

transitions when the anomalous  $d\alpha_V/dT$ ,  $dC_p/dT$ , and  $dK_s/dT$  factors are not carefully evaluated.

(e) *Pressure induced phase changes*

An alternative explanation for the deviation of Bridgman's data for Gd from the Murnaghan equation with  $K'_s$  is that a structural phase transition is induced near 25 kbar, as suggested by one of Bridgman's studies [35] and which seems to be indicated in more recent studies of Gd [36]. The deviations of Bridgman's data, shown in Fig. 4, are, however, gradually increasing from 10 kbar and show no clear indication of a sharp change in the equation of state as would be expected for a structural change. A more clear association between the equation of state and a phase transition is found in the case of Er, where Drickamer *et al.* [37], have measured the changes in lattice constants with pressure to 200 kbar. Distinct changes in the pressure derivatives of the  $c_0$  and  $a_0$  lattice constants occur at approximately 90 kbar. The diffraction data indicate that the high pressure phase has the double hcp symmetry. The  $P$ - $V$  plot of the diffraction data for Er is shown in Fig. 5, where the Murnaghan equation and Bridgman's data are also shown for comparison. From  $P = 0$  to  $P = 94$  kbar, the Murnaghan equation with  $(K'_T)_0 = 3.256$  falls well within the error bars of the diffraction data. At  $P > 94$  kbar the diffraction data show that the appropriate  $(K'_T)_0$  is considerably greater than that used in the Murnaghan equation.

### 5. SUMMARY

The pressure derivatives of the elastic moduli in the paramagnetic hcp rare earth metals, Gd, Dy and Er, have been used as a measure of the relative importance of the electrostatic forces in determining the elastic properties of lanthanide metals. For Er, the pressure derivatives of the shear moduli can be closely approximated by an electrostatic model, assuming no change in valence with volume but a change in the Coulomb sum

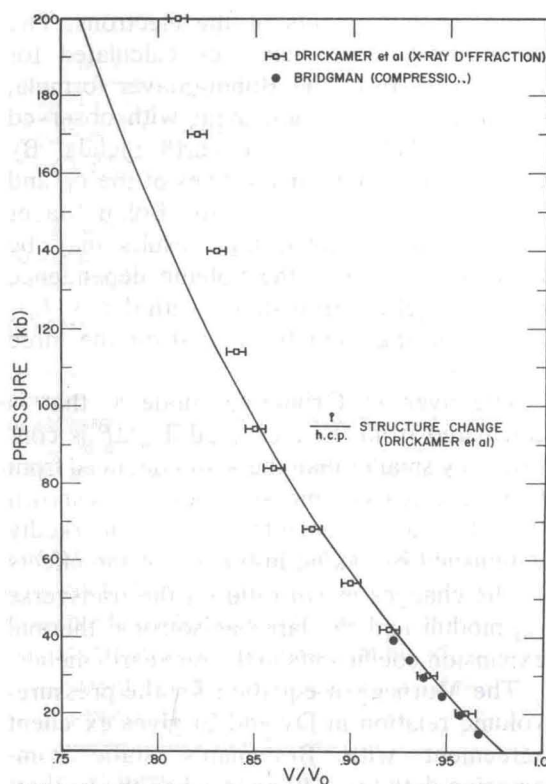


Fig. 5. Comparison of Murnaghan equation for Er with  $P$ - $V$  data obtained from X-ray diffraction measurements up to 200 kbar. Question mark denotes that crystal structure at  $P > 90$  kbar is not established.

parameter with  $c/a$  ratio. The results for Gd and Dy are quite similar to each other but different from Er. By deduction it is concluded that the band structure produces negative contributions to the pressure derivatives of the shear moduli in all three metals and that this contribution is considerably larger in Gd and Dy.

The pressure derivatives of the bulk moduli for the three metals are smaller than in other solids and indicate that the repulsive forces between ions can be safely neglected in understanding the elastic moduli.

The longitudinal wave velocities and their pressure derivatives are also interpreted on a nearly electrostatic model, where the ions are immersed in an electron sea and their vibrational frequencies are affected by the charge

screening movements of the electrons. The longitudinal wave velocities calculated for this model, from the Bohm–Staver formula, are in remarkable agreement with observed values in all three rare earth metals. By treating the volume derivatives of the  $c_{11}$  and  $c_{33}$  values on the basis of the Bohm–Staver equation it is shown that results may be understood through the volume dependence of density of electron states, with  $d \ln N(E_f)/d \ln V$  varying from 0.7 to 2.0 for the three metals.

The average Grüneisen mode  $\gamma_i$  that is calculated from the measured  $dc_{ij}/dP$  is considerably smaller than the  $\gamma(\alpha_V)$  deduced from thermal expansion measurements. It is shown that the disagreements can be markedly diminished by taking into account the effects of the changes in  $c/a$  ratio on the transverse  $c_{44}$  moduli and the large anisotropic thermal expansion coefficients in the rare earth metals.

The Murnaghan equation for the pressure-volume relation in Dy and Er gives excellent agreement with Bridgman's static compression data to  $\sim 40$  kbar, when the isothermal values of  $dK_T/dP$  computed from the present data are used in the equation of state. For Gd there is significant disagreement above  $\sim 20$  kbar. This may arise from a very large difference between  $dK_s/dP$  and  $dK_T/dP$  at 298°K. Because the Curie temperature occurs at 291°K, there are very large values of  $d\alpha_V/dT$  and  $dC_p/dT$  that are difficult to evaluate accurately and thus lead to large errors in calculating  $dK_T/dP$ . An alternative explanation is that a pressure induced phase change occurs in Gd at  $P \sim 20$  kbar. It is shown that a phase change in Er near 90 kbar produces a relatively sharp deviation at  $P > 95$  kbar between X-ray diffraction data of Drickamer *et al.*, and the Murnaghan equation.

*Acknowledgements*—Measurements of elastic moduli at temperatures below 273°K were carried out at Argonne National Laboratory, under auspices of the Division of Research, U.S. Atomic Energy Commission. Work supported by National Science Foundation grant GK-29750.

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