

## HYDROSTATIC PRESSURE DERIVATIVES OF THE SINGLE CRYSTAL ELASTIC MODULI OF Gd, Dy AND Er\*

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**Abstract**—The hydrostatic pressure derivatives of the single crystal elastic moduli of Gd, Dy and Er have been measured at 298°K, to pressures near 5 Kbar. The very small pressure derivatives of the adiabatic bulk moduli indicate that a small ion core model should be appropriate for interpreting the data. The long-range electrostatic contributions to the shear moduli have a dominant influence on the pressure derivatives of the shear moduli of Er, whereas the Gd and Dy data evidently reflect band structure contributions. The values of the longitudinal stiffnesses correspond remarkably well with the Bohm-Staver model for velocity of waves in an ion plasma dispersed in a sea of electrons, where the ionic interaction is purely Coulombic. This model is extended to provide an interpretation of the volume derivatives of the longitudinal moduli in terms of the volume derivative of the density of electron states at the Fermi energy.

The Grüneisen parameters calculated from averages of the acoustic model gammas are in relatively poor agreement with those determined from thermal expansion data. An explanation based on the changes in  $c/a$  ratio with volume change is tested quantitatively and found to be reasonably successful. The values of  $dK_T/dP$ , where  $K_T$  is the isothermal bulk modulus, are applied to the Murnaghan equation of state and give excellent agreement with Bridgman's direct compression data for Dy and Er to 40 Kbar. For Gd, Bridgman's data indicate either that  $(dK_T/dP)_{P=0}$  should be considerably larger than deduced from the adiabatic  $dK_A/dP$  measurements or that a phase change occurs near 20 Kbar. The occurrence of a phase change in Er at  $\sim 90$  Kbar is definitely indicated when comparing the Murnaghan equation with X-ray diffraction data.

### 1. INTRODUCTION

MEASUREMENTS of the hydrostatic pressure derivatives of elastic moduli in ionic crystals have proven to be invaluable in testing the validity of the simple central force Born model, where one is concerned with an electrostatic potential that is  $1/r$  dependent and a repulsive potential varying as  $1/r^n$ . The values of the exponent  $n$  deduced from such work have provided a basis for understanding several properties of ionic materials that are of broad interest [1]: (a) the variations of  $dK/dP$  and  $d\mu/dP$ , where  $K$  is the bulk modulus and  $\mu$  is the isotropic shear modulus, with composition and crystal structure, (b) the anisotropy in the single crystal shear moduli

and their pressure derivatives, and (c) the variation in the Grüneisen parameter,  $\gamma$ . In metals the extraction of information from the elastic moduli and their pressure derivatives is, in general, considerably more complex because of the free electron and band structure contributions, that presumably become more important in the higher order elastic moduli [2]. There are, nevertheless, some extreme cases such as the noble metals where the core repulsion has a dominating influence and the third-order elastic moduli or the  $dc_{ij}/dP$  can be useful in evaluating the repulsive potentials [3]. In the opposite situation where the ion cores are widely separated, the shear moduli are almost totally given by the electrostatic component,

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$$c_{ij}^e = \frac{M_{ij} Z_{\text{eff}}^2}{\Omega_0 r_0}, \quad i = j \quad (1)$$

where,  $M_{ij}$  is a Coulomb sum factor that depends on structure and mode of shear strain,  $Z_{\text{eff}}$  is the effective valence on the ion,  $\Omega_0$  is the atomic volume and  $r_0$  is the undeformed ionic radius. The volume derivatives of the shear moduli in such cases should correspond to

$$\pi_{ij}^e = \frac{d \ln c_{ij}^e}{d \ln V} = -\frac{4}{3} \quad (2)$$

where  $V$  is the total volume and  $M_{ij}^e$  and  $Z_{\text{eff}}$  are assumed independent of  $V$ . In several metals where equation (2) may be expected to hold, the experimental data indicated that factors other than the electrostatic forces dominate the  $dc_{ij}/dP$ . In the bcc alkali metals [2], for example, the values of  $c_{44}$  and  $c'$  are almost completely derived from equation (1), whereas the values for  $\pi_{44}$  and  $\pi_{c'}$  in Na and K are about a factor of two greater in magnitude than the  $-4/3$  given by equation (2). These large deviations are attributed either to the effects of volume on the band structure contributions or to changes in  $Z_{\text{eff}}$  with volume. The deviations from the purely electrostatic model are even more pronounced in the polyvalent cases of Al and Mg, where again the repulsive potential has only a minor role but the band structure effects on the pressure derivatives of the model are very large [4].

The rare earth metals form another group where the electrostatic potential can be expected to have a dominant influence on the elastic moduli at least in the paramagnetic structures. The principal magnetic properties of the heavy rare earths in particular, Gd through Tm, conform to a simple model of tripositive ions embedded in a sea of  $5d$  and  $6s$  valence electrons. Since the  $4f$  electrons are closely bound to the ions with radii considerably smaller than the interatomic radii, the ionic repulsion should be a minimum factor in the bonding, as in the alkali metals. The values of the second order  $c_{ij}$  in these hexagonal close packed (*hcp*) structures,

together with recent calculations by Cousins [5], do in fact indicate that the repulsive potentials play a minor role and that this simple electrostatic model is nearly sufficient to explain the variation of the shear moduli with atomic number. Cousins has computed Coulomb sum factors,  $M_{ij}$ , for the three principle shear moduli in *hcp* structures as a function of the axial,  $c/a$ , ratio. If we use these values of  $M_{44}$  in equation (1), together with a  $Z_{\text{eff}} = 3$  we find, for example, that the electrostatic contributions to  $c_{44}$ ,  $c'_{44}$ , for Gd, Dy, Ho and Er are at most 30 per cent larger than the measured room temperature values [6-9]. The measurements of the hydrostatic pressure derivatives of the shear moduli in Gd, Dy, and Er that are reported here provide a more sensitive test of the electrostatic model and also provide some information in regard to the importance of the band structure energy in evaluating the effects of pressure on other properties of rare earth metals.

The value of  $M_{ij}$  to be used in equation (1) will necessarily change with  $c/a$  ratio in *hcp*, or any uniaxial, crystal. In such crystals the isothermal linear compressibilities parallel and perpendicular to the 'c' axes,  $\beta_{\parallel}$  and  $\beta_{\perp}$ , respectively, generally are different in magnitude. This produces a change in  $c/a$  ratio with hydrostatic pressure and introduces a small change in equation (2) for uniaxial crystals, where

$$\pi_{ij}^e = \frac{d \ln c_{ij}^e}{d \ln V} = -\frac{4}{3} + \left( \frac{\partial M_{ij}}{\partial (c/a)} \right)_V \times \frac{c/a}{M_{ij}} (\beta_{\parallel} - \beta_{\perp}) / \beta_V \quad (3)$$

and  $\beta_V$  is the isothermal volume compressibility. A recent analysis of the measured  $dc_{44}/dP$  values for *hcp* Ti and Zr metals [10] suggested that the second term on the right of equation (3) has a very prominent effect in determining whether  $c_{44}$  increases or decreases with volume. This term also becomes somewhat significant in influencing  $dc_{44}/dP$  in Gd