Elastic Moduli and Ultrasonic Attenuation of Gadolinium, Terbium, Dysprosium, Holmium, and Erbium from 4.2 to 300°K

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The longitudinal and transverse acoustic velocities and the ultrasonic attenuations in high-purity polycrystalline gadolinium, terbium, dysprosium, holmium, and erbium metals have been measured by a pulse technique at a frequency of 10 MHz between 4.2 and 300°K. The variations with temperature of the Young moduli E, shear moduli G, adiabatic compressibilities K_s, and Debye temperatures Θ_D have been determined. The anomalies observed in the elastic and anelastic behavior were correlated with the magnetic transitions known to occur in these metals. The behavior of the elastic properties and ultrasonic attenuations in the vicinity of the majority of the magnetic transition points was in accord with the criteria of Landau *et al.*'s theories of second-order phase changes. Exceptions are the ferromagnetic transitions in terbium and dysprosium, and the change in the antiferromagnetic structure of erbium at 56°K. The character of the elasticity anomalies in these three cases tends to indicate that they are of first order. The abrupt change in the easy direction of magnetization in gadolinium at 224°K is sharply manifested in the elastic and anelastic properties. Determination of these properties in holmium revealed an anomalous behavior at 70°K. The temperature variation of the Debye temperatures in gadolinium, terbium, dysprosium, holmium, and erbium depicts the elasticity behavior. The limiting Debye temperatures at 0°K are, in general, higher than those obtained from specific-heat measurements.

INTRODUCTION

THE metals of the heavy rare-earth series, from gadolinium to thulium, provide a system which exhibits a complex magnetic spin structure with strong dependence on temperature.[1] They crystallize in a single hexagonal close-packed structure with a c/a ratio relatively constant (1.59–1.57).[2] However, the so-called "lanthanide contraction" may affect the Brillouin zone boundaries and thus influence various physical properties.

The electronic configurations of the heavy rare-earth elements differ from each other only in the number of the electrons in the $4f$ shell. As distinct from the elements of the iron group, the uncompensated electron spins in the $4f$ shell of the rare-earth metals, are screened by the higher-lying $5s$ and $5p$ electron shells. Therefore, the direct exchange interaction between $4f$ electrons of neighboring atoms is greatly impeded or even totally prevented. It is assumed that indirect exchange, via the conduction electrons, occurs in the rare-earth metals.[3,4] Their magnetic behavior results from these localized $4f$ electrons. As the temperature is reduced below certain critical points, there appear magnetic order-disorder transitions, as well as transitions between different types of ordering. They arise from the energy balance among long-range exchange interaction anisotropy resulting from crystal-field–spin-orbit effects and direct exchange. Kittel[5] has formulated the theory of exchange magnetostriction which shows the interaction between the magnetic and elastic forces. In some cases this mechanism can lead to first-order magnetic transitions.

By cooling through the magnetic ordering points, the rearrangement of the spins will give rise to a change in those contributions to the total energy that are due to the interatomic magnetic interaction. Since the elastic constants are second derivatives of the thermodynamic potential with respect to strain, a magnetic contribution should be expected in the vicinity of any magnetic ordering transition. The magnitude of the elastic modulus anomaly will depend on the magnetostriction deformations created during the magnetic transformation.

The behavior of the elastic moduli in the vicinity of a second-order phase transition was described by the phenomenological theory of Landau and Lifshitz.[6] The critical fluctuations of the spins in the neighborhood of a phase transition will interact with the acoustical phonons of the sound wave giving rise to anomalies in the ultrasonic attenuation. Landau and Khalatnikov[7] showed that the attenuation should display a maximum on the low-temperature side of the transition point. Since a relaxation mechanism was postulated, the position of this attenuation peak with respect to the critical temperature should depend on the frequency of the ultrasonic waves.

The measurements reported in the present paper are concerned with the behavior of the elastic moduli and ultrasonic attenuation of the heavy rare-earth metals: Gd, Tb, Dy, Ho, and Er. The data provide an additional insight, and a confirmation of the anomalous behavior noted in various other physical properties, e.g., heat capacity, electrical and thermal resistivities, neutron-

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diffraction, thermal expansion, and magnetic moment measurements in the temperature range between 4.2 and 300°K.[8] Furthermore, the elastic properties are of fundamental importance in the interpretation of high-pressure measurements, magnetostriction, etc. The limiting value of the Debye temperature at 0°K, as obtained from elastic measurements is useful in the analysis of specific-heat data since it provides an independent estimate of the lattice contribution of the calorimetrically measured total heat capacity. This evaluation is particularly important in metals that have a high electronic component or a magnetic component in the total specific heat.

EXPERIMENTAL DETAILS

The high-purity (99.9%) polycrystalline specimens, supplied by Johnson-Matthey Co., England, were in the form of flat disks, 12 mm in diameter and about 5 mm thick. The samples were hand-lapped to a parallelism of faces of better than 2 parts in 10^4. The thickness of the disk was measured on a calibrated indicator stand to within $\pm 5\times 10^{-4}$ mm.

Elastic moduli and attenuation measurements were made at a frequency of 10 MHz by an ultrasonic pulse technique. Pulses of 0.5 μsec duration were generated by an Arenberg model PG-650C pulse generator. The reflected, unrectified rf signals were amplified and displayed on the screen of a Tektronix 545A oscilloscope, the timing circuit of which was checked by means of a Hewlett-Packard 524 counter and a Tektronix 180A quartz signal generator. The echo pattern, including the calibrated oscilloscope grid, was automatically recorded at a speed of 4 frames per min by means of a Robot camera system (Robot Foto and Elektronik, Duesseldorf, West Germany). The film was subsequently read on a film analyzer (Vanguard Instrument Corp., Roosevelt, N.Y.).

Acoustical transit times were determined from the distances between corresponding cycles of several successive echoes. Knowledge of the instantaneous thickness of the specimen (by the aid of the coefficient of thermal expansion), enables the calculation of the longitudinal (C_l) and transverse (C_t) sound velocities. The adiabatic elastic moduli (E=Young modulus, G=Shear modulus, K_s=compressibility) were found through the following relationships:

$$G=\rho C_t^2, \qquad E=2G(1+\sigma), \qquad K_s=3(1-2\sigma)/E,$$

where ρ is the density of the specimen. Poisson's ratio σ is given by

$$\sigma=\frac{2-(C_l/C_t)^2}{2[1-(C_l/C_t)^2]}.$$

The Debye temperature was derived from the acoustic velocities using the well-known relations[9,10]

$$\Theta_D=h/K(3N\rho/4\pi M)^{1/3}C_m,$$

where h is Planck's constant, K is Boltzmann's constant, N is Avogadro's number, and M is the atomic weight. The value C_m is an average sound velocity, according to the basic assumptions of the Debye theory of specific heat. In the case of a polycrystalline specimen that can be assumed elastically isotropic (small grain size relative to acoustic wavelength), where the transverse and longitudinal sound velocities are invariant with respect to the direction of propagation of the elastic wave, C_m will be

$$C_m=\{\tfrac{1}{3}[(2/C_t^3)+(1/C_l^3)]\}^{-1/3}.$$

The relative ultrasonic attenuation was calculated from the exponential decay of the echoes, and expressed in dB μsec^{-1}.

$$\alpha=\frac{20\log_{10}(A_1/A_n)}{(n-1)t},$$

where A_1, A_n are the amplitudes of the 1st and the nth pulse, respectively, and t is the measured transit time between two successive pulses.

The transit time-measurement procedure was checked by means of velocity determination on three aluminum specimens of various thicknesses. The estimated experimental errors in the sound velocity is less than 0.2%, i.e., 0.4% in the elastic moduli. The relative, point-to-point precision was better by a factor of 4. The ultrasonic attenuation was determined to within 1%.

Thin layers of Dow Corning Compound 7, Dow Corning 200 (viscosities of 6000 and 10^6 cP) were found to give satisfactory acoustic couplings between the quartz transducers and the surfaces of the metallic specimens for both longitudinal and transverse modes of vibration over the whole temperature range.

Conventional cryogenic techniques were employed. The measurements were mostly carried out during the warmup from liquid-helium to room temperature at a rate of about 0.5°K min^{-1}. The temperature was measured with a helium gas thermometer in the region of 4.2 to 35°K. From 35 to 310°K a Au–Co versus Cu thermocouple was used. Both were checked against a calibrated germanium resistance thermometer and melting points of CS_2 (164.5°K), CCl_4 (250.6°K), and ice (273.15°K). The estimated error in temperature is ±0.5°K.

The variation of the acoustical path length of the specimens was calculated using the average coefficients

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[9] J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1965), Vol. 2, p. 219.

[10] H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 213.

TABLE I. Average coefficients of thermal expansion and the room-temperature densities of the samples.

Element	Density g cm^{-3}	Average linear coefficient of thermal expansion °K^{-1}
Gd	7.890	8.28×10^{-6}
Tb	8.271	10.3×10^{-6}
Dy	8.530	10.0×10^{-6}
Ho	8.802	10.7×10^{-6}
Er	9.061	12.3×10^{-6}

of thermal expansion as given by Gschneidner.[11] The room-temperature densities of the samples were determined by means of a fluid-displacement technique, using monobromobenzene. The average coefficients of thermal expansion and the room-temperature densities are given in Table I.

RESULTS AND DISCUSSION

1. Gadolinium

Gadolinium metal is generally considered a "normal" ferromagnet[2] at temperatures below its Curie point of 292°K. However, Belov *et al.*[12] observed an anomalous behavior in the temperature variation of the magnetization in weak fields (10–15 Oe) exhibiting a maximum at about 210°K. In this temperature region, anomalies were also found in the coercive force and in the remanent magnetization.[12] Belov concluded that antiferromagnetism exists in gadolinium below 210°K, and that it can be destroyed by a weak field.

The suggested existence of antiferromagnetism in gadolinium triggered a variety of experiments. Graham[13] has found no evidence of bumps in the low-field magnetization curves of single-crystal specimens. He, and other workers,[14,15] observed that the easy direction of magnetization varies with temperature, forming a cone of easy magnetization with a maximum angle of about 70° with respect to the hexagonal axis. The electrical resistivity[16] does not exhibit any anomalies in its behavior below the Curie point, although the slope of the resistivity versus temperature changes slightly below 210°K. But thermal conductivity,[17] on the other hand, does show a pronounced minimum at 230°K, which was attributed to the rapidly varying angle of the easy cone of magnetization. Difficulties are encountered in obtaining reliable neutron diffraction data because of the very high neutron absorption of gadolinium. Nevertheless, neutron diffraction studies[18,19] indicated that gadolinium behaves as a normal ferromagnet. Above 284°K the magnetic moment is directed along the c axis, while below this temperature, the direction varies continuously, with the cone angle reaching a maximum at 195°K. Recent initial-susceptibility measurements[20] show a minimum at 170°K, where according to Graham[13] the easy direction of magnetization is very nearly in the basal plane. With increasing temperature the initial susceptibility reaches a maximum at about 220°K before forming a knee at the Curie point. Coefficients of thermal expansion show a complex temperature dependence along both axes.[21] Along the c axis, the coefficient was found to be negative from 150 up to 292°K, with a maximum at 220°K. Finally, the saturation magnetostriction constants[22,23] behave anomalously in this temperature region. A change in sign is observed[23] at 230°K with a minimum at 260°K, before vanishing at the Curie temperature, in agreement with the results of Belov *et al.*[12]

The objective of the simultaneous measurement of the elastic moduli and ultrasonic attenuation, reported here, was to gain additional insight into the anomalies found by Belov[12] and Graham.[13]

The temperature dependence of the elastic moduli of polycrystalline gadolinium is shown in Fig. 1. G and E represent the shear and Young moduli, respectively. A steady increase in both E and G with decreasing temperature, from 310 to 295°K, can be observed. Both moduli diminish drastically at the Curie point of 292.5°K. The behavior of the elastic moduli in the vicinity of the Curie point in gadolinium is represented by a λ-type anomaly in the adiabatic compressibility K_s (Fig. 2). A similar peak was also observed in the heat capacity.[24] This is in qualitative agreement with the phenomenological theory of second-order phase transitions of Landau and Lifshitz.[6] In accord with the theory of Landau and Khalatnikov,[7] both attenuations (longitudinal α_l and transverse α_t) behave anomalously and exhibit a peak on the low-temperature side of the Curie point. Unfortunately, a single ultrasonic frequency has been employed in the present study and therefore the relaxation times and the activation energies

[11] K. Gschneidner, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, p. 275.
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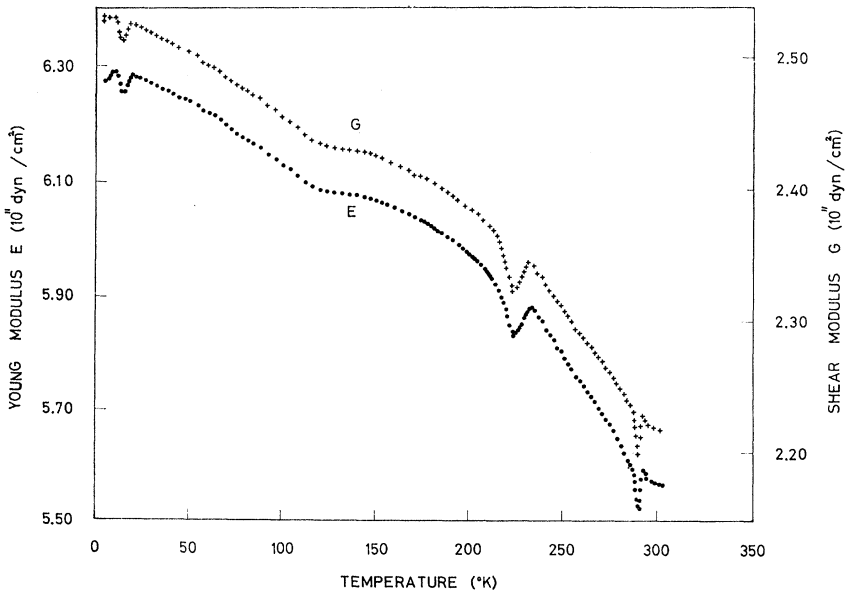

FIG. 1. Temperature variation of the Young (E) and shear (G) moduli of polycrystalline gadolinium.

involved in the paramagnetic-ferromagnetic transition could not be established.

A second anomaly, in the elastic moduli, compressibility, and ultrasonic attenuations (Figs. 1–3), was observed at 224°K. The minimum in the compressibility curve is at 235°K, increasing rather slowly (compared with the drastic rise at the Curie point) to its peak at 224°K. The transition at 224°K corresponds to the anomalous behavior of gadolinium in this temperature range. It is probably associated with the abrupt change in the easy direction of magnetization as found by Graham.[13] The attenuation behavior (Fig. 3) lends support to such a mechanism rather than to the helical reordering, as was assumed by Belov.[12] The attenuation of the transverse waves, α_t, indicates the presence of a magnetic transition. However, the attenuation of the longitudinal waves, besides the expected peak, keeps growing with decreasing temperature to about 170°K, then levels off. This gradual increase may be associated with additional alignment of interacting spins into a direction at right angles to the prior ferromagnetic alignment. The spins in this prevailing direction interact anelastically with the propagating acoustic phonons. The longitudinal attenuation will be preferentially increased while the attenuation of the transverse waves should diminish with temperature, thus compensating

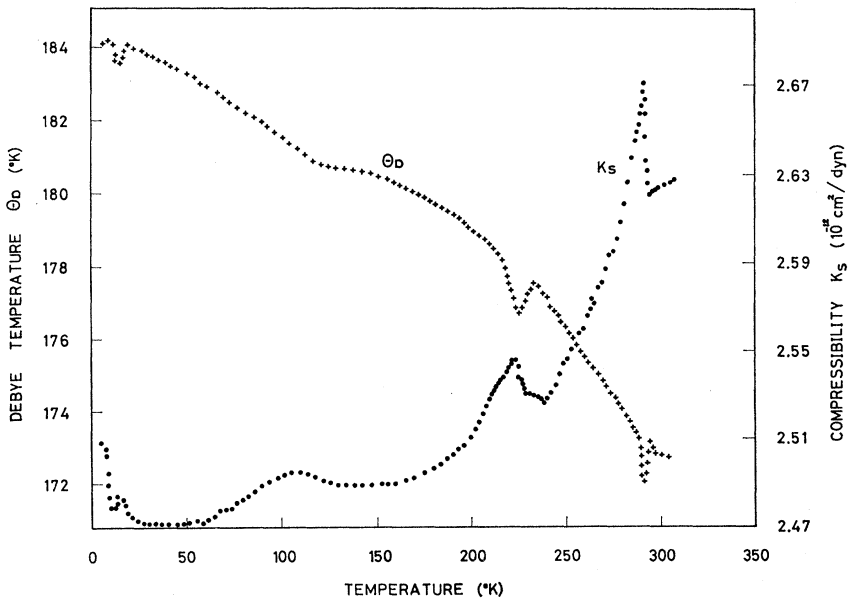

FIG. 2. Temperature variation of the adiabatic compressibility (K) and the Debye temperature (Θ_D) of polycrystalline gadolinium.

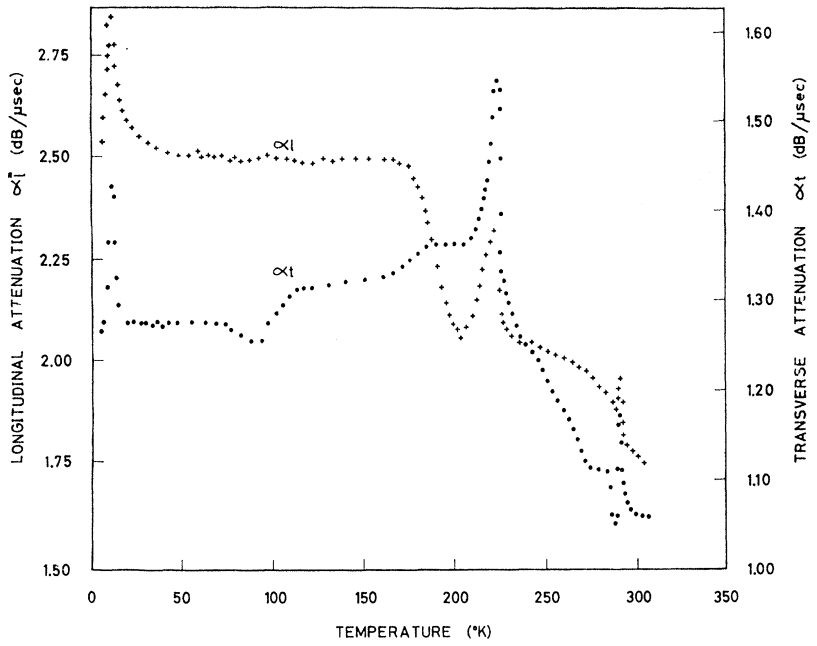

FIG. 3. Temperature variation of the longitudinal (α_l) and transverse (α_t) attenuation of polycrystalline gadolinium.

to some extent the increase in the longitudinal attenuation. Such a behavior is manifested in Fig. 3. In this temperature region the thermal conductivity[17] shows a pronounced minimum, whereas no such effect was observed in the electrical resistivity.[16] This illustrates the similarity in behavior between acoustical and thermal phonons and is in agreement with the observations of the present work. Fisher,[25] has detected a sharp increase in the acoustic attenuation at temperatures below 218°K, which prevented him from carrying out any single-crystal elastic-moduli measurements in the temperature range between 218 and 200°K.

Figures 1 and 2 show that the temperature dependence of the elastic moduli and the compressibility varies rather smoothly down to about 115°K, where a change in slope of the elastic moduli curves can be observed. At this temperature the compressibility displays a broad maximum and the transverse attenuation (Fig. 3) drops to a lower value. It is possible that in this region the easy cone of magnetization changes its angle with respect to the hexagonal axis. Graham[13] and Will *et al.*[18,19] reported such a shift at about 165°K.

At 15°K depressions in the elastic moduli are observed. The ultrasonic attenuations (Fig. 3) also show rather sharp and well-defined peaks. Arajs[17] and Aliev[26] found a maximum in the thermal conductivity of gadolinium at about 16°K. The anomalies in the elastic and anelastic behavior observed at 15°K are probably associated with this change in the transport properties.

Figure 2 shows the temperature dependence of the Debye temperature Θ_D as derived from the variation of the elastic velocities with temperature. The Debye temperature is essentially a representation of a certain averaging procedure of the acoustic velocities, which is the basis of the Debye theory of specific heat. Therefore, it is not surprising that its temperature dependence is very similar to that of the elastic moduli and includes all the anomalies observed. From the third law of thermodynamics, it is expected that the Debye temperature should approach the absolute zero with zero slope. This is the so-called limiting Debye temperature, which is of importance in the calculations of many physical parameters of solids. The limiting Debye temperature of gadolinium found in this investigation is $\Theta_D = 184$°K. This value is significantly higher than 152°K obtained from specific-heat measurements.[24] The calculation of the Debye temperature from the measured specific heat suffers from several uncertainties; e.g., difficulty in the accurate determination of the electronic and magnetic contributions to the heat capacity. The elastic-constants method is free from these difficulties. Recently, Lounasmaa,[27] assuming a zero-magnetic contribution to the specific heat, estimated the Debye temperature for gadolinium as being 195°K.

2. Terbium

Neutron diffraction studies[28,29] showed that metallic terbium experiences two magnetic transformations. The

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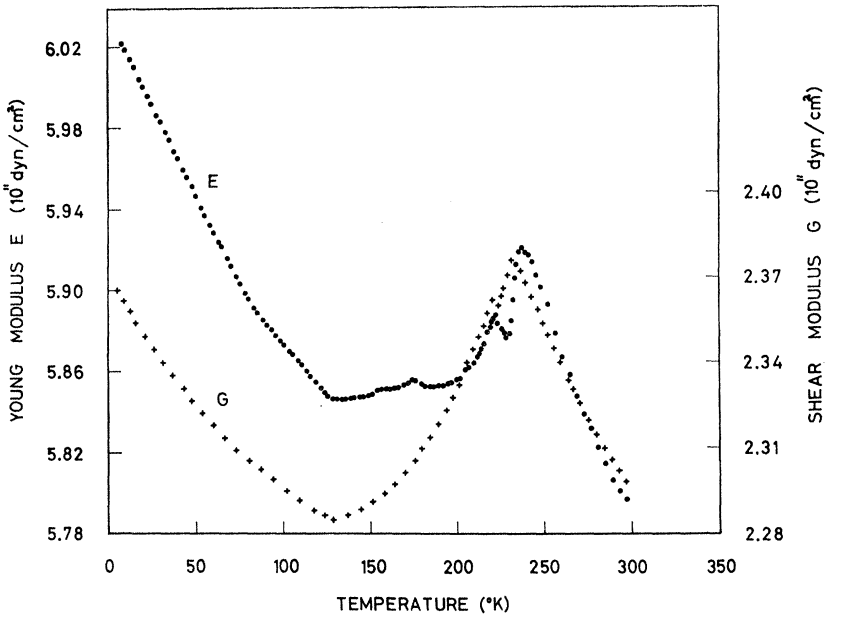

FIG. 4. Temperature variation of the Young (E) and shear (G) moduli of polycrystalline terbium.

paramagnetic helicoidal antiferromagnetic transition occurs at 229°K. This antiferromagnetic structure exists in the temperature interval between 229 and 221°K, and can be destroyed in relatively weak magnetic fields ($H_c = 200$ Oe). The transition into a ferromagnetic structure, with collinear ordering, takes place at 221°K. At this temperature a jump is observed in the atomic volume, accompanied by a rhombic distortion of the crystal lattice,[30] i.e., the first derivative of the thermodynamic potential, signifying that the antiferromagnetic to ferromagnetic transition is of the first order. Magnetic measurements on single-crystal and polycrystalline terbium[31–33] confirmed that the metal is ferromagnetic below 221°K and paramagnetic above 230°K.

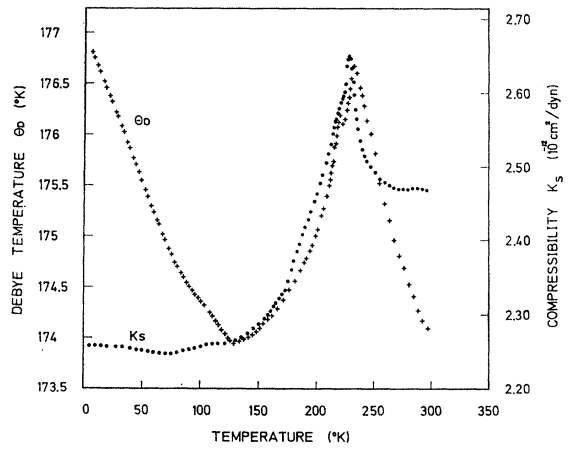

FIG. 5. Temperature variation of the adiabatic compressibility (K_s) and the Debye temperature (Θ_D) of polycrystalline terbium.

In contrast to the x-ray studies,[30] the transition to the ferromagnetic state is only slightly observable in the variation with temperature of the specific heat[34] and the electrical[35] and thermal[36,37] conductivities; the paramagnetic to antiferromagnetic change is generally more pronounced, yielding a λ-type jump in the specific heat[34] at 229°K.

The Young modulus E, and to some extent the shear modulus G (Fig. 4) show a dip in their variation with temperature at 228°K, which is the Néel point of terbium. A corresponding jump of about 7.3% (similar to that in the specific heat)[34] is observed in the adiabatic compressibility K_s (Fig. 5). This is in agreement with the Landau-Lifshitz theory of second-order transitions.[6] Figure 6 shows that the ultrasonic attenuation of the longitudinal waves, α_l, exhibits a peak on the low-temperature (ordered) side of the Néel point, which is in qualitative accord with the Landau-Khalatnikov theory.[7] The attenuation of the shear waves, α_t, begins growing with decreasing temperature below the Néel point, but for some reason does not show a pronounced

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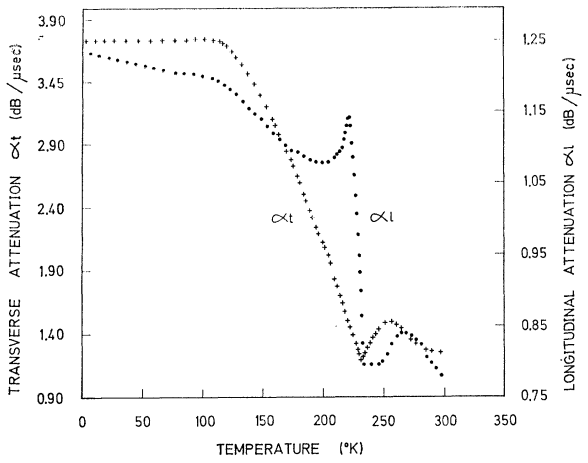

FIG. 6. Temperature variation of the longitudinal (α_l) and transverse (α_t) attenuation of polycrystalline terbium.

peak. Possibly, both longitudinal and transverse attenuations are affected by the subsequent transformation to the ferromagnetic state with decreasing temperature. One reason may be the narrowness of the temperature interval of existence of the antiferromagnetic state in terbium.

The ultrasonic attenuations display subsidiary peaks centered about 260°K. A similar behavior was observed in α-manganese[38] and europium,[39] and was attributed to the possible formation of short-range order in the paramagnetic state, preceding the magnetic order-disorder transition.

The elastic moduli (Fig. 4) do not display any striking discontinuities at the Curie point proper (221°K). However, with decreasing temperature below the Curie point, the moduli decrease in magitude attaining minima at about 130°K. It is interesting to note that at this temperature the Hall coefficient is at its maximum.[40] The adiabatic compressibility (Fig. 5) decreases smoothly with decreasing temperature.

The behavior of the elastic moduli and ultrasonic attenuations below the Curie point of terbium, is probably attributable to the first-order character of this antiferromagnetic-ferromagnetic transition. One would suspect that this phase change is temperature-dependent, where the rate of temperature variation has some effect on the transformation kinetics. Hystereses loops and similar thermal effects are expected. These points should be elucidated before an attempt can be made to explain the elastic and anelastic behavior of terbium in the vicinity, and below, its Curie point.

Figure 5 shows the variation of the Debye temperature Θ_D from 300 to 4.2°K. As expected, its behavior is similar to that of the elastic moduli. The limiting value of the Debye temperature (extrapolated to 0°K) is 177°K, compared with a value of 150°K, estimated from specific-heat measurements.[11]

3. Dysprosium

Specific-heat measurements[41] on dysprosium show the existence of two maxima, at 174 and 84°K. The high-temperature peak displays a definite λ character, and was attributed to the paramagnetic-antiferromagnetic transition. The peak at 84°K is smaller, and indicates the Curie point of dysprosium. Corresponding anomalies were also observed in the electrical[42,43] and thermal[43] conductivities. Magnetization measurements[44] show that dysprosium single crystals are highly anisotropic with spontaneous magnetic moments oriented parallel to the planes of the hexagonal layers. At about 108°K, dysprosium becomes isotropic in the basal plane.[44] Neutron diffraction[29,45] shows that dysprosium is similar to terbium in its magnetic behavior. The helical magnetic structure in dysprosium exists in the temperature interval between 179 and 85°K. The antiferromagnetic ordering is parallel to basal planes of the hexagonal lattice and the magnetic moment in successive planes is turned through an initial turn angle of 43°. This angle is temperature-dependent, becoming 26° at the Curie point (85°K). Below 85°K the turn angle drops to zero and the structure becomes normal ferromagnetic, with moments parallel to the hexagonal layers.

Although Banister *et al.*[46] have not noted any changes

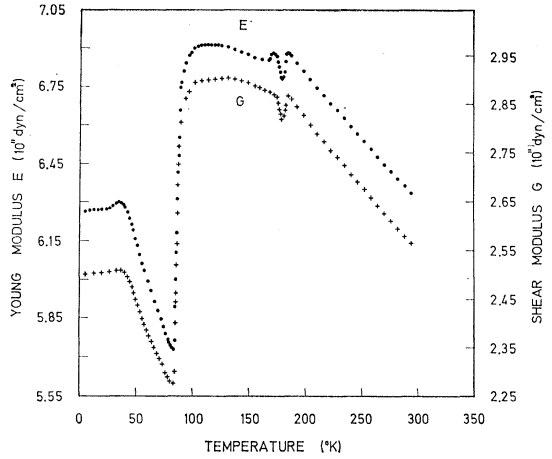

FIG. 7. Temperature variation of the Young (E) and shear (G) moduli of polycrystalline dysprosium.

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in the crystal symmetry at the Curie point, recent lattice-parameter measurements[47,48] indicate sharp discontinuities and distortions in the hexagonal lattice symmetry that can be ascribed to a first-order transition. On the passage from the helical to the ferromagnetic state, at 85°K, the large spontaneous magnetostriction distorts the lattice from hexagonal to orthorhombic.[49,50]

The Young (E) and shear (G) moduli of dysprosium (Fig. 7) exhibit a rather strong temperature dependence in the paramagnetic region. It is noteworthy that the adiabatic compressibility K_s (Fig. 8) displays a negative temperature coefficient, i.e., compressibility increases with decreasing temperature. The reason for this behavior is not clear. With decreasing temperature, at the Néel point (178°K), the elastic moduli show prominent dips. Corresponding attenuation anomalies, characteristic of second-order phase transitions,[7] are observed in both longitudinal (α_l) and transverse (α_t) wave attenuations (Fig. 9).

The behavior of the adiabatic compressibility in the antiferromagnetic region of dysprosium (Fig. 8) is rather peculiar. With decreasing temperature the compressibility increases up to a flat maximum at 148°K, followed by a minimum at about 105°K. It is possible that this behavior is associated with the reported variations in the antiferromagnetic structure at these temperatures.[44,48,51]

The transition to the ferromagnetic state is marked by a drastic dip in the elastic moduli at 86°K (Fig. 7)

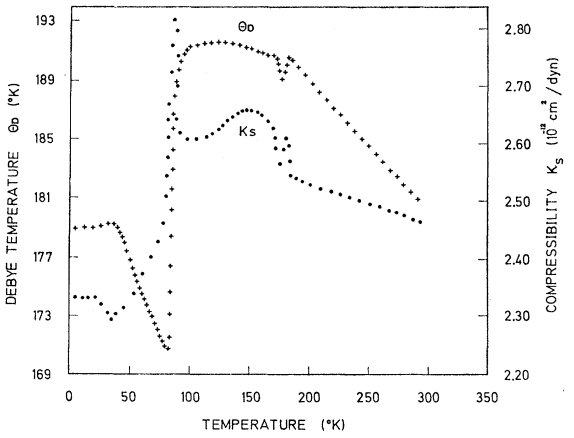

FIG. 8. Temperature variation of the adiabatic compressibility (K_s) and Debye temperature (Θ_D) of polycrystalline dysprosium.

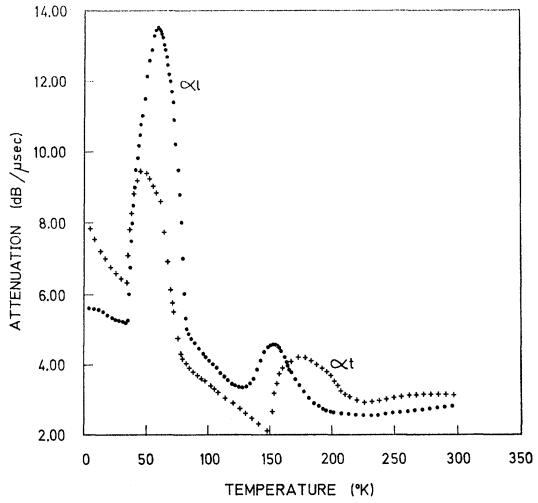

FIG. 9. Temperature variation of the longitudinal (α_l) and transverse (α_t) attenuation of polycrystalline dysprosium.

and by a corresponding peak in the adiabatic compressibility (Fig. 8). In contrast to the behavior in the vicinity of a second-order phase change, where the discontinuous jumps in the elastic properties can be visualized as being superimposed on a continuous curve,[38,39] the elastic moduli in dysprosium below 86°K recover to values which are significantly different from those in the antiferromagnetic state. Such a behavior indicates the possibility of occurrence of a crystallographic symmetry change that accompanies the magnetic reordering. The nature of the elasticity anomaly at 86°K is consistent with a first-order phase transition, and thus confirms the behavior of other physical properties.[47,48] The anomalous magnitude of the attenuation peaks in dysprosium, at temperatures below the ferromagnetic transition point, provides further support that the phase change is of first-order. In addition to the attenuation resulting from the rearrangement of the spins, there is probably another contribution that is due to the change in the crystal symmetry.

The temperature variation of the Debye temperature Θ_D in dysprosium is presented in Fig. 8. Its behavior is similar to that of the elastic moduli. The limiting value of Θ_D extrapolated to 0°K, is 179°K. The room-temperature value of Θ_D is 181°K. The Debye temperatures obtained from elastic measurements are different from those calculated from specific-heat data,[11] 172±35°K and 158°K, at 0°K and room temperature, respectively.

4. Holmium

Similar to terbium and dysprosium, holmium was also found to display two magnetic transitions at low temperatures. Specific-heat measurements[52] revealed

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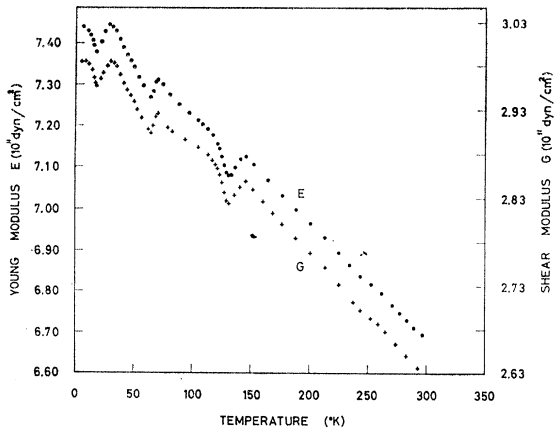

FIG. 10. Temperature variation of the Young (E) and shear (G) moduli of polycrystalline holmium.

two peaks. A λ-type anomaly occurs at 131.6°K, and a smaller, more symmetrical and thermal-history-dependent peak at 19.4°K. Neutron diffraction confirmed this behavior.[53,54] It showed that below its Néel point (133°K) holmium has a helical structure in which the c axis is the screw axis. The antiferromagnetic structure of holmium is intermediate between those of dysprosium and erbium. Magnetic[55,56] and electrical resistivity[56–58] measurements have shown that the ferromagnetic transition, with a Curie point at 20°K, is less drastic than in dysprosium, and takes place via a ferromagnetic

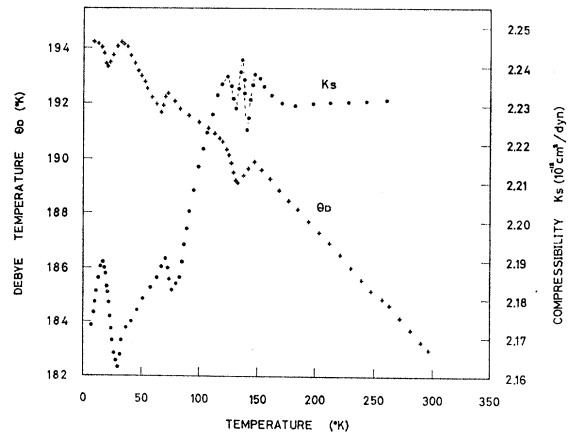

FIG. 11. Temperature variation of the adiabatic compressibility K_s and the Debye temperature Θ_D of polycrystalline holmium.

helix in which the magnetic moment has components both along the hexagonal axis and the basal plane. It is noteworthy that, whereas the antiferromagnetic transition is barely noticeable in the curve of the thermoelectric power versus temperature, the ferromagnetic phase change exhibits a sharp minimum at 19°K.[59,60]

The antiferromagnetic transition in holmium is marked by a dip in the elastic moduli at 132°K (Fig. 10). A corresponding peak is formed in the adiabatic compressibility at this temperature (Fig. 11). The anomalies in the ultrasonic attenuations (Fig. 12) are rather small and shallow. The transition appears to be of the second order.

The temperature dependence of the elastic moduli and ultrasonic attenutations in holmium reveals pronounced peaks at 72°K. The nature of these maxima is not clear. They point towards the possibility of changes in the

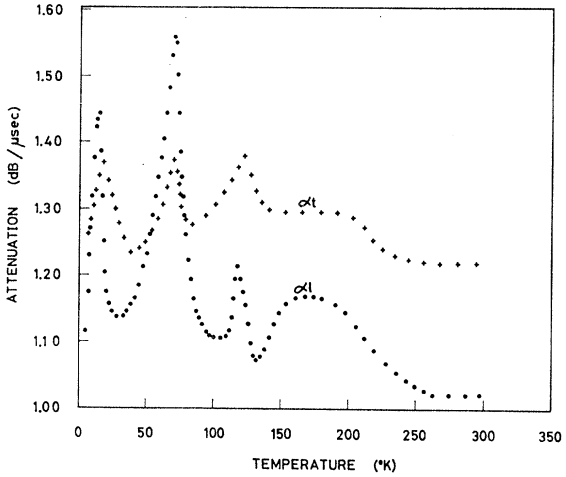

FIG. 12. Temperature variation of the longitudinal (α_l) and transverse (α_t) attenuation of holmium.

antiferromagnetic structure, similar to those in gadolinium at 224°K or erbium at 56°K. The anomaly in holmium at 72°K was not observed in the temperature dependence of other physical properties, e.g., neutron diffraction.[53]

The minima in the elastic moduli at 20°K (Fig. 10) are connected with the ferromagnetic phase change in holmium. The behavior of the elastic moduli and the ultrasonic attenuations (Fig. 12) suggests that this transition is of the second order.

5. Erbium

Erbium exhibits three distinct magnetic phases which were observed by neutron diffraction.[61] The metal is

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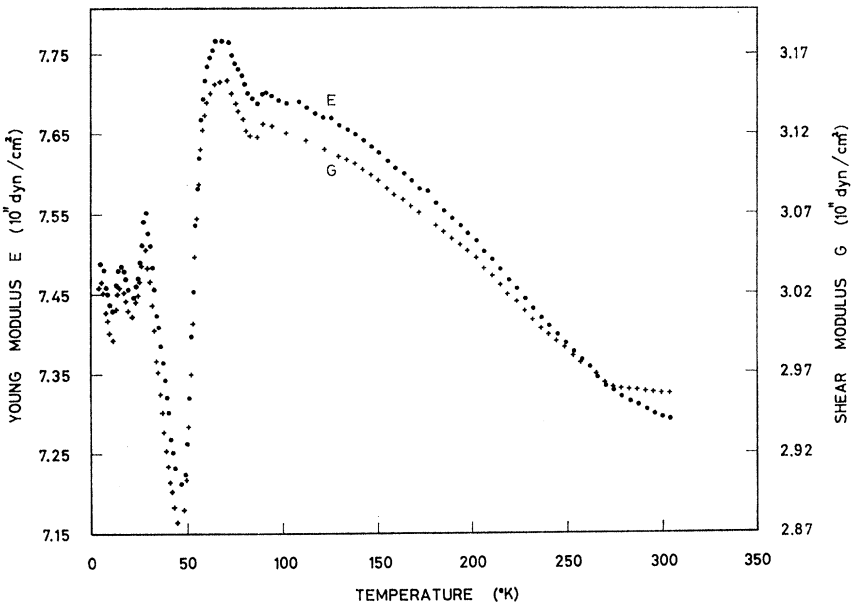

FIG. 13. Temperature variation of the Young (E) and shear (G) moduli of polycrystalline erbium.

paramagnetic above 85°K. In the temperature interval between 85 and 53°K the c axis of the magnetization is observed to be sinusoidally modulated. No ordering was found in the basal plane. Below 53°K the sinusoidal variation transforms into a square-wave modulation and helical ordering is observed in the basal plane. At 20°K the anisotropy energy spontaneously causes a transition to conical ferromagnetism in which the easy magnetic directions are the generators of the cones. Heat-capacity measurements are consistent with the neutron diffraction observations.[62] At 84°K a flat maximum was observed which drops rapidly with increasing temperature. The peak at 53°K is rather rounded, whereas the peak at 20°K was found to be symmetrical and showed thermal hysteresis. Magnetic[63,64] and electrical resistivity[57,64,65] measurements confirm, in essence, the existence of the transitions at 84 and 20°K. The antiferromagnetic phase change at 53°K is not noticeable in polycrystalline specimens, but is clearly observable in the electrical resistivity curve of single crystals along the c axis.[64]

The elastic moduli, E and G, in polycrystalline erbium

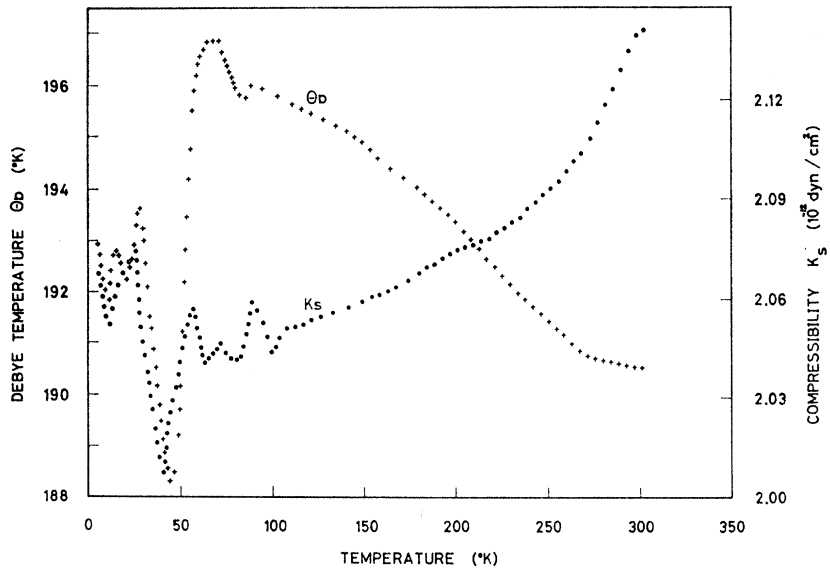

FIG. 14. Temperature variation of the adiabatic compressibility (K_s) and the Debye temperature (Θ_D) of polycrystalline erbium.

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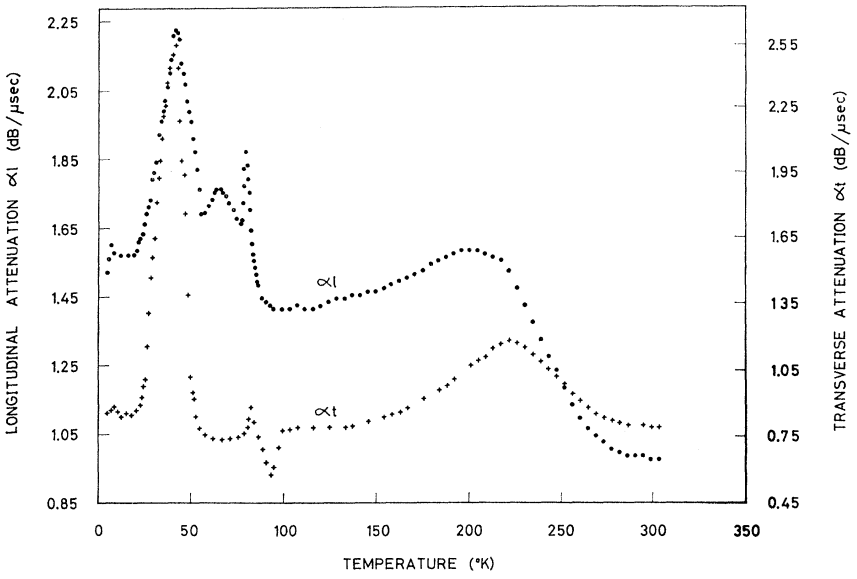

FIG. 15. Temperature variation of the longitudinal (α_l) and transverse (α_t) attenuation of polycrystalline erbium.

increase quite smoothly with decreasing temperature (Fig. 13). The paramagnetic to antiferromagnetic transition is marked by a small dip in the elastic moduli at 86°K. A corresponding peak is formed in the adiabatic compressibility curve (Fig. 14). This transition is of the second order, as evidenced by the characteristic rise of the ultrasonic attenuations, (Fig. 15) at the transition point. In addition, the attenuations exhibit flat maxima at about 220°K, which are probably related to formation of short-range order preceding the para-antiferromagnetic phase change.

In the temperature interval between 67 and 44°K, the elastic moduli decrease drastically by about 8%, followed by an increase at lower temperatures. On the adiabatic compressibility curve (Fig. 14) a small peak is formed at 56°K. With decreasing temperature, the compressibility decreases to a minimum at 44°K. Figure 15 shows the temperature variation of the ultrasonic attenuations α_l and α_t. The attenuations exhibit prominent peaks at 44°K, i.e., at the temperature where the elastic moduli (Fig. 13) and the adiabatic compressibility (Fig. 14) are at their minima. The behavior of the elastic moduli, adiabatic compressibility, and ultrasonic attenuations in this temperature range indicates the presence of a complex transition mechanism. The peak in the compressibility at 56°K is apparently related to the change in the antiferromagnetic structure of erbium, as manifested by various physical properties quoted before. But in contrast to other properties, the elastic and anelastic ones emphasize the probable occurrence of a first-order transition which is a consequence of the magnetic phase change at 56°K. With decreasing temperature, the elastic moduli and ultrasonic attenuations show an anomalous behavior at about 20°K. It is apparently connected with the transition from the antiferromagnetic to the ferromagnetic state. The limiting Debye temperature Θ_D in the ferromagnetic range (Fig. 14) is 192°K, as compared with 134°K deduced from specific-heat measurements.[11]

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