the c/a ratio with pressure, the computed $\bar{\gamma}_H$ cannot be expected to agree with $\gamma(\alpha_V)$ unless the atomic configurational change with volume, $\mathrm{d}(c/a)/\mathrm{d}V$, is the same during thermal expansion as in the application of hydrostatic pressure.

Since

$$\left(\frac{\partial \ln (c/a)}{\partial \ln V}\right)_T = \frac{\beta_\parallel - \beta_\perp}{\beta_v} \tag{15}$$

during hydrostatic compression and

$$\left(\frac{\partial \ln (c/a)}{\partial \ln V}\right)_P = \frac{\alpha_\parallel - \alpha_\perp}{\alpha_V} \tag{16}$$

during thermal expansion, one is in a position to predict whether $\gamma_H = \gamma_H(\alpha_V)$, if $\mathrm{d}c_{ij}/\mathrm{d}(c/a)$ can be evaluated. Thus one finds for Mg, where $(\partial(c/a)/\alpha_V)_T \simeq (\partial(c/a)/\alpha_V)_P$, the evaluation of γ_H from the experimental $\mathrm{d}c_{ij}/\mathrm{d}P$ gives excellent agreement with $\bar{\gamma}_H(\alpha_V)$. In Zr and Ti[10], however, the experimental $\mathrm{d}c_{ij}/\mathrm{d}P$ lead to large differences between γ_H and $\gamma_H(\alpha_V)$, primarily because of the small values of $\mathrm{d}c_{44}/\mathrm{d}P$. The present authors have shown that the assumption of a negative $\mathrm{d}c_{44}/\mathrm{d}(c/a)$ contribution accounts for the small values of $\mathrm{d}c_{44}/\mathrm{d}P$ and can also account for a major part of the difference in $\bar{\gamma}_H$ and $\gamma_H(\alpha_V)$ when the differences between $(\partial c/a/\partial V)_T$ and $(\partial(c/a)/\partial V)_P$ are considered[10]. The procedure that was used for the latter consideration requires only the following simple adjustment of the $\mathrm{d}c_{ij}/\mathrm{d}P$ values that are used for computing $\bar{\gamma}_H$:

$$\left(\frac{\mathrm{d}c_{ij}}{\mathrm{d}P}\right)^* = (\mathrm{d}c_{ij}/\mathrm{d}P)_{\text{obs.}} - \left(\frac{\partial c_{ij}}{\partial c/a}\right)_V \left(\frac{\partial c/a}{\partial P}\right)_T + \frac{\partial c_{ij}}{\partial c/a}\left(\frac{\partial c/a}{\partial V}\right)_p \frac{\mathrm{d}V}{\mathrm{d}P} \tag{17a}$$

$$= \left(\frac{\mathrm{d}c_{ij}}{\mathrm{d}P}\right)_{\text{obs.}} + \beta_V \frac{c}{a}\left(\frac{\partial c_{ij}}{\partial c/a}\right)_V \times \left[\left(\frac{\beta_\parallel - \beta_\perp}{\beta_V}\right) - \left(\frac{\alpha_\parallel - \alpha_\perp}{\alpha_V}\right)\right] \tag{17b}$$

where $(\mathrm{d}c_{ij}/\mathrm{d}P)^*$ is the effective value to be used in computing the $\gamma^P(q)$. In view of the very large values of $(\alpha_\parallel - \alpha_\perp)$ that are found in the *hcp* rare earth metals, the comparisons of $\bar{\gamma}_H$ and $\bar{\gamma}_H(\alpha_V)$ for Gd, Dy and Er provide a severe test of the reasoning that leads to equation (17b). We see immediately that the computed values of $\bar{\gamma}_H$ from the observed values of the $\mathrm{d}c_{ij}/\mathrm{d}P$, using equations (12), (13) and (14), are considerably smaller than $\gamma_H(\alpha_V)$. Since the $(\beta_\parallel - \beta_\perp)/\beta_V$ values are relatively small, the $\bar{\gamma}_H$ evidently reflect the small volume dependence of the transverse $C_p(q)$ that are numerically dependent on π_{44} and π_{66} for all three metals. The wide differences between $\bar{\gamma}_H$ and $\bar{\gamma}_H(\alpha_V)$ may presumed to arise from the relatively large value of $\partial c^e_{44}/\partial(c/a)$, as given by Cousins[5]. For all three metals $\partial c^e_{44}/\partial(c/a) \sim 10\partial c^e_{66}/\partial(c/a)$, therefore a simple adjustment of the $\mathrm{d}c_{44}/\mathrm{d}P$ value for each metal, using equation (17b) and $[\partial c_{44}/\partial(c/a)] = Z^2/a_0 28 \times 10^{12}$ dynes/cm^2, should provide a semiquantitative test of our assumptions. These results are given in Table 11 as γ^*_H. The latter values give a reasonably good approximation to the $\gamma_H(\alpha_V)$ and lead to the conclusion that the $\gamma_H(\alpha_V)$ contain a significantly large contribution from the dependence of transverse mode frequencies on the c/a ratio.

(d) *Comparison of dK_T/dP with Bridgman's compression data*

The value of $(\partial K_T/\partial P)_T$ plays a central role in the equation of state. Anderson[31] has shown that the initial value of $\mathrm{d}K_T/\mathrm{d}P$ as determined from ultrasonic data as $P \to 0$, giving $(K'_T)_0$, can successfully predict the change of volume of many solids over a wide range of pressures, when used in conjunction with either the Murnaghan[32] or Birch[33] equations. The latter equations are derived from the expansion of the basic equation, $P = -\mathrm{d}\phi/\mathrm{d}V$, where ϕ is the strain energy. Using finite strain theory, Murnaghan's equation predicts the following relation

between V/V_0 and P:

$$\frac{V}{V_0} = [1 + (K_T')_0 P/(K_T)_0]^{-1/(K_T')_0}. \quad (18)$$

We should then find that equation (18) agrees with the direct measurements of volume changes in Gd, Dy and Er that were carried out by Bridgman [34] in 1954. Since the Bridgman measurements extend only to approximately 40 kbar the comparison is not a severe test of the Murnaghan equation and the agreement should be better than a comparison with very high pressure data, such as encountered with shock-wave results. This is indeed found to be true, as shown in Fig. 4, for Dy and Er. There are obvious differences for Gd at the higher pressure range that suggest that our use of $(K_s')_0$, rather than $(K_T')_0$ is not a good approximation. As stated in an earlier section, above, the calculation of K_T' from K_s' in this case is extremely difficult because of the proximity of the Curie temperature to room temperature i.e., the values of $\mathrm{d}\alpha_V/\mathrm{d}P$ or $\mathrm{d}\beta_V/\mathrm{d}T$ are subject to very large errors. We may conclude from Bridgman's data that $(K_T')_0$ is enhanced by the effects of the magnetic transition on K_T as well as on α_V.

The magnitude of the enhancement in Gd is quite large, as shown in Table 12, where the values of $\mathrm{d}K_T'/P$ derived from Bridgman's data are compared with the ultrasonic values. Bridgman K_T' is that obtained from expressing the compression data as a polynomial in P, as follows:

$$V/V_0 = 1 - aP + bP^2$$

$$1/K_0 = a - 2bP$$

$$\mathrm{d}K_0/\mathrm{d}P = 2bK_0^2 = K_0'.$$

The reasonable agreement between the K_0' and K_T' values for Dy and Er indicates that a major part of the difference between K_0' and K_s' for Gd can be attributed to the isothermal–adiabatic conversion. We believe that this is the first experimental evidence that the $K_s' \rightarrow K_T'$ conversion, and thus the equation of state, can be subject to considerable error near magnetic

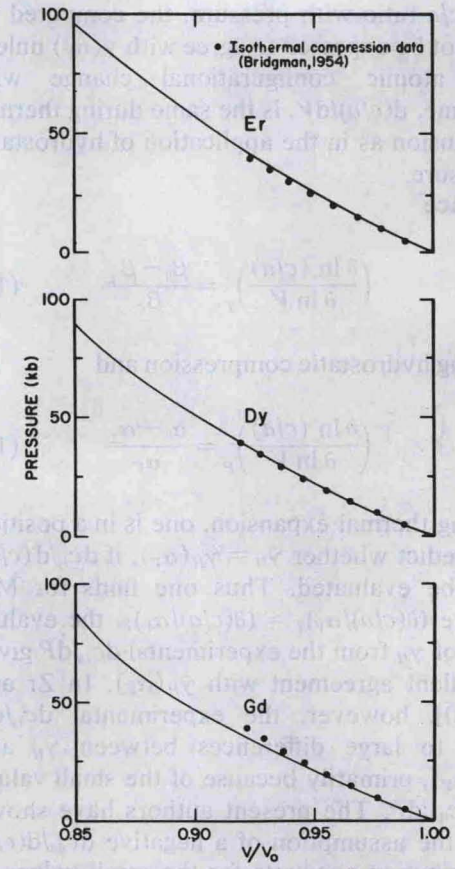

Fig. 4. Pressure-volume curves for Gd, Dy and Er obtained from the Murnaghan equation of state and $(K_T')_0$ values given in Table 12. (K_s' was used for Gd curve). Data points are from direct compression measurements by Bridgman.

Table 12. Comparison of ultrasonic K_T' with K_0' determined from Bridgman's compression data

Metal	K_0' (Ref. 34)	K_s' (Present work)	K_T'
Gd	4·517	3·283	
Dy	3·305	3·214	3·228
Er	3·634	3·302	3·256