

TABLE III

Pressure derivatives of adiabatic and isothermal compressibilities and bulk modulus

	$d\beta_{\perp}/dp$	$d\beta_{\parallel}/dp$	$d\beta_v/dp$	$dK/dp$
	$10^{-21} \frac{\text{cm}^4}{\text{dyne}^2}$			
Adiabatic 298 K	-0.0054	-0.0117	-0.0225	3.22
Isothermal 298 K	-0.0052	-0.0114	-0.0223	3.11
Adiabatic 273 K	-0.0046	-0.009	-0.0180	2.57
Isothermal 273 K	-0.0035	-0.006	-0.0125	1.68

Conversion to isothermal moduli and their pressure derivatives: Because of the anomalous thermal expansion coefficient parallel to the "c" axis [11],  $\alpha_{\parallel}$ , and the relatively large  $d\alpha_{\parallel}/d[p] = -d\beta_{\parallel}/dT$  in the temperature range of our measurements, the difference between adiabatic and isothermal elasticity parameters becomes quite significant, as noted in Tables II and III. For this conversion we used the Voigt equations for each of the  $c_{ij}$  [12], the zero applied field thermal expansion data of Bozorth and Wokiyoma [11] and the published values of  $C_p$  (measured heat capacity) near  $T_c$  [13]. The remarkably small  $(dK/dp)_T$ , where K is the bulk modulus should be noted; this derivative is seldom less than 4, whereas in ferromagnetic Gd it is 1.68.

Discussion

The anomaly in  $c_{33}$  near  $T_c$ : The effects of the transition to the ferromagnetic state on the temperature dependence of  $c_{33}$  are of interest because they are typical of the anomalies observed at many higher order phase transitions. In the case of Gd we observe the anomalous effects beginning at approximately 40 K above  $T_c$  and the largest effects occurring between  $T_c$  and 2.5 to 3 K below  $T_c$  (Fig. 4). Since the thermal expansion anomaly also begins about 30 K above  $T_c$  it may be presumed that part of the  $c_{33}$  anomaly is a result of the increase in volume on cooling through  $T_c$ . We

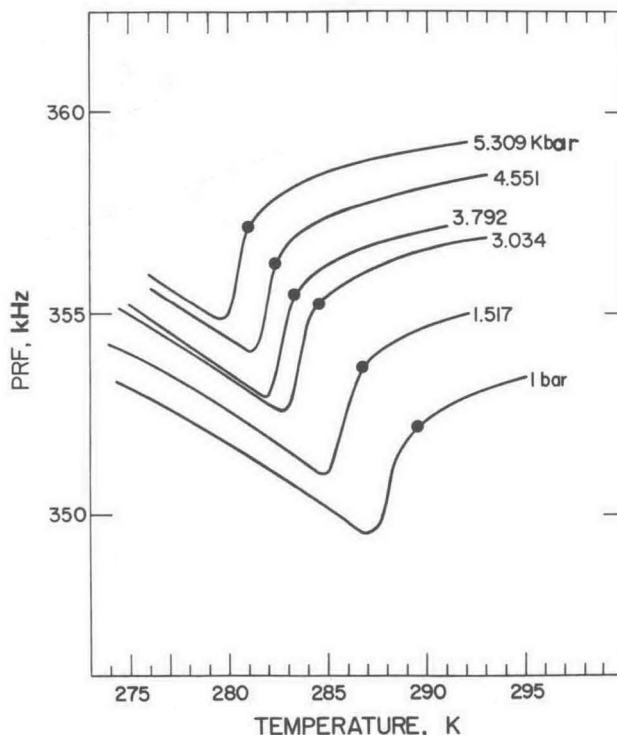


FIG. 4

Variation of pulse repetition frequency for the  $c_{33}$  mode through the ferromagnetic transition as a function of hydrostatic pressures (●) corresponds to  $T_c$  estimated from changes in slope.

TABLE IV

Evaluation of the intrinsic temperature effect on the  $c_{ij}$  of Gd from Eq. (3) of text.

Temp.	Modulus	$\left(\frac{1}{m} \frac{\partial m}{\partial T}\right)_p$	$\left(\frac{\alpha_v}{\beta m} \frac{dm}{dp}\right)_T$	$\left(\frac{1}{m} \frac{dm}{dT}\right)_v$
298 K	$c_{33}$	$+ 2.08 \times 10^{-4}$	$- 1.74 \times 10^{-4}$	$0.34 \times 10^{-4}$
	$c_{11}$	- 4.00	- .60	- 4.60
	$c_{44}$	- 4.83	- .06	- 4.89
	$c_{66}$	- 4.34	- .33	- 4.67
	B	+ 2.14	- 1.58	- 0.56
	$c_{33}$	$97 \times 10^{-4}$	$- 5.50 \times 10^{-4}$	91.5
273 K	$c_{33}$	- 16.9	- .94	- 17.84
	$c_{11}$	- 9.8	- .64	- 10.4
	$c_{44}$	- 10.3	- .31	- 10.6
	$c_{66}$	- 6.1	- .35	- 6.5
	B	- 8.76	- 1.00	- 9.76

can now investigate this presumption via the pressure coefficients that are given above and the relation

$$\frac{1}{m} \frac{dm}{dT} = \frac{1}{m} \left(\frac{\partial m}{\partial T}\right)_v - \frac{\alpha_v}{(\beta_v)_T m} \left(\frac{\partial m}{\partial p}\right)_T \quad (3)$$

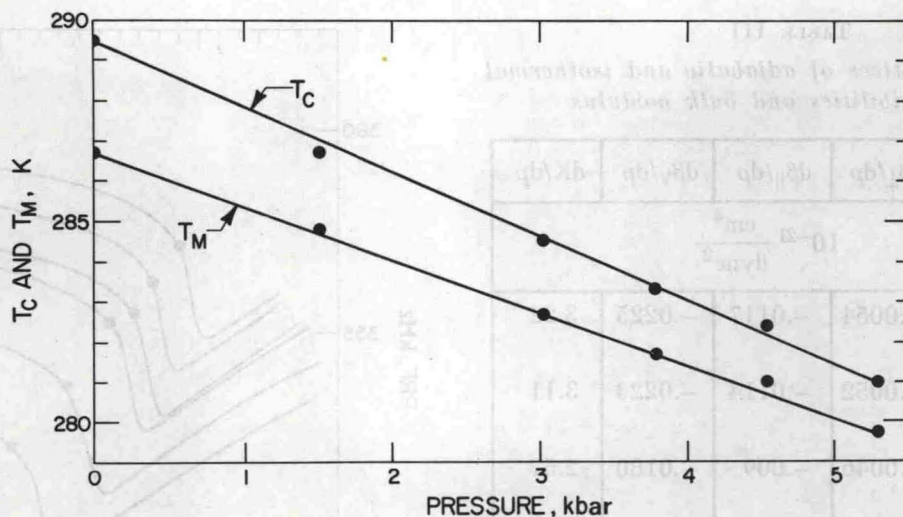


FIG. 5  
Variation of  $T_c$  and  $T_m$  (minimum  $c_{33}$ ) with hydrostatic pressure.

where  $m$  is the modulus and  $\alpha_V$  is the volume expansion coefficient. The  $(\partial m/\partial T)_V$  term is the intrinsic part of the temperature dependence which is due to effects other than static volume change. Table IV gives the evaluations for the three terms of equation (3) as applied to the  $c_{ij}$  and bulk modulus. At 298 K the observed temperature derivatives of  $c_{11}$  and the shear moduli are almost completely due to the intrinsic effects, whereas the  $c_{33}$  and  $K$  derivatives are primarily caused by the anomalous thermal expansion. Below  $T_c$ , however, the volume change contribution to  $c_{33}$  is almost insignificant. The very large  $dc_{33}/dT$  between  $T_c$  and the temperature of the minimum  $c_{33}$ ,  $T_m$ , is evidently due to a coupling between the compressional wave and the spontaneous magnetic dipole alignment along the "c" axis. The abrupt change to a negative  $dc_{33}/dT$  are perhaps associated with a rapid increase in magnetic anisotropy energy at  $T < T_m$  and a consequent loss of coupling between the magnetic structure and the "c" axis strain.

The effects of high pressures on the  $c_{33}$  curves are shown in Fig. 4. From the data at 1 bar and the magnetization data it is deduced that  $T_c$ , noted by (0) in Fig. 4, is that point on each curve where  $dc_{33}/dT$  begins to increase sharply on cooling from above  $T_c$ . The variations of the  $T_c$  and  $T_m$  deduced from the data of Fig. 4 are shown in Fig. 5.

The straight line through the indicated  $T_c$  connects the two end points. The slope of this line is  $-1.60$  K/kbar, which is remarkably near the values for  $dT_c/dp$  deduced from several sets of

magnetization measurements [14]. The pressure dependence of  $T_m$  is given by a straight line with a slope of  $-1.36$  K/kbar. The difference  $(T_c - T_m)$  is clearly decreased with increasing hydrostatic pressure.

*Grüneisen parameters,  $\gamma_L$  and  $\gamma_H$* : It has been shown that the hydrostatic pressure derivatives of the  $c_{ij}$  can be used in deriving average Grüneisen  $\gamma$ 's at low and high temperatures,  $\gamma_L$  and  $\gamma_H$  [15]. These computed  $\gamma$ 's closely approximate that obtained from the lattice contributions to the thermal expansion coefficients:

$$\gamma_{th} = \frac{\alpha_V V}{c_V (\beta_V)_T} = - \frac{d \ln \bar{\omega}_i}{d \ln V} \quad (4)$$

where  $\alpha_V$  is separated from the spontaneous magnetization effects,  $c_V$  is the heat capacity at constant volume,  $V$ , and  $\bar{\omega}$  is the average lattice frequency of vibration. The  $(\partial \ln c_{ij}/dp)_T$  values enable the approximation of  $(\partial \ln \omega_i/\partial p)_T$  which, in turn, are related to the individual mode  $\gamma_i$ , where  $i$  is a given mode of wave propagation. By simple averaging of the  $\gamma_i$  over 300 directions [16] and 3 polarizations using 298 K and 273 K values for  $dc_{ij}/dp$  and  $c_{ij}$  of Gd, we obtain values of  $\gamma_H$  of 0.35 and 0.26, respectively, compared to values of approximately 0.45 for  $\gamma_{th}$ . Since the  $\gamma_{th}$  calculation involves an estimate of the normal  $\alpha_V$  and  $c_V$  values near  $T_c$  the agreement with the computed  $\gamma_H$  is reasonably good. Both give remarkably small  $\gamma$ 's for a metal above its Debye temperature.