former were coated with a thin (~ 300 Å) layer of gold by vapor deposition, in order to prevent their being charged up by the incident electron beam when imaged in the scanning electron microscope. Germanium had sufficient conductivity that no such conducting layer

was necessary. Figure 1 shows an indenter resting at zero load on a typical germanium specimen.

The principal experimental difference between the present work and that of Gane and Bowden¹ was that the tips used as indenters in the current experiments were those having the most nearly spherical ends. Tip radii were typically 2000–5000 Å, and were measured

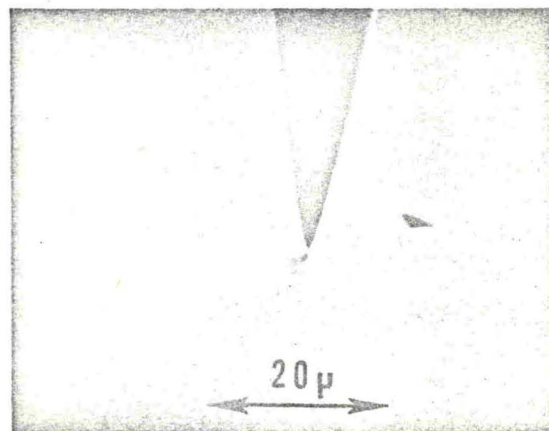


FIG. 1. A titanium carbide tip resting at zero load on a {111} germanium surface. Note the dislocation etch pit.