

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. Ruoff<sup>2</sup> 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.<sup>7</sup> 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

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

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

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

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,