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TEMPERATURE AND PRESSURE EFFECTS ON THE ELASTIC MODULI OF GADOLINIUM SINGLE CRYSTALS

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ABSTRACT

The effects of hydrostatic pressures up to 3 kbar on the single crystal elastic moduli of Gd metal have been measured at 298 K and 273 K. In addition, the effect of pressure on the temperature dependence of c_{33} between 298 and 273 K has been observed. With exception for the c_{44} shear mode the pressure coefficients of the stiffness moduli and the Gruneisen mode gammas are significantly decreased by ferromagnetic ordering. The isothermal pressure derivative of the bulk modulus is 1.68 at 273 K in contrast to 3.11 at 298 K.

The effects of ferromagnetic ordering observed in the temperature dependence of the elastic moduli are mostly intrinsic effects not caused by the volume magnetostriction. The pressure dependence of T_c as indicated by the c_{33} modulus is — 1.60 K/kbar.

RÉSUMÉ

Les effets de la pression hydrostatique jusqu'à 3 kbar sur les modules élastiques d'un monocristal de Gd ont été mesurés à 298 K et 273 K. De plus, on a observé l'effet de la pression sur la variation thermique de c_{33} entre 298 K et 273 K. L'ordre ferromagnétique réduit sensiblement les coefficients de pression des modules d'élasticité, à l'exception de c_{44}, et les gammas de Grüneisen. La dérivée isotherme, par rapport à la pression, du coefficient en volume est 1,68 à 273 K au lieu de 3,11 à 298 K.

Les effets de l'ordre ferromagnétique que l'on constate dans la variation thermique du module élastique sont dus essentiellement à des effets intrinsèques qui ne résultent pas de la magnétostriction en volume. La variation de T_c avec la pression indiquée par le module c_{33} est de — 1,60 K/kbar.

Introduction

Several papers have recently appeared which pertain to certain aspects of ultrasonic wave propagation in ferromagnetic Gd metal. Luthi et al. have shown a pronounced peak in ultrasonic attenuation for the c_{33} longitudinal mode near T_c ($\sim$ 290 K) which arises from the volume magnetostriction coupling mechanism [1]. Long, et al. have published some data regarding the effects of changes in magnetic anisotropy constants on c_{33} at 236 K, which indicate a type of ΔE effect [2]. Brooks et al. have calculated the effect of magnetoelastic coupling on the temperature dependence of the magnetic anisotropy constants [3]. Rosen has measured the changes in polycrystalline elastic parameters with temperature [4]. The present

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work presents the effects of temperature and high pressure on all of the single crystal elastic stiffness moduli of Gd.

The purpose of the work it twofold : (1) to determine whether the indirect exchange interaction between the *f* electrons and the conduction band, which leads to the observed magnetic structures in rare earth metals, produces significant intrinsic changes in the elastic moduli, (2) to obtain some basic information about the Grüneisen constants for the lattice vibrational modes in the paramagnetic and ferromagnetic phases. The measurements of the temperature dependence of the elastic moduli at atmospheric pressure are included in the Proceedings of the 6th Rare Earth Conference [5] ; in this paper we will only briefly review this part of the work and concentrate on the derivation and use of the high pressure measurements carried out at the University of Hawaii.

Experimental procedure

The five independent elastic stiffness moduli for h.c.p. crystals are determined by measuring the velocities of pulsed ultrasonic waves propagated parallel, perpendicular, and 45° to the " c " axis. The relationship of the moduli to the wave modes are given in Table I. The diagonal moduli c_{ij} $(i = j)$ are determined directly from ρv^2, where ρ is the mass density and v is the particular wave velocity. The calculation of c_{13} involves the quasicompressional wave velocity, as well as c_{11}, c_{33} and c_{44} [6].

The purity of our Gd crystals has not been chemically evaluated. On the basis of the magnetic Curie temperature ($T_c = 289.5$ K) that was carefully measured for this material, we estimate from the relation of Cadieu and Douglas [7] that the resistivity ratio $R_{273\,K}/R_{4\,K}$ was approximately 25.

TABLE I

Relation of elastic moduli to acoustic wave modes propagated in Gd crystals

Modulus	Wave propagation direction	Type mode
c_{11}	90° to "c"	compressional
c_{33}	parallel to "c"	compressional
c_{44}	parallel to "c"	shear 90° to "c"
c_{44}	90° to "c"	shear parallel to "c"
$c_{66} = \frac{1}{2}(c_{11} - c_{12})$	90° to "c"	shear 90° to "c"
c_{13}	45° to "c"	quasi-compressional (Q.L.)

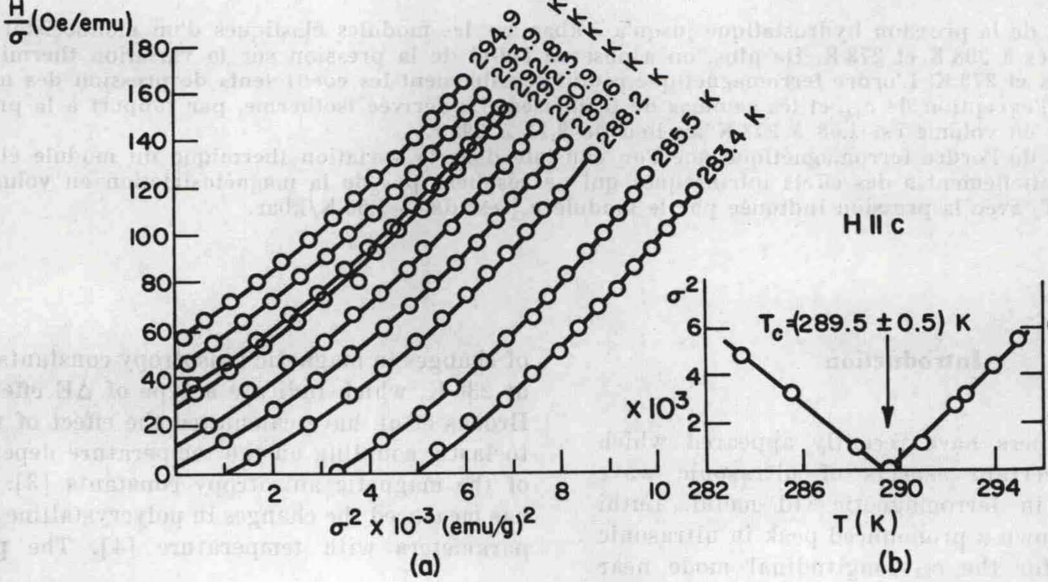

FIG. 1

Determination of the magnetic Curie temperature T_c, from magnetization (σ) vs. field (H) data for $H_{\parallel}$ "c".

The H/σ vs σ^2 plots that were measured for this Gd are shown in Fig. 1 (H is the magnetic field and σ is the induced magnetization along the « c » axis) [8].

The effects of pressure on all of the elastic moduli at 293 K (paramagnetic phase) and 273 K (ferromagnetic phase) and on c_{33} at various intermediate temperatures were measured by the pulse superposition method [9]. Nitrogen gas was the hydrostatic pressure medium and pressure measurements were obtained from a calibrated manganin pressure cell.

The corrections to the basic data that are necessary to account for path length and density changes with pressure were made by computing the linear and volume compressibilities at each interval of pressure using the following equations :

$$(c_{ij})_p = \left[\left(\frac{f_p}{f_0}\right)^2 \frac{(1 + (\beta_\perp)_T \Delta p)^2}{1 + (\beta_{||})_T} \right] (c_{ij})_0 \ ; \quad c_{ij} = c_{33} \text{ or } c_{44} \quad (1)$$

$$(c_{ij})_p = \left(\frac{f_p}{f_0}\right)^2 (1 + (\beta_{||})_T \Delta p)(c_{ij})_0 \ ; \quad c_{ij} = c_{11} \text{ or } c_{66} \quad (2)$$

where f_p/f_0 is the ratio of the pulse repetition rate frequencies at pressure $[p]$, to that at one atmosphere, f_0 ; $(\beta_\perp)_T$ and $(\beta_{||})_T$ are the isothermal linear compressibilities perpendicular and parallel to the " c " axis, respectively, at the start of the pressure interval denoted by $[\Delta p]$, arbitrarily chosen as 300 bar.

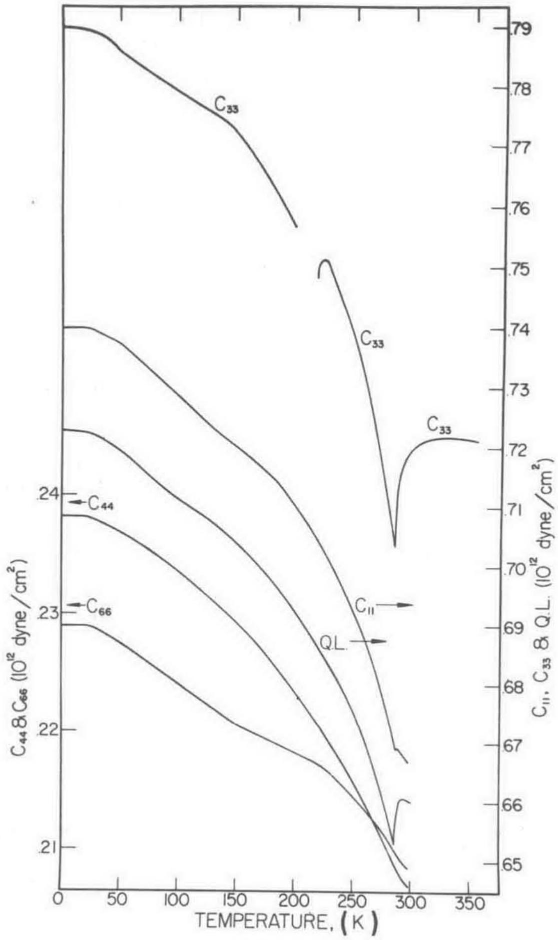

FIG. 2

Temperature dependence of the c_{ij} of Gd.

Results

Variation of c_{ij} with T at zero applied pressure : Curves obtained from plotting the measured c_{ij} as a function of temperature at ambient pressures are shown in Fig. 2. The effects of the paramagnetic transition on the compressional modes, c_{33}, c_{11} and Q. L. are clearly observed with c_{33} showing by far the greatest effects at $T < 330$ °K. The slope inversion for the c_{33} curve occurs at (286.5 ± 1) K, which is approximately 3 K less than T_c, the measured magnetic Curie temperature. The c_{11} curve changes slope abruptly at 289 K and c_{11} is constant between 289 and 286 K, at which point there is again an abrupt change. The c_{44} and c_{66} (shear moduli) curves both change slopes abruptly at 289 K. The effects between 286 and 289.5 K are then clearly associated only with compressional modes and evidently arise from the volume changes produced by the acoustic waves; i.e. shear waves do not change the volume. The much greater effect on c_{33} than c_{11} is to be expected if the modulus decrease is caused by an interaction between the strain and the magnetic anisotropy in Gd [10].

The effect on c_{33} that are implicitly due to the anomalous thermal expansion are considered in the analysis of the high pressure data. The anomaly in the c_{33} curve between 225 K and 210 K is evidently associated with the temperature change in the easy direction of magnetization and has been closely examined in a recent paper by Long et al. [2].

The adiabatic linear and volume compressibilities peak at 286 K; $(\beta_\perp - \beta_{||})$ is positive at $T > 286$ K and negative at $T < 286$ K.

Effects of high pressure : The results of the measurements of the changes in repetition rate frequencies with increasing hydrostatic pressure up to 3.034 kbar, are shown in Fig. 3. These measurements were made at 298 K and 273 K, as noted in the curve identification titles. There are 3 distinct anomalies : (1) the 298 K data for the c_{33} mode and the Q.L. mode deviates from a linear pressure-frequency relation at higher pressures ; (2) the c_{44} mode frequencies, measured either by wave propagations parallel or perpendicular to the " c " axis initially decreases very slightly with pressure at 298 K but there is no net change between zero applied pressure and 3.03 kbar ; (3) at 273 K the frequency for the c_{44} mode increases with initial pressure but no significant change occurs above 1 kbar.

The changes in wave velocity with pressure reflect the reductions in thickness of the crystals with increasing pressure as well as the basic frequency data given in Fig. 3. For both shear modes, c_{44} and c_{66}, the wave velocities have negative pressure coefficients at 298 K as well as 273 K. Since the density changes are inversely related to approximately the 3rd power of the change in thickness, all of the stiffness moduli have positive pressure coefficients. The effect of ferromagnetic ordering, as reflected in the differences between the 298 K and 273 K data, is to decrease the pressure coefficients of c_{11}, c_{33}, c_{13} and c_{66} whereas the pressure coefficient of c_{44} is increased. The slopes of the linear parts of the pressure-modulus curves are given in Table II.

TABLE II

Pressure derivatives of adiabatic and isothermal c_{ij}

	$\frac{dc_{11}}{dp}$	$\frac{dc_{12}}{dp}$	$\frac{dc_{13}}{dp}$	$\frac{dc_{33}}{dp}$	$\frac{dc_{44}}{dp}$	$\frac{dc_{66}}{dp}$
Adiabatic 298 K	3.118	2.393	3.553	6.019	.07	.362
Isothermal 298 K	2.78	2.18	3.26	6.41		
Adiabatic 273 K	2.437	1.740	2.683	3.77	.29	.334
Isothermal 273 K	1.94	1.33	1.63	2.93		

The changes in adiabatic linear and volume compressibilities with pressure are given in Table III. The initial slope of the $\beta_{\parallel}$ vs pressure plot is about twice that for $\beta_{\perp}$, at both 298 K and 273 K.

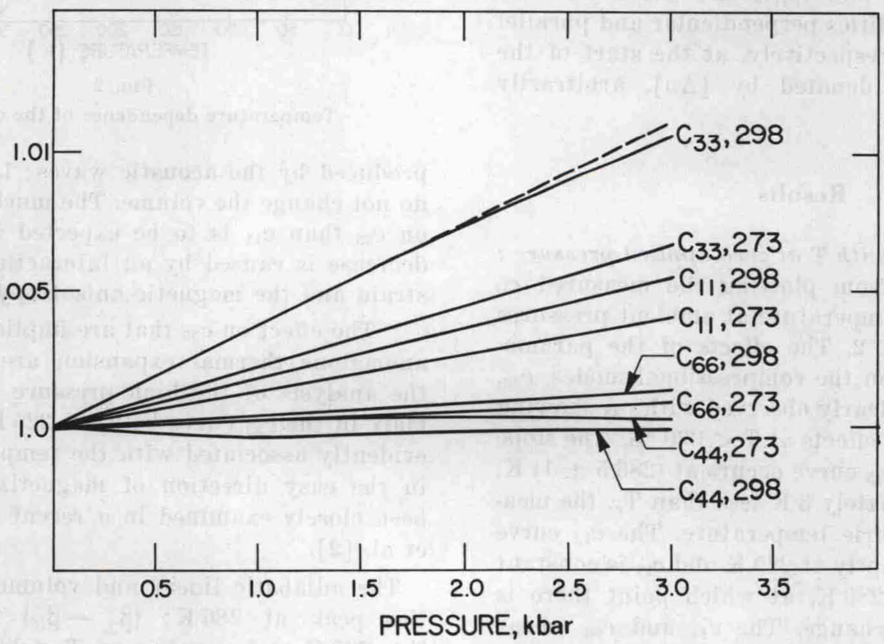

FIG. 3

Pressure dependence of the ratio of the pulse repetition rate frequency at pressure p, to that at one atmosphere for the propagation modes corresponding to the c_{ij} at 298 K and 273 K.

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
	$10^{-21}\,\dfrac{cm^4}{dyne^2}$			
Adiabatic 298 K	–.0054	–.0117	–.0225	3.22
Isothermal 298 K	–.0052	–.0114	–.0223	3.11
Adiabatic 273 K	–.0046	–.009	–.0180	2.57
Isothermal 273 K	–.0035	–.006	–.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

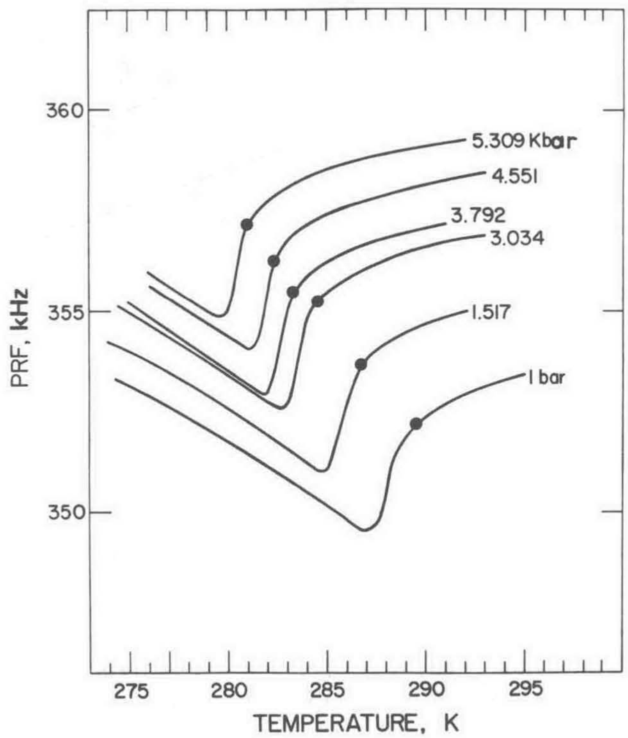

FIG. 4

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 × 10^{-4}	– 1.74 × 10^{-4}	0.34 × 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
288 K	c_{33}	97 × 10^{-4}	– 5.50 × 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

$$\frac{1}{m}\frac{dm}{dT} = \frac{1}{m}\left(\frac{\partial m}{\partial T}\right)_V - \frac{\alpha_V}{(\beta_V)_T}\frac{1}{m}\left(\frac{\partial m}{\partial p}\right)_T \qquad (3)$$

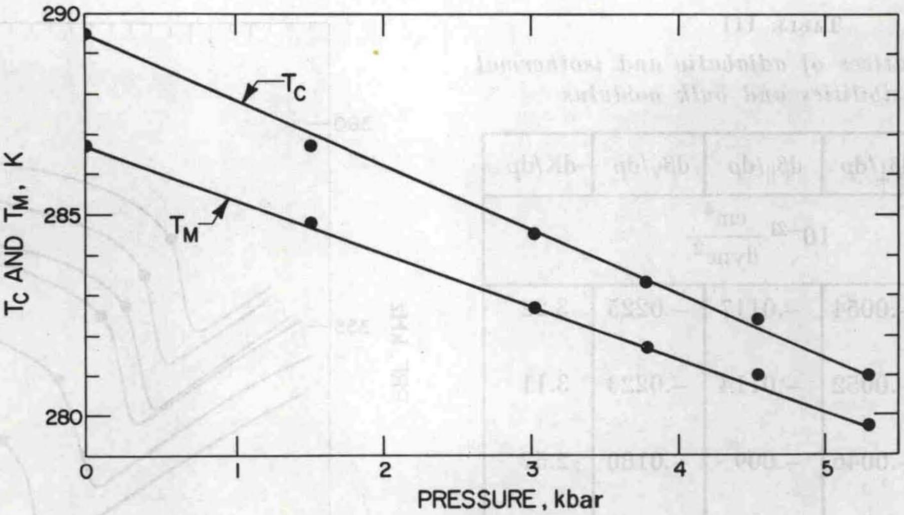

FIG. 5
Variation of T_c and T_m (minimum c_{33}) with hydrostatic pressure.

where m is the modulus and α_V is the volume expansion coefficient. The $(\partial m/\partial T)_V$ term is the intrinsic part of the temperature dependencewhich 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.

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

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

where α_V is separated from the spontaneous magnetization effects, c_V is the heat capacity at constant volume, V, and $\overline{\omega}$ 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 γ_i, where i is a given mode of wave propagation. By simple averaging of the γ_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 γ_H of 0.35 and 0.26, respectively, compared to values of approximately 0.45 for γ_{th}. Since the γ_{th} calculation involves an estimate of the normal α_V and c_V values near T_c the agreement with the computed γ_H is reasonably good. Both give remarkably small γ's for a metal above its Debye temperature.

The low temperature γ, γ_L, is computed by weighting the individual γ_i, computed from the c_{ij} at 4 K and dc_{ij}/dp at 273 K, according to the inverse 1/3 power of the wave velocity.

The γ_L computed for Gd is 0.13. At present time there are no direct determinations of γ_L that can be used to test the accuracy of that computed from the c_{ij} data. Andres dilatation measurements in the range of 2 K to 25 K were, unfortunately, not adequate for separating the lattice, electronic, and magnetic contributions to the low temperature thermal expansion [17]. Consequently, we have a value of 0.2 for $(\gamma_L + \gamma_e + \gamma_m)$ where γ_e is related to the volume dependence of the electronic density of states. Subtracting the computed γ_L from Andre's total γ_{Lth} suggests that γ_e for Gd is a very small number on the order of 0.1, if we neglect γ_m.

It has been proposed [18] that the change in T_c with pressure, assuming a free electron model for Gd, is related to γ_e as follows :

$$-\frac{1}{T_c(\beta_V)_T}\frac{dT_c}{dp} = \frac{d\ln T_c}{d\ln V} = \gamma_e - 1 + 2\frac{\partial \ln(I)}{\partial \ln V} \simeq 1.8$$

where I represents the strength of the exchange interaction between ion and *s* electron spins. If we assume γ_e to be 0.1 it is clear that dT_c/dP arises almost completely from the volume dependence of the exchange interaction, with the shift in $N(E_F)$ having a very minor role.

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Commentaires

Comments

H. G. HOPKINS. — I was very much struck with the extremely large differences between the adiabatic and isothermal values of the elastic constants in your work. These values are normally coincident for all practical purposes, e.g. for isotropic or polycrystalline materials. Are the present results peculiar to Gadolinium ?

E. S. FISHER. — The large difference is created by the large thermal expansion coefficient in the temperature range of the magnetic transition, i.e. α_V is in the range -5 to -10×10^{-5}. We used the relations of Voigt for evaluating the isothermal values of each of the c_{ij}.