

and Er and becomes very important in the interpretation of the differences between the Grüneisen parameter, $\bar{\gamma}_H$, as calculated from the averaging of the mode γ 's that are based on the present experimental data and the $\gamma_H(\alpha_V)$ that are derived from thermal expansion and heat capacity measurements. The mode gammas are derived here from a modification of the following equation that applies to cubic symmetry [11]:

$$\gamma_i = -\frac{1}{6} + \frac{1}{2} \left(\frac{\partial \ln c_i}{\partial \ln V} \right)_T \quad (4)$$

where i refers to a specific normal mode of vibration in a given crystallographic direction and c_i is the stiffness modulus for this mode.

In addition to the electrostatic contribution to the pressure derivatives of the shear moduli, c_{44} , c_{66} and $C_H = 1/6 (c_{11} + c_{12} + 2c_{33} - 4c_{13})$, we have here attempted to calculate the screened electrostatic contributions to dc_{11}/dP and dc_{33}/dP , (pressure derivatives of the longitudinal modes) via the Bohm-Staver [12] formula for the vibrational frequency of metal ions in an electron plasma. This appears to be a novel but simple approach that may prove useful in extracting valuable information regarding the contribution of the electronic Grüneisen γ , γ_e , to the γ_i for longitudinal modes of lattice vibration.

2. EXPERIMENTAL PROCEDURES

The Gd, Dy and Er single crystals that

were used in this study were precisely those used in earlier studies [6, 7] of the temperature dependence of the c_{ij} . The Dy crystals were prepared by prolonged annealing of an arc melted button obtained from pure sponge material. Because the ultrasonic wave velocities in Dy appeared to be uniquely sensitive to purity, as described in Ref. [7], a special effort was made to prepare relatively clean single crystals where the cross-checks on the various moduli were consistent to within 0.3 per cent. The Er and Gd crystals were made by a similar annealing procedure, but the starting materials were made by casting into Ta crucibles. The single crystals did contain a large number of microscopic inclusions, presumed to be complex compounds containing Ta, but the cross-checks on the zero pressure wave velocities indicated no significant effects of the impurities.

Three crystals of each metal were prepared for propagating waves parallel, perpendicular and near 45° of arc to the 'C' axis, i.e. hexagonal, axis. Table 1 relates the elastic moduli measured in the experiments to the crystal and transducer orientations. The ultrasonic path lengths varied from 2 to 3 mm, among the crystals used in this study.

The apparatus for measuring the wave velocities under hydrostatic gas pressures up to 72,000 psi, or 4.964 Kbar is described in a prior publication [13]. Briefly, this consisted of an ultrasonic pulse superposition machine with carrier r.f. frequencies of 30 MHz.

Table 1. Relations of measured wave velocities to elastic stiffness moduli

Crystal specimen	Direction of wave propagation	Type of mode	Direction of particle motion	Elastic modulus determined from measured velocity
A	⊥ to "C"	long.	⊥ to "C"	c_{11}
	⊥	shear	∥	c_{44}
B	⊥	shear	⊥	c_{66}
C	~ 45°	long.	45°	c_{RS}^*
	∥	long.	∥	c_{33}
	∥	shear	⊥	c_{44}

* $c_{RS} = \frac{1}{4}(c_{11} + c_{33} + 2c_{44} + [(c_{11} - c_{33})^2 + 4(c_{13} + c_{44})^2])^{1/2}$.

Temperatures were carefully regulated at $298 \pm 0.1^\circ\text{K}$.

The process of evaluating wave velocity and modulus changes from the changes of p.r.f. (pulse repetition rate frequency) with pressure is also described in Ref. [13]. This procedure is essentially based on recomputing the linear and volume compressibilities at steps of 4000 psi, 0.267 Kbar, so as to closely approximate the path length and density at each data point. The data points used for the calculations were, in turn, taken from linear equations obtained by a least-square fit to the initial data. The coefficients of correlation, r , or the estimated probable error for each data point, based on regression analyses for each set of data, provide the basis for the estimated probable errors in dc_{ij}/dP that are given in the results.

3. RESULTS

(a) Zero pressure results

The *hcp* rare earth metals display a variety of ordered magnetic arrangements [14]. The highest ordering temperature among this group occurs at Gd, (element 64) and decreases with increasing atomic number. Gadolinium goes directly from the paramagnetic state to a ferromagnetically ordered state, with T_c at approximately 291°K for the crystals used here [15]. There are indications, however, that some degree of spontaneous magnetic moment ordering exists at temperatures above T_c , extending to about 330°K [16]. This short range interaction between the ions, or between the conduction electrons and the ions, manifests itself, at $T > T_c$, in the lattice properties as an anomalous thermal expansion at zero magnetic field with the c_0 lattice constant expanding with decreasing temperature. The modulus c_{33} is strongly influenced by the anomalous thermal expansion and dc_{33}/dT has a positive value at 298°K . The dc_{ij}/dT for the other principal moduli are, however, not significantly affected by the preliminary magnetic interactions and show significant changes only at T_c , as shown

in Fig. 1. (These data were previously published in a conference proceedings [6] and are shown here because the values of dc_{ij}/dP at 298°K may well be influenced by the close proximity of T_c to the temperature of measurement). Hydrostatic pressures have the effect of decreasing T_c in Gd at the rate of $1.5 \pm 1^\circ\text{K}$ per Kbar [17]. Some measurements of the effect of pressure on the variation of c_{33} at T near T_c are reported in Ref. [15].

The Curie temperature, T_c , of Dy is 87°K , but an antiferromagnetically ordered phase exists between the paramagnetic and ferromagnetic state. Between 87 and 179°K the magnetic moments are aligned parallel within each basal plane, but the difference in direction of alignment in adjacent basal planes produces a helix, or spiral, magnetic structure, with a temperature dependent turn angle. The large effects of these phase changes on

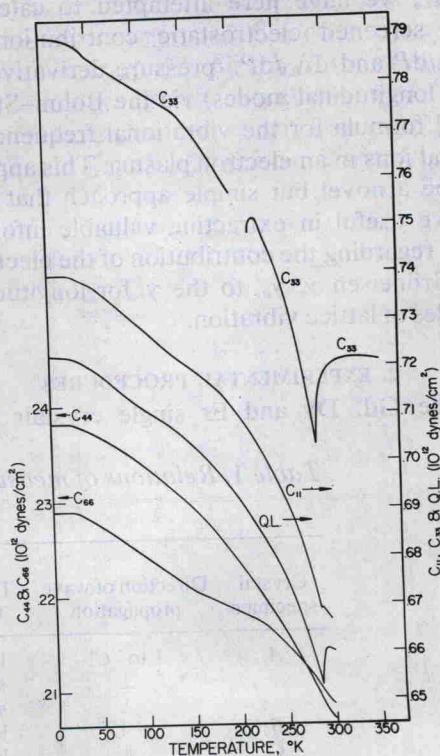


Fig. 1. Elastic moduli at zero magnetic field vs temperature for Gd, where $T_c = 291^\circ\text{K}$. Anomaly in c_{33} at $\sim 215^\circ\text{K}$ is related to change in direction of easy magnetization.