Magneto-Elastic Interactions in Gadolinium*

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(Received 19 August 1968)

The effect of the change in easy direction of magnetization on the elastic constants c_{33} and c_{44} has been measured in single-crystal gadolinium by means of a pulse-echo technique. One of the constants c_{33} exhibited a sharp decrease of about 2% over the temperature range -37 to -51°C after which it slowly returned to its normal, monotonic increasing behavior with decreasing temperature. Magnetic fields of up to 8 kOe, either parallel or perpendicular to the unique axis of the hexagonal crystal, were applied to the sample. These decreased the absolute magnitude of the change in c_{33}. It is thought that the acoustic wave is coupled to the spin structure by volume magnetostriction.

I. INTRODUCTION

In recent years, considerable interest has been shown in the study of the magnetic structures of the lanthanide series or the rare-earth elements. Many of these elements, including gadolinium, assume magnetic configurations which depart from simple ferromagnetic alignment below their Curie temperature. In particular, gadolinium is a simple ferromagnet in the temperature range from about -37 to 17°C, its Curie point. Below -37°C the direction of easy magnetization is no longer aligned along the unique axis of the hexagonal crystal but may lie anywhere on a cone of directions about this axis with equal configurational energy. The cone half-angle has been measured by several investigators[1–3] using neutron diffraction techniques. Cable and Wollan found that below -41°C it rapidly increased, until near -93°C, it reached a maximum of 65° and then decreased to 32° at lower temperatures.

Callen and Callen,[4] citing the experimental data of Coleman,[5] point out that near -37°C the magnetostriction coefficient of Gd suffers a change of sign and have derived a theory of the temperature dependence of this coefficient. It is convenient to follow the notation of Cooper[6] who has divided the total Hamiltonian for gadolinium into three parts,

$$\mathcal{H}=\mathcal{H}_{\mathrm{EX}}+\mathcal{H}_{\mathrm{CF}}+\mathcal{H}_{\mathrm{MS}}, \tag{1}$$

where these terms represent the exchange, crystal-field, and magnetostrictive contributions, respectively. The exchange term

$$\mathcal{H}_{\mathrm{EX}}=-\sum_{i\neq j} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j \tag{2}$$

comes from the usual Ruderman-Kittel interaction.[7–9]

The crystal-field term is given by

$$\mathcal{H}_{\mathrm{CF}}=\sum_i P_2 S_{i\zeta}^2+P_4 S_{i\zeta}^4+P_6 S_{i\zeta}^6 +P_6^6[Y_6^6(\mathbf{S}_i)+Y_6^{-6}(\mathbf{S}_i)], \tag{3}$$

where the P_j are Lagrange polynomials, $S_{i\zeta}$ is the projection of the total magnetic moment along the unique axis of the hexagonal crystal, i.e., $S_{i\zeta}=\bar{S}\cos\theta$, where $\bar{S}$ is the equilibrium spin value per ion at a given temperature. The $Y_k^l(\mathbf{S}_i)$ are operator equivalents of spherical harmonics.[10]

The magnetostrictive term has been given by Callen and Callen.[11]

$$\mathcal{H}_{\mathrm{MS}}=\mathcal{H}_E+\mathcal{H}_M, \tag{4}$$

where $\mathcal{H}_E$ is the contribution to the elastic energy due to homogeneous strain components and $\mathcal{H}_M$ is due to the magneto-elastic interaction.

$$\mathcal{H}_E=\tfrac{1}{2}c_{11}^{\alpha}(\epsilon^{\alpha,1})^2+c_{12}^{\alpha}\epsilon^{\alpha,1}\epsilon^{\alpha,2}+\tfrac{1}{2}c_{22}^{\alpha}(\epsilon^{\alpha,2})^2 +\tfrac{1}{2}c^{\gamma}[(\epsilon_1^{\gamma})^2+(\epsilon_2^{\gamma})^2]+\tfrac{1}{2}c^{\epsilon}[(\epsilon_1^{\epsilon})^2+(\epsilon_2^{\epsilon})^2]. \tag{5}$$

Here, the symmetry strains are given in terms of the Cartesian strains by

$$\begin{aligned}
\epsilon^{\alpha,1}&=\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz},\\
\epsilon^{\alpha,2}&=\tfrac{1}{2}(\sqrt{3})[\epsilon_{zz}-\tfrac{1}{3}\epsilon^{\alpha,1}],\\
\epsilon_1^{\gamma}&=\tfrac{1}{2}[\epsilon_{xx}-\epsilon_{yy}],\\
\epsilon_2^{\gamma}&=\epsilon_{xy},\\
\epsilon_1^{\epsilon}&=\epsilon_{yx},\\
\epsilon_2^{\epsilon}&=\epsilon_{xz},
\end{aligned} \tag{6}$$

and where the symmetry elastic constants are given in terms of the conventional Cartesian elastic constants by

$$\begin{aligned}
c_{11}^{\alpha}&=\tfrac{1}{9}[2c_{11}+2c_{12}+4c_{13}+c_{33}],\\
c_{12}^{\alpha}&=\tfrac{2}{3}(\sqrt{3})[-c_{11}-c_{12}+c_{13}+c_{33}],\\
c_{22}^{\alpha}&=\tfrac{2}{3}c_{11}+\tfrac{2}{3}c_{12}-(8/3)c_{13}+\tfrac{4}{3}c_{33},\\
c^{\gamma}&=2[c_{11}-c_{12}],\\
c^{\epsilon}&=4c_{11}.
\end{aligned} \tag{7}$$

* Work supported in part by U. S. Office of Naval Research, Acoustics Program and in part by the University of California, Los Angeles Space Science Center.

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[11] See Ref. 4.

One should note that $\mathcal{H}_E$ is essentially a classical additive term and includes only homogeneous strain components ϵ_{xx}, ϵ_{yy}, ϵ_{zz}, ϵ_{xy}, ϵ_{yz}, and ϵ_{zx}. The nonhomogeneous strains or phonon modes are not included. The shear strains are defined by

$$\epsilon_{xy}=\frac{1}{2}\left[\left(\frac{\partial u_y}{\partial x}\right)+\left(\frac{\partial u_x}{\partial y}\right)\right]. \tag{8}$$

The one-ion magnetoelastic term in the Hamiltonian for the ith ion is

$$\begin{aligned}\mathcal{H}_M{}^{(i)}=&-\tilde{B}_{12}{}^{\alpha}\epsilon^{\alpha,1}\left(\frac{\sqrt{3}}{2}\right)[(S_i{}^z)^2-\tfrac{1}{3}S(S+1)]\\&-\tilde{B}_{22}{}^{\alpha}\epsilon^{\alpha,2}\left(\frac{\sqrt{3}}{2}\right)[(S_i{}^z)^2-\tfrac{1}{3}S(S+1)]\\&-\tilde{B}^{\gamma}\{\epsilon_1\gamma\tfrac{1}{2}[(S_i{}^x)^2-(S_i{}^y)^2]+\epsilon_2\gamma\tfrac{1}{2}[S_i{}^xS_i{}^y+S_i{}^yS_i{}^x]\}\\&-\tilde{B}^{\epsilon}\{\epsilon_1\epsilon\tfrac{1}{2}[S_i{}^yS_i{}^z+S_i{}^zS_i{}^x]+\epsilon_2\tfrac{1}{2}[S_i{}^xS_i{}^z+S_i{}^zS_i{}^x]\},\end{aligned} \tag{9}$$

where the $\tilde{B}_{jj'}{}^{\zeta}$ are phenomenological magneto-elastic coupling constants. This term considers explicitly only the lowest-order contributions: those linear in strain components and of zeroth and second order in spin. The linear spin components have not been included because they are not symmetric under time reversal and thus do not exist except as linear functions of magnetic field. There are six spin operators of zeroth and second order including $(S^x)^2+(S^y)^2+(S^z)^2$, $[(S^z)^2-\frac{1}{3}S(S+1)]$, $[(S^x)^2-(S^y)^2]$, $\frac{1}{2}[S^xS^y+S^yS^x]$, $\frac{1}{2}[S^yS^z+S^zS^y]$, and $\frac{1}{2}[S^xS^z+S^zS^x]$. The antisymmetric products $[S^xS^y-S^yS^x]=iS^z$ are of first order because of the spin commutation rules. The magnetoelastic coupling constants $\tilde{B}_{jj'}{}^{\zeta}$ contain both the temperature and field dependence. Subscripts j and j' follow a similar convention to that of the symmetrized elastic constants, and the superscripts refer to the order of the spin operators associated with it. The complex behavior of the coupling constants has been more fully treated by Callen and Callen[11] and will not be discussed here.

The elastic constants of a material are calculated by obtaining the second derivatives of the total energy with respect to strain.

$$c_{ij}=\frac{\partial E}{\partial\epsilon_i\partial\epsilon_j}, \tag{10}$$

where i and j are the directions of propagation and displacement, respectively, of an acoustic wave in the sample. Thus, elastic constants would respond to changes in magnetic structure as reflected by changes in the magnetostrictive terms in the Hamiltonian. Since it is those terms which are quadratic in strain which survive second differentiation and, therefore, contribute to the elastic constants, the matrix elements of $\mathcal{H}_M$ must be calculated as second-order perturbations to the total energy. This work is currently being undertaken.

II. EQUIPMENT AND SPECIMEN

The method used to determine sound velocities is that originally suggested by Williams and Lamb.[12]

A continuous rf wave is gated and introduced into the sample by means of a quartz transducer. Another transducer, placed parallel to the first on an opposite face, is used to monitor the pulse and its subsequent reflections. By lengthening the duration of the input pulse it may be made to overlap its own reflection as seen at the receiving transducer. The carrier frequency may be then adjusted so as to obtain an antiresonance. This is displayed as an amplitude minimum on an oscilloscope, and the corresponding antiresonant frequency is read from a digital frequency counter. With the knowledge of this frequency and the number of the harmonic which it represents, one may determine a time of flight and the propagation velocity.

A block diagram of the experimental equipment is shown in Fig. 1. The 5-MHz output from a Hewlett-Packard model 650A tunable continuous wave oscillator was buffered by a Keithley 121R wide-band amplifier and the resultant signal then gated by a Saunders Associates DS13 switch and driver. The gate was driven by a Hewlett-Packard model 214A pulse generator which also triggered the horizontal synchronization of the oscilloscope.

The pulsed cw output from the gate was then amplified by a General Radio Company type 1233-A power amplifier and introduced into the sample by either an X-cut (longitudinal wave) or an AC-cut (transverse wave) quartz transducer.

The signal from the receiving transducer was amplified by a Keithley 104 wide-band amplifier and, after passing through a tuned filter to eliminate noise, was displayed on the vertical axis of an oscilloscope. Precise measurements of the antiresonant frequency were made with a Hewlett-Packard model 5253B digital frequency counter.

The specimen was 99.999% pure gadolinium purchased from Alpha Inorganic in the form of a single crystal grown in random orientation. It was heat treated three times before the final measurements. An initial treatment was 5 h at 700°C then 1 h at 500°C. The sample was allowed to cool overnight to room temperature. A series of magnetic measurements were made and it was found that it would be necessary to recut the specimen to avoid undesirable effects due to sample geometry. The heat treatment before and after recutting was at 700°C for 4 h whereupon it was slowly cooled to room temperature overnight.

The final specimen was a right circular cylinder of $\frac{3}{16}$ in. diam with its end faces cut perpendicular to the

[12] J. Williams and J. Lamb, J. Acoust. Soc. Am. **30**, 308 (1958).

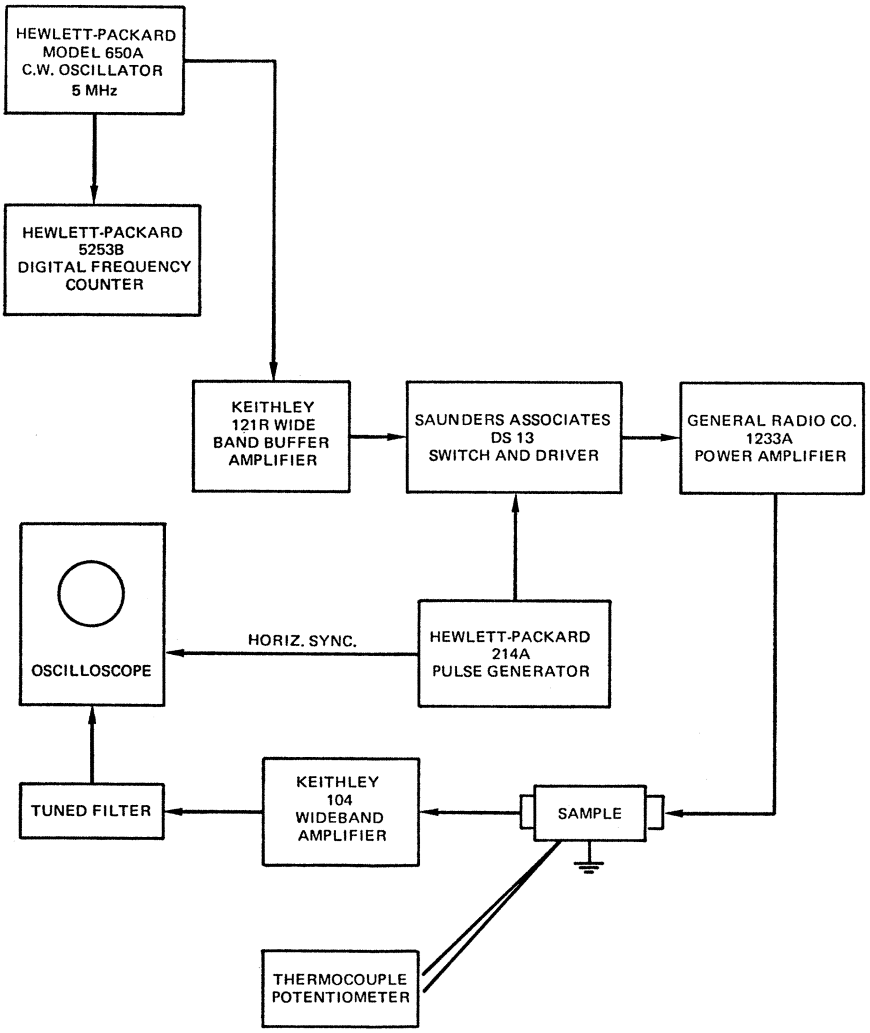

FIG. 1. Schematic circuit diagram.

unique axis by a Metals Research Ltd., Servomet spark cutter. The orientation of the unique axis was determined on a General Electric XRD-5 x-ray spectrometer to within $\pm 1°$. The length of the specimen, measured to within one part in 10^4, was 0.1324 in.

One-eighth-in.-diam X-cut or AC-cut quartz transducers with a resonant frequency of 5 MHz and an overtone polish were wrung onto the parallel faces of the specimen using a thin film of bonding material. Three types of bonds were used. Though Dow Corning 276-V9 and Nonac stopcock grease were used on early runs, Vac Seal, a silicone vacuum sealant made by the Space Environment Laboratories, Inc., Boulder, Colo., was the most dependable. The Vac Seal was cured 2 h at 250°C after wringing on.

Finally, the sample and transducers were mounted in a rectangular frame which subsequently was placed in the magnetic field produced by a Varian 15-in. low-impedance magnet. Temperature was controlled automatically with an accuracy of ± 0.1°C.

III. RESULTS

A description of the formal procedures involved in the calculation of elastic constants has been given by Williams and Lamb.[12] From plots of these data we estimate the Curie temperature of gadolinium to be 17 ± 1°C and the temperature at which the ferromagnetic spin alignment breaks away from the unique axis to be -37 ± 1°C.

Figure 2 shows the elastic constant c_{33} versus temperature. The lower plot is that with no applied field and the upper curve shows c_{33} in the presence of an 8-kOe field in the basal plane (added to show the general extent of the interaction). It should be remembered that c_{33} is measured by propagating a longitudinal wave along the unique axis of the hexagonal crystal. The cusp at 17°C points out the Curie temperature.

A similar plot is shown in Fig. 3 for the elastic constant c_{44}. c_{44} is measured by propagating a transverse wave along the unique axis of the hexagonal crystal. The displacement direction is perpendicular to this

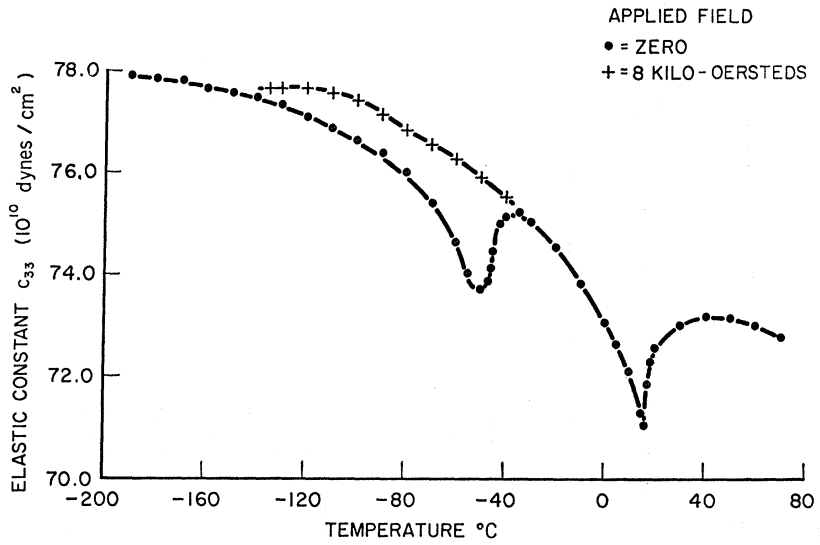

FIG. 2. Elastic constant c_{33} versus temperature. A plot of the 8-kOe data has been added to indicate the range of the magnetic interaction.

axis but otherwise may be arbitrarily oriented. There are only slight perturbations in the vicinity of the Curie point and at lower temperatures. The lack of an appreciable effect in c_{44} indicates that a volume-dependent mechanism such as magnetostriction might be responsible for coupling.

Subsequently, an examination of the anomaly at −37°C in the presence of a magnetic field was undertaken. In Fig. 4, we have plotted c_{33} versus temperature in the vicinity of the minimum for several values of magnetic field applied parallel to the basal plane. It should be noted that the position of the minimum shifts to lower and lower temperatures with increasing field.

Basal-plane anisotropy was checked on a steep portion of the curve (i.e., 3 kOe and −52.4°C) in order to magnify any effects. The vertical scale of Fig. 5 has been enlarged to 1.5 times that of Fig. 4. One cannot clearly pick out any definite pattern of anisotropy in these data though sixfold symmetry might be expected. The basal-plane field measurements of Fig. 4 were taken with the magnet oriented at 30° arbitrary relative angle, as indicated in Fig. 5.

The final measurement was c_{33} versus temperature in the presence of a magnetic field applied along the unique axis. In Fig. 6, we find no temperature displacement of the minimum with increasing field as before. Fields as high as 10 kOe were applied, but the results lay so close to the 8-kOe plot that it was not instructive to show it. The estimated scatter in measurements of velocity is 0.2%.

During the course of this experiment it was brought to our attention that the elastic constants of gadolinium had been measured by Fisher and Dever.[13] They saw

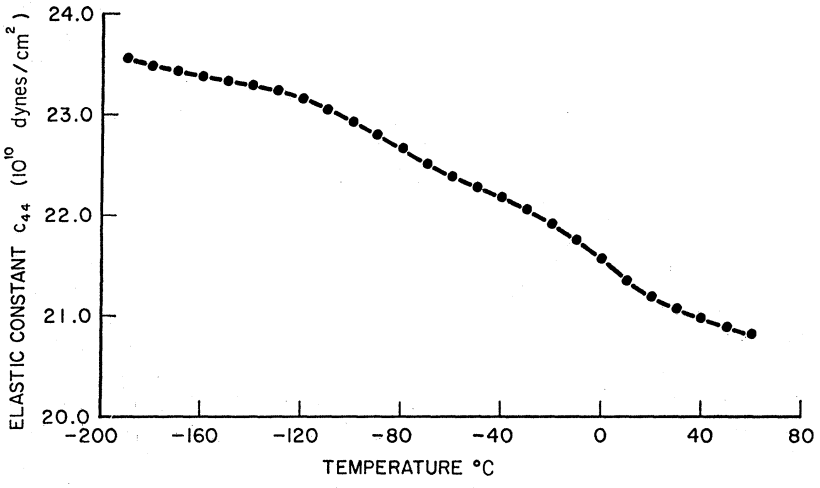

FIG. 3. Elastic constant c_{44} versus temperature.

[13] E. S. Fisher and D. Dever, in Proceedings of an Oak Ridge Conference on Rare Earths, 1968, p. 522–533 (unpublished).

the beginnings of the anomaly in c_{33} which we were examining but were unable to study it in detail.

IV. DISCUSSION

Two elastic constants of gadolinium have been measured over a moderate temperature range. One has been examined more closely under the presence of a magnetic field. The shear wave elastic constant c_{44} shows no appreciable fluctuations from generally monotonic decreasing behavior over the temperature range

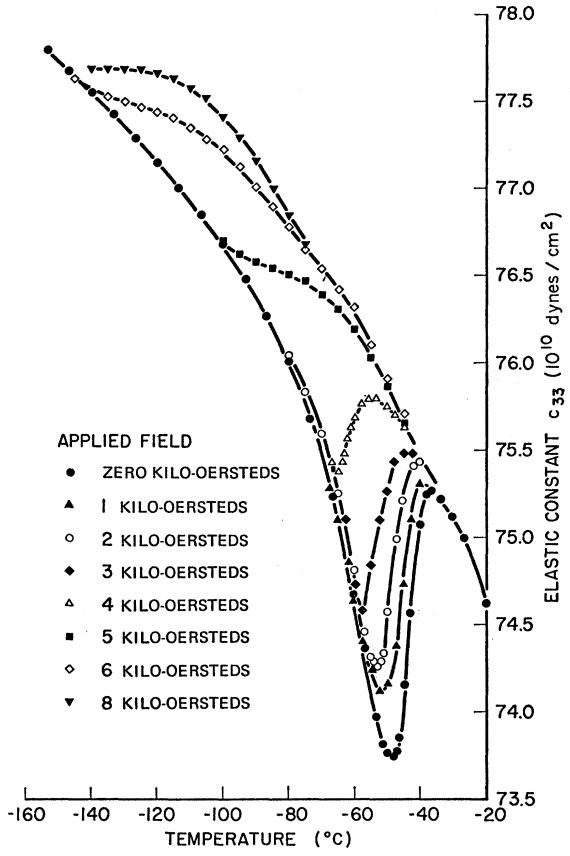

FIG. 4. Elastic constant c_{33} versus temperature plotted for various values of magnetic field applied in the basal plane.

from −190 to 60°C. Juxtaposed the longitudinal wave elastic constant c_{33} shows changes of about 2% which mark the Curie point at 17°C and an anomalous region from −37°C to approximately −160°C. The presence of the effect in the longitudinal case is evidence that a volume-dependent interaction may be responsible, and the extremely close temperature correlation with the change in magnetic structure indicates a magnetostrictive effect.

The experiments with an applied magnetic field confirm the fact that the dip is indeed due to a magnetic

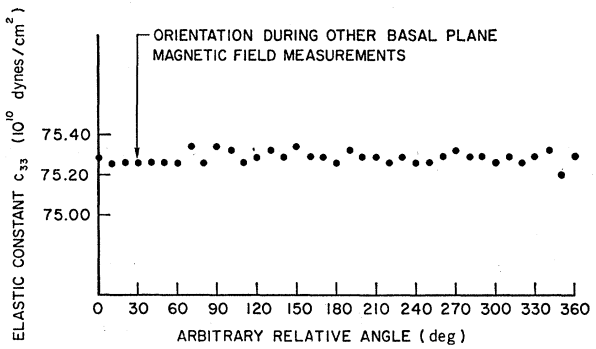

FIG. 5. Elastic constant c_{33} versus arbitrary relative angle within the basal plane at a temperature of −52.4°C and a 3-kOe field.

interaction and must then be directly associated with the change in allowed directions of easy magnetization.

These results strongly suggest that magneto-elastic terms in the Hamiltonian of gadolinium and possible of other rare earths play a major role in determining macroscopic properties. In particular, it is suggested that any band calculation which might be attempted

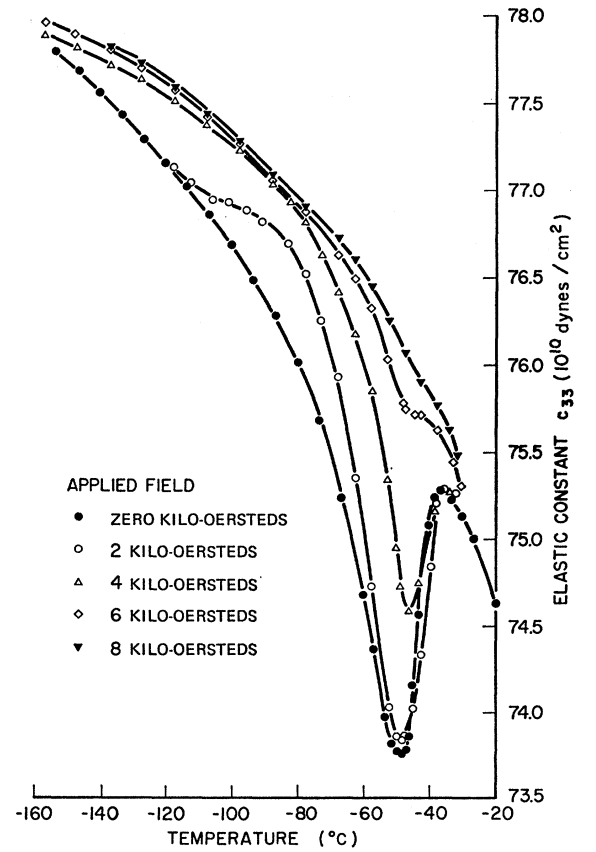

FIG. 6. Elastic constant c_{33} versus temperature plotted for various values of magnetic field applied along the unique axis of the crystal.

for these metals without considering such terms would be ignoring important contributions.

As has been mentioned earlier, the change in the direction of easy magnetization occurs coincidently in temperature with a change in sign of the magnetostriction constant λ^γ. This constant has been given by Callen and Callen[14] as

$$\lambda^\gamma=\left(\frac{1}{c^\gamma}\right)\sum_f \tilde{B}^\gamma(f)\mathfrak{L}_f(T,H)+\left(\frac{1}{c^\gamma}\right)\sum_{(f,g)}\tilde{D}^\gamma(f,g)\mathfrak{L}_{fg}(T,H). \quad (11)$$

Here, $\mathfrak{L}_f(T,H)$ and $\mathfrak{L}_{fg}(T,H)$ are the correlation functions containing the temperature and field dependence of the magnetostriction constants, and $\tilde{D}^\gamma(f,g)$ is a two-ion magneto-elastic constant. In this discussion we will consider only one-ion terms, though two-ion terms might also be considered as well.

If a longitudinal wave is propagated along the unique axis in order to measure c_{33}, the only strain induced (to first order) is ϵ_{zz}. Thus, on examining the magneto-elastic Hamiltonian [given in Eq. (9)] for terms that might influence the elastic constants we find that

$$\tilde{B}_{22}{}^\alpha\epsilon^{\alpha,2}\tfrac{1}{2}(\sqrt{3})[(S_i{}^z)^2-\tfrac{1}{3}S(S+1)], \quad (12)$$

as well as the first term in $\mathfrak{IC}_M$ representing uniform volume dilitation could be considered. It is speculated that the $\tilde{B}_{22}{}^\alpha$ term represents the important contribution to c_{33}.

If the energy contribution due to magneto-elastic terms is considered a second-order perturbation to the exchange Hamiltonian, then $\mathfrak{IC}_M$ matrix elements will include terms proportional to

$$\{\tilde{B}_{22}{}^\alpha\epsilon^{\alpha,2}\tfrac{1}{2}(\sqrt{3})[(S_i{}^z)^2-\tfrac{1}{3}S(S+1)]\}^2. \quad (13)$$

The elastic constant $c_{33}=\partial^2E/\partial\epsilon_{zz}{}^2$ will then be proportional to

$$\{\tilde{B}_{22}{}^\alpha[(S_i{}^z)^2-\tfrac{1}{3}S(S+1)]\}^2 \quad (14)$$

and, therefore, strongly dependent on the size of $S_i{}^z$.

If we assume that the behavior of λ^γ is the driving mechanism for the anomaly and seek terms in $\mathfrak{IC}_M$ with coefficients having a λ^γ dependence, we find such a dependence in

$$\tilde{B}^\gamma\epsilon_2{}^\gamma\tfrac{1}{2}(S_i{}^xS_i{}^y+S_i{}^yS_i{}^x). \quad (15)$$

The $\tilde{B}^\gamma$ term would be the major contributor to c_{44}. Since the effect seen in c_{44} is small, we must assume the same of $\tilde{B}^\gamma$.

We finally suggest that these two terms

$$\tilde{B}_{22}\epsilon^{\alpha,2}\tfrac{1}{2}(\sqrt{3})[(S_i{}^z)^2-\tfrac{1}{3}S(S+1)] \quad (16)$$

and

$$\tilde{B}^\gamma\epsilon_2{}^\gamma\tfrac{1}{2}[S_i{}^xS_i{}^y+S_i{}^yS_i{}^x] \quad (17)$$

are strongly coupled by the spin components through the minimization of energy with respect to magnetic moment orientation.

Further experimental and theoretical work is in progress to determine the nature of these types of interactions in gadolinium and other rare earths.

ACKNOWLEDGMENTS

The authors wish to thank Professor Phillip Pincus, Professor W. Gilbert Clark, and Dr. Bernard Cooper for their assistance and valuable comments.

[14] See Ref. 4.