

table are from relativistic APW calculations of Keeton and Loucks [22] and the corresponding  $V_l$  values, again for  $Z = 3$ , are within 12 per cent of the observed.

The calculation of the volume derivatives of  $c_{11}$  and  $c_{33}$  from equation (10) is subject to considerable question because of the assumption of a spherical Fermi surface. In this overly simplified model the volume dependence of the velocity is derived entirely from the change in  $E_f$  on the basis of a spherical Fermi surface and values of  $\pi_{ij}$  for longitudinal modes turns out to be

$$\pi_l = -\frac{5}{3}.$$

It is, however, of interest to note that the observed  $\pi_{11}$  values for Gd and Dy given in Table 4 are very close to  $-5/3$  and that the  $\pi_{11}$  value for Er and  $\pi_{33}$  values for all three metals are within a factor of two of the spherical Fermi surface model. There is, then, qualitative value in reformulating the free electron gas model so as to relate  $\pi_{ij}$  to the volume dependence of the density of electron states,  $N(E_f)$ . We then find that

$$\pi_l = -1 - \frac{d \ln N(E_f)}{d \ln V} \quad (9)$$

where in the free electron model

$$\frac{d \ln N(E_f)}{d \ln V} = \frac{2}{3}.$$

The latter quantity is of particular interest [23] in understanding the observed effects of hydrostatic pressures on  $T_c$  and or  $T_N$  and it is therefore of interest to propose some reasonable estimates of this number from our data. The anisotropy, i.e. differences between  $\pi_{11}$  and  $\pi_{33}$ , presents a problem in literal interpretation of the data. If the anisotropy is indeed caused by the  $d \ln N(E_f)/d \ln V$  term, we conclude that the change in  $N(E_f)$  with volume change is considerably larger along the  $c$  axes of Gd and Dy than in perpendicular

directions. This situation is, evidently not related to  $d(c/a)/dV$ , is perhaps related to the symmetry of the conduction band energies (and their proximity) to  $E_f$ . For Gd and Dy we conclude that  $0.7 < d \ln N(E_f)/d \ln V < 2.0$ , whereas for Er,  $1.5 < d \ln N(E_f)/d \ln V < 2.0$ .

### (c) Analysis of the Grüneisen parameters

One of the unique characteristics of the hcp rare earth metals are the relatively small values of the Grüneisen parameter,  $\gamma$ , that is obtained from thermal expansion measurements, as follows:

$$\gamma(\alpha_V) = \frac{\alpha_V K_T}{\rho C_V} = \frac{\alpha_V K_S}{\rho C_P} \quad (10)$$

where  $\alpha_V$  is the volume thermal expansion coefficient and  $C_V$  and  $C_P$  are the constant volume and constant pressure specific heat coefficients, respectively. Since all of the factors that enter into the above equation are sensitive to magnetic ordering, the characterization of the lattice contribution to  $\gamma(\alpha_V)$  of the paramagnetic phases of the rare earths is not straightforward. The values of  $\gamma(\alpha_V)$  given in Table 11 illustrate the problem encountered for Gd. Gschneidner's values [24, 25] evidently represent  $\gamma$  at 298°K, based on  $\alpha_V$  and  $C_P$  values that are definitely influenced by the fluctuations in magnetic order that are present at 10°K above  $T_c$ . The third value listed for  $\gamma_H(\alpha_V)$  is obtained from  $\alpha_V$ ,  $K_T$ ,  $\rho$ , and  $C_V$  at 673°K [27, 28], where all of the parameters are more likely to represent the paramagnetic lattice properties. The values of  $\gamma_H(\alpha_V)$  for Dy and Er as calculated from the  $K_S$  values given in Table 2 and the  $\alpha_V$  and  $C_P$  values [26-28] at 298°K are also listed in Table 11, along with those given by Gschneidner's [24, 25].

Direct estimates of  $\gamma$  can be arrived at by various means from the relation.

$$\bar{\gamma} = -\frac{d \ln \bar{\omega}}{d \ln V} \quad (11)$$

Table 11. Comparison of the average Grüneisen parameter  $\gamma_H(\alpha_V)$ , as determined from thermal expansion and specific heat data, with that calculated from the measured  $dc_{ij}/dP$ ,  $\bar{\gamma}_H$ , and the adjusted  $dc_{ij}/dP$  [equation (17b)],  $\bar{\gamma}_H^*$ . The thermal expansion coefficients and  $c_p$  values used for evaluating  $\bar{\gamma}_H(\alpha_V)$  are listed

	$\gamma_H(\alpha_V)$	$\bar{\gamma}_H$	$\bar{\gamma}_H^*$	$\alpha_{  } \times 10^{-6}/^\circ\text{K}$	$\alpha_{\perp} \times 10^{-6}/^\circ\text{K}$	$\alpha_V \times 10^{-4}/^\circ\text{K}$	$C_p$ cal/g, $^\circ\text{K}$
Gd	0.52 (Ref. [24])	0.370	0.82	13.0	6.3	25.6	0.0374
	0.55 (Ref. [25])						
	0.79						
Dy	0.78 (Ref. [24])	0.42	0.83	15.6	7.13	29.9	0.0412
	0.68 (Ref. [25])						
	0.83						
Er	1.01 (Ref. [24])	0.80	1.20	20.92	7.89	36.7	0.0405
	0.88 (Ref. [25])						
	1.08						

where  $\bar{\omega}$  represents the average vibrational frequency of the lattice modes. The method proposed by Sheard for calculating  $\bar{\gamma}$  [see equation (4)] from the pressure derivatives of the  $c_{ij}$  has been shown to give reasonably good agreement with  $\gamma(\alpha_V)$  obtained from highly precise measurement of  $\alpha_V$  at low and high temperatures in various solids, including Mg and Cd in the family of *hcp* metals [11, 29]. This method is in principle an approximation based on the assumption that only low frequency acoustic modes contribute to  $\bar{\gamma}$ , but its success in giving good agreement with  $\gamma(\alpha_V)$  at high temperatures indicates either that  $\gamma(\alpha_V)$  at high temperatures is in fact dominated by the acoustic modes or that  $\bar{\gamma}$  evaluated from low frequency acoustic modes is also representative of  $\bar{\gamma}$  for the high frequency modes.

The procedure for equating the  $dc_{ij}/dP$  values to  $\bar{\gamma}$  in uniaxial crystals has been given by Gerlich [29], as an approximation from the general strain approach given by Brugger [30]. The individual mode  $\gamma$ 's for hydrostatic strain are obtained from a variation of equation (4), where the factor  $-1/6$  is replaced by  $-1/2$  plus the ratio of the linear compressibility to volume compressibility in the direction of wave propagation,  $q$ . The mode  $\gamma$ 's,  $\gamma^p(q)$  for each of the three wave modes for a given propagation, are obtained from solutions of

the Christoffel eigen matrix, where the matrix elements are functions of the principal  $dc_{ij}/dP$  given as  $dC_p(q)/dP$ , where  $p$  represents the displacement polarization for a given wave mode. The general equation for computing  $\gamma^p(q)$  is then

$$\gamma^p(q) = \frac{\beta_q}{\beta_v} - \frac{1}{2} \left[ 1 + \frac{d \ln C_p(q)}{d \ln V} \right] \quad (12)$$

where

$$\frac{d \ln C_p(q)}{d \ln V} = \pi^p(q) = - \frac{K_T}{C_p(q)} \frac{dC_p(q)}{dP}, \quad (13)$$

and for computing the average value of  $\gamma^p(q)$  at temperatures where all the lattice vibrational modes contribute to  $C_p$ , the specific heat,

$$\bar{\gamma}_H = \sum_1^{3N} \gamma^p(q) / 3N \quad (14)$$

where  $N$  represents the number of  $q$  directions for which the  $\gamma^p(q)$  have been calculated. For sufficient  $N$  and systematic choices of  $q$ , the computed  $\bar{\gamma}_H$  should provide a reasonably good approximation to the  $\gamma(\alpha_V)$  determined from  $\alpha_V$  at high temperatures, if the principal  $dc_{ij}/dP$  are derived strictly from the volume dependence of the  $c_{ij}$ .

If, however, the measured  $dc_{ij}/dP$  contain a significant contribution from the change in