SALA-K 73-0237

Elastic constants of holmium between 78 and 300 K*

K. Salama, F. R. Brotzen, and P. L. Donoho
Rice University, Houston, Texas 77001
(Received 24 July 1972)

The adiabatic elastic constants of holmium were determined in the temperature range from 78 to 300 K, using high-purity single crystals. The constants were obtained from the ultrasonic-wave velocities (20 MHz) measured by the pulse-superposition method. The values of the constants at room temperature in units of 10^{11} dyn/cm^2 are $c_{33}=8.015$, $c_{44}=2.592$, $c_{11}=7.612$, $c_{12}=2.600$, and $c_{13}=2.072$. Using these values, the Debye temperature was computed to be 181 K. The sound velocities tend to vary with temperature in an anomalous fashion near the Néel temperature ($T_N=131$ K). Attenuation and sound-velocity measurements near T_N permit an estimate of the relaxation time for spin fluctuations, which was found to be 3×10^{-10} sec.

INTRODUCTION

Like most other heavy rare-earth metals, holmium changes its magnetic configuration as it is cooled from the paramagnetic state. At the Néel temperature ($T_N=131$ K), the paramagnetic state gives way to a helimagnetic arrangement which, upon further cooling, changes into a ferromagnetic structure at the Curie temperature ($T_C=20$ K). Neutron-diffraction studies[1,2] revealed that the magnetic components on the basal plane of the hexagonal crystal structure retain their helical configuration down to the lowest temperatures studied, while a ferromagnetic component along the c axis exists below T_C. The elastic properties are strongly affected by these magnetic transitions, as was shown by Rosen[3] who observed anomalies in the isotropic elastic moduli of holmium near these transitions.

Investigations of the elastic constants of heavy rare-earth metals had been limited to dysprosium[4] and gadolinium,[5] and a complete set of these constants for terbium has become available only recently.[6] Knowledge of the elastic properties of the rare earths is necessary not only for an analysis of the interesting magnetoelastic behavior of these elements but also for many of their technological applications.

SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

Single crystals of holmium were acquired from Metals Research Ltd., Cambridge, England, in the form of cylinders about 6 mm in diameter. The crystals were spark cut to a length of about 6 mm and subsequently electropolished so that the faces were parallel within less than 1°. Three samples were required for this investigation: (i) a crystal having two parallel surfaces normal to the c axis (=[0001]), (ii) a crystal having two parallel surfaces normal to the b axis (=[10$\bar{1}$0]), and (iii) a crystal having two parallel surfaces at 45° between the c and b planes, i.e., (0001) and (10$\bar{1}$0), respectively. The samples were electropolished to remove surface layers, and their orientation was checked by means Laue back-reflection patterns to fall within 2° of the desired directions.

Measurements of the sound velocities were carried out by the pulse-superposition method originally described by McSkimin.[7] Details of the method used in this investigation are given in Ref. 6. The relationship between different wave velocities and the elastic constants is given in Table I. For the calculation of the elastic constants a density of 8.803 g/cm^3 was used,[8] which was not corrected for thermal expansion.

RESULTS AND DISCUSSION

A compilation of the elastic constants of holmium is given in Table II. The constants c_{33}, c_{44}, and c_{11} were determined directly from the sound velocities v_1, v_2, and v_3, in accordance with Table I. c_{12} was obtained from the measurements of v_4 and the values of c_{11}. The attenuation of shear waves propagating in the [10$\bar{1}$0] was so high at temperatures below T_N that sufficiently strong echoes became unobservable and v_4 could not be determined at low temperatures. Combination of v_{QL} and v_{QS} and use of c_{33}, c_{44}, and c_{11} yielded the values for c_{13}, as shown in relations (5) and (6) in Table I. Table II in-

TABLE I. Relations between measured sound velocities and elastic constants.

Velocity	Crystal axis	Displacement direction	Relation
(1) v_1	[0001]	[0001]	$\rho v_1^2=c_{33}$
(2) v_2	[0001]	Any direction in the (0001)	$\rho v_2^2=c_{44}$
(3) v_3	[10$\bar{1}$0]	[10$\bar{1}$0]	$\rho v_3^2=c_{11}$
(4) v_4	[10$\bar{1}$0]	[$\bar{1}$2$\bar{1}$0]	$\rho v_4^2=c_{66}=\frac{1}{2}(c_{11}-c_{12})$
(5) v_{QL}	Quasilongitudinal along an axis 45° between [0001] and [10$\bar{1}$0]		$\rho v_{QL}^2=\frac{1}{4}(c_{11}+c_{33}+2c_{44})+\frac{1}{2}[\frac{1}{4}(c_{11}-c_{33})^2+(c_{13}+c_{44})^2]^{1/2}$
(6) v_{QS}	Quasishear along an axis 45° between [0001] and [10$\bar{1}$0]		$\rho v_{QS}^2=\frac{1}{4}(c_{11}+c_{33}+2c_{44})-\frac{1}{2}[\frac{1}{4}(c_{11}-c_{33})^2+(c_{13}+c_{44})^2]^{1/2}$

Copyright © 1973 American Institute of Physics

AUG 6 1973

TABLE II. The elastic constants of holmium in units of 10^{11} dyn/cm^2 and the compressibilities in units of 10^{-11} cm^2/dyn.

Temperature (K)	c_{33} [a]	c_{44} [b]	c_{11} [c]	c_{12} [d]	c_{13} [e]	$K_{\|\|}$ [f]	$K_\perp$ [g]	K_V [h]
80	8.084	2.922	8.125		2.048			
90	8.033	2.885	8.081		2.052			
100	7.982	2.847	8.035		2.055			
110	7.930	2.809	7.993		2.060			
120	7.879	2.772	7.950	2.538	2.059	0.0859	0.0785	0.2429
125	7.852	2.754	7.942	2.580	2.123	0.0853	0.0778	0.2409
130	7.828	2.748	7.935	2.627	2.083	0.0854	0.0776	0.2416
135	8.056	2.746	7.922	2.654	2.076	0.0839	0.0781	0.2400
140	8.085	2.742	7.913	2.653	2.071	0.0836	0.0783	0.2400
150	8.107	2.734	7.893	2.649	2.067	0.0833	0.0785	0.2404
160	8.116	2.725	7.875	2.647	2.065	0.0832	0.0787	0.2406
170	8.118	2.716	7.857	2.643	2.063	0.0831	0.0789	0.2409
180	8.117	2.709	7.838	2.640	2.059	0.0831	0.0791	0.2413
190	8.112	2.700	7.817	2.635	2.057	0.0831	0.0793	0.2417
200	8.107	2.692	7.798	2.630	2.057	0.0830	0.0795	0.2420
210	8.101	2.684	7.780	2.628	2.056	0.0830	0.0797	0.2424
220	8.093	2.675	7.762	2.625	2.055	0.0830	0.0798	0.2427
230	8.085	2.668	7.742	2.622	2.053	0.0830	0.0800	0.2431
240	8.076	2.659	7.725	2.619	2.056	0.0830	0.0802	0.2437
250	8.067	2.650	7.705	2.615	2.056	0.0830	0.0804	0.2437
260	8.058	2.639	7.686	2.612	2.059	0.0830	0.0805	0.2440
270	8.048	2.627	7.668	2.610	2.062	0.0829	0.0807	0.2442
280	8.038	2.616	7.650	2.606	2.063	0.0829	0.0808	0.2446
290	8.027	2.604	7.631	2.603	2.063	0.0829	0.0810	0.2449
300	8.015	2.592	7.612	2.600	2.072	0.0828	0.0811	0.2451

[a] Using relation (1), Table I.
[b] Using relation (2), Table I.
[c] Using relations (5) and (6), Table I, and footnotes a and b.
[d] Using relation (4), Table I, and footnote c.
[e] Using relation (5), Table I, and footnotes a, b, c, and d.

[f] $K_{\|\|}=(c_{11}+c_{12}-2c_{13})\ [c_{33}(c_{11}+c_{12})-2c_{13}^2]^{-1}$.
[g] $K_\perp=(c_{33}-c_{13})\ [c_{33}(c_{11}+c_{12})-2c_{13}^2]^{-1}$.
[h] $K_V=K_{\|\|}+2K_\perp$.

cludes a tabulation of compressibilities of holmium, which were computed according to the formulas in the footnotes f, g, and h to Table II. The error in the constants whose values were obtained directly from measured sound velocities is estimated to be less than 0.5%, but may be as high as 3% in the case of the indirectly determined constants, such as c_{13}.

Thermal expansion and dimensional changes of the specimens associated with the magnetic transition have only a small effect on the numerical values of the elastic constants.[9] The changes introduced by neglecting these effects lie, therefore, within the experimental error.

The temperature dependence of the elastic constants of holmium are illustrated in Figs. 1–4. In the paramagnetic range, i.e., at $T > T_N = 131$ K, all constants except c_{13} exhibit the usual behavior of decreasing values as the temperature is raised. The constants undergo pronounced changes as T_N is approached. The change is

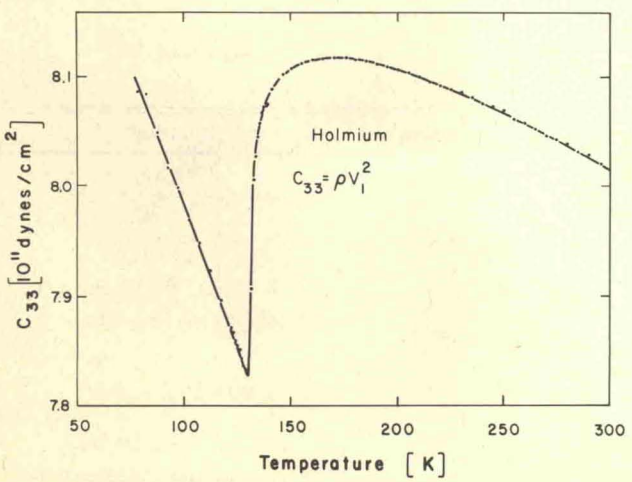


FIG. 1. Temperature dependence of the adiabatic elastic constant c_{33} in holmium.

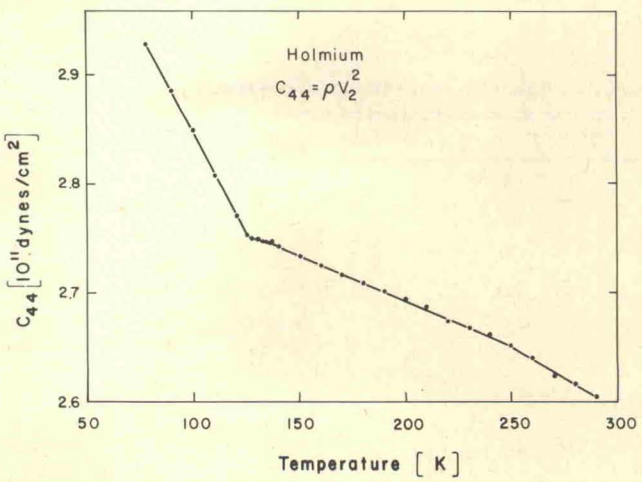


FIG. 2. Temperature dependence of the adiabatic elastic constant c_{44} in holmium.

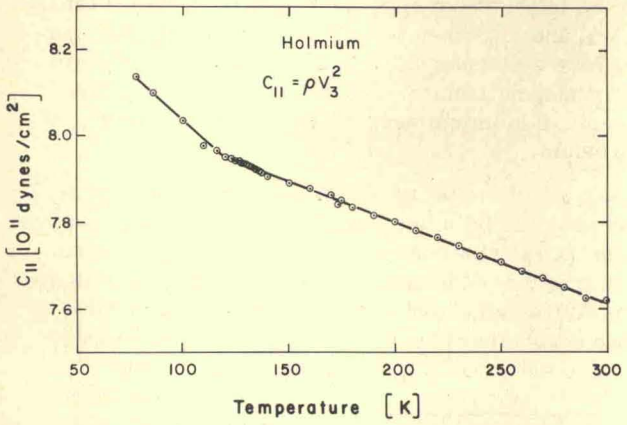


FIG. 3. Temperature dependence of the adiabatic elastic constant c_{11} in holmium.

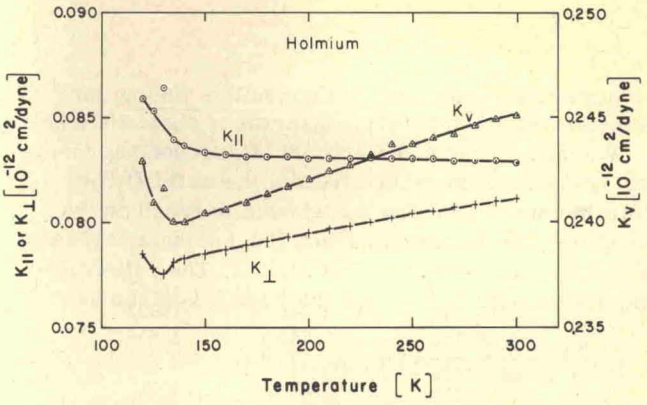


FIG. 5. Temperature dependence of the directional compressibilities $K_{\parallel}$ and $K_{\perp}$ and the volume compressibility K_V of holmium.

particularly evident in the case of c_{33}, Fig. 1, and resembles strongly the change in c_{33} near T_N for dysprosium[4] and terbium.[6] The steeper slope of c_{44} below T_N (Fig. 2) is also noted for this elastic constant in terbium and dysprosium. Comparison of the other elastic constants for holmium and terbium is hampered by the narrowness of the antiferromagnetic temperature range for terbium ($T_N = 229$ K and $T_C = 221$ K), which causes an overlap of the effects of the two transitions. Such comparisons are possible, however, for holmium and dysprosium, and similarities in the temperature dependence of c_{11} (Fig. 3) and c_{13} (Fig. 4) of these two metals can be detected. In the case of c_{12} (Fig. 4), the impossibility of obtaining meaningful data for holmium in the helimagnetic range precludes comparisons with other elements.

The compressibilities as functions of the temperature are shown in Fig. 5. They were calculated from the elastic constants given in Table II. It is noteworthy that the changes of the compressibilities of holmium at T_N are rather small compared to those observed in terbium.[6] This difference can be attributed to a large variation of the compressibilities near the Curie temperature and a relatively small one near the Néel temperature. This behavior was also observed in the case of dysprosium by Rosen and Klimker.[4] The large variation in holmium at T_C was not observed in the work reported here, since $T_C = 20$ K, and the measurements given here extended only to 78 K. In terbium, however, the helimagnetic phase extends over a temperature range of only 8°, so that the effects of the two phase transitions on the compressibilities clearly overlap.

Knowledge of the elastic constants makes possible the calculation of the Debye temperature. By the method of direct integration for hexagonal crystals,[10] using the elastic constants at 300 K listed in Table II, the Debye temperature for holmium was found to be 181 K, which agrees with the value of 184 K computed by Rosen[11] from the moduli of polycrystalline holmium. Both these values are, however, higher than the calorimetrical result of 161 K.[12]

Lüthi *et al.*[13] observed that in holmium, as well as in gadolinium, terbium, and dysprosium, the relative change in the longitudinal sound velocity in the c direction, $\Delta v_l/v_l$, near the magnetic transition is a logarithmic function of the reduced temperature, $\epsilon = (T - T_N)/$

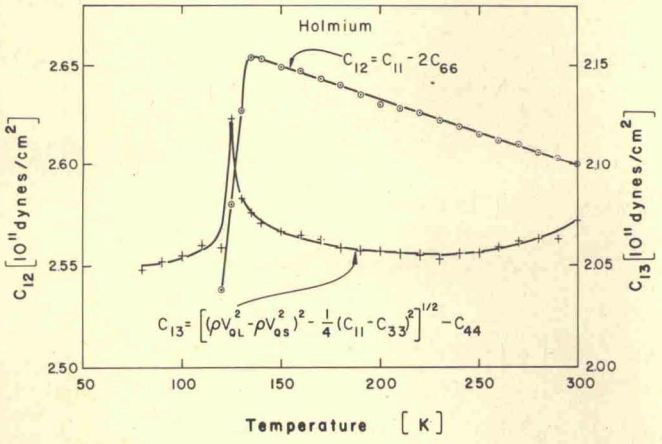


FIG. 4. Temperature dependence of the adiabatic elastic constants c_{12} and c_{13} in holmium.

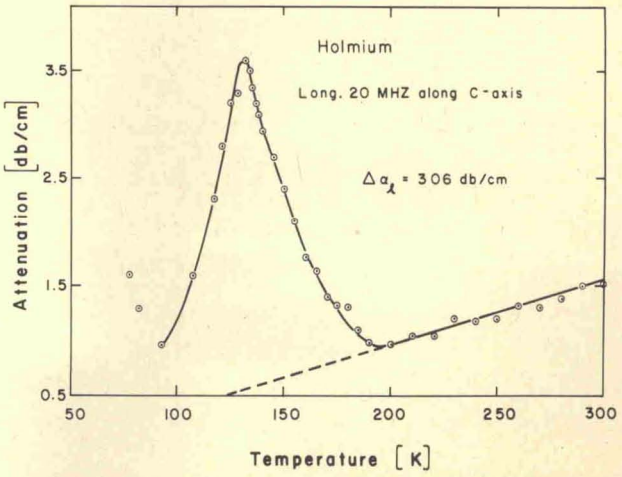


FIG. 6. Temperature dependence of the ultrasonic attenuation in holmium single crystals; longitudinal waves at 20 MHz propagating along the c axis.

T_N, i.e.,

$$\Delta v_1/v_1 \sim -\ln\epsilon. \tag{1}$$

The present investigation confirmed this finding for holmium over a temperature interval of about 30° above T_N. Velocity changes and critical attenuation near magnetic transitions have been treated theoretically by several authors.[14,15] The model used is based on the spin-phonon interaction in which the dominant part is the volume-magnetostrictive coupling. The relaxation time characterizing the spin fluctuation is given by

$$\tau = \frac{v_1}{\omega^2}\frac{\Delta\alpha_l}{(-\Delta v_1/v_1)}. \tag{2}$$

In Eq. (2), $\Delta v_1/v_1$ is the relative change in the longitudinal sound velocity in the c direction, measured at T_N. $\Delta\alpha_l$ denotes the attenuation coefficient at T_N after subtracting the background attenuation obtained by extrapolation from the truly paramagnetic state (Fig. 6) and was found to be 3.06 dB/cm. The value for $\Delta v_1/v_1$ at T_N was obtained by assuming that v_1 increased linearly as the temperature was lowered and was found to be 2.16×10^{-2}. Equation (2) then yields a relaxation time $\tau \cong 3\times10^{-10}$ sec, or about one-half of the value found for terbium.[6] This is to be compared with 2.6×10^{-10} sec obtained by Lüthi *et al.*[12] in holmium.

CONCLUSIONS

The elastic constants of holmium in the paramagnetic state, except c_{13}, have the normal tendency to rise as the temperature is lowered. Since the temperature range of this investigation did not include the Curie point ($T_C = 20$ K), anomalies in the temperature dependence of the elastic constants refer only to the Néel point ($T_N = 131$ K). The constant c_{33} forms a cusplike minimum at T_N, while c_{13} has a sharp maximum at this magnetic transition. c_{44} and c_{11}, when plotted as functions of temperature, have a steeper slope in the helimagnetic than in the paramagnetic state. The general behavior of the constants of holmium near T_N is comparable to that of dysprosium.

An analysis of the sound velocities and attenuation of sound waves in holmium near T_N yields a relaxation time for the spin fluctuations of 3×10^{-10} sec. This is about one-half of the value computed for terbium.[6] The Debye temperature calculated from the room-temperature elastic constants of holmium is 181 K, approximately 20° above the value determined calorimetrically.[12]

*Research carried out under Advanced Research Projects Agency contract.

[1]W. C. Koehler, H. R. Child, E. O. Wollan, and J. Cable, J. Appl. Phys. **34**, 1355 (1963).
[2]W. C. Koehler, J. Appl. Phys. **36**, 1078 (1965).
[3]M. Rosen, Phys. Rev. **174**, 504 (1968).
[4]M. Rosen and H. Klimker, Phys. Rev. B **1**, 3748 (1970).
[5]M. Long, A. R. Wazzan, and R. Stern, Phys. Rev. **178**, 775 (1969).
[6]K. Salama, F. R. Brotzen, and P. L. Donoho, J. Appl. Phys. **43**, 3254 (1972).
[7]H. J. McSkimin, J. Acoust. Soc. Am. **33**, 606 (1961).
[8]C. S. Barrett and T. B. Massalski, *Structure of Metals* (McGraw-Hill, New York, 1966), p. 631.
[9]J. J. Rhyne, S. Legvold, and E. T. Rodine, Phys. Rev. **154**, 266 (1967).
[10]G. A. Alers, *Physical Acoutics*, edited by W. P. Mason (Academic, New York, 1965), Vol. III B, p. 16.
[11]M. Rosen, Phys. Rev. Lett. **19**, 695 (1967).
[12]K. A. Gschneider, Jr., *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 370.
[13]B. Lüthi, T. J. Moran, and R. J. Pollina, J. Phys. Chem. Solids **31**, 1741 (1970).
[14]K. Kawasaki and A. Ikushima, Phys. Rev. B **1**, 3143 (1970).
[15]H. S. Bennett, Phys. Rev. **185**, 801 (1969).