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MAGNETOELASTIC COUPLING IN PARAMAGNETIC DYSPROSIUM

by

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Abstract

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The magnetic field dependence of the velocities of 20 MHz longitudinal acoustic waves has been measured in the temperature range 180K-300K for fields from 0-17.65 kOe. By choosing the propagation axis to be the b- or c-axis, the field dependence of the elastic constants C_{11} and C_{33} is obtainable. Corrections for the magnetostrictive effects, necessary for a consistent treatment of the problem, are included in the analysis. The resulting values of $\Delta C_{11}(\vec{H}, T)$ and $\Delta C_{33}(\vec{H}, T)$, in conjunction with the theoretical work of Southern and Goodings, allows calculation of five of the magnetoelastic constants of Dysprosium in the paramagnetic region. The temperature dependence of these magnetoelastic constants is examined, in the light of the theory, and is compared to that temperature dependence of the same five magnetoelastic constants, of Terbium, found by Salama, Melcher, and Donoho.

To Jonita

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I. Introduction

MOTIVATION

This thesis reports on an investigation of the magnetoelastic properties of Dysprosium. In particular, the magnetic field dependence of the longitudinal elastic constants C_{11} and C_{33} was experimentally measured, in the paramagnetic region. Using a theory developed by Southern and Goodings,¹ the five magnetoelastic coupling constants appearing in the expressions for $\Delta C_{11}(H)$ and $\Delta C_{33}(H)$ were calculated from the experimental data.

MAGNETIC BEHAVIOR OF DYSPROSIUM

The ground state electronic configuration of Dy is $[\text{Xe}] 6s^2 4f^{10}$. In a solid, the two 6s electrons and one 4f electron are lost to the conduction band.² The 5s and 5p electrons have larger mean radii than the remaining 4f electrons, and they tend to shield the 4f electrons from their external environment, principally the crystal field.³ The crystal field perturbation of the free ion states is thus small, and the orbital angular momentum is not quenched. The spin-orbit interaction is stronger than the crystal field, so each ion can be characterized by its L, S, and J quantum numbers. Using Hund's rules, the ground state of Dy in a solid is then ${}^6\text{H}_{15/2}$ which corresponds to 10 Bohr magnetons per ion. The experimental saturation magnetization

agrees well, the measured value being 10.33 Bohr magnetons per ion.⁴ The small crystal field does, however, affect the magnetization by making it anisotropic. In Dy for example, the a-axis is the easy axis of magnetization and the c-axis is the hard axis.⁴

At low temperatures, the exchange interaction between ions induces magnetic ordering of the moments of the ions. In zero applied field, Dy undergoes a transition from paramagnetic to antiferromagnetic at the Neel point $T_N = 179\text{K}$.⁴ In this phase, the moments are constrained to lie in the basal plane. The moments in each plane perpendicular to the c-axis are parallel to each other, but the orientation of the moments changes from plane to plane. The angle between the moments in two adjacent planes is constant throughout the crystal, but is temperature dependent. Below the Curie point $T_C = 85\text{K}$, Dy is ferromagnetic, the a-axis being the easy axis.⁴

More relevant to this thesis is the fact that the magnetic 4f electrons can interact with deformations or stresses in the crystal. A well known example of these magnetoelastic interactions is the extremely large magnetostriction observed in rare earth metals, Dy in particular.⁵ This magnetostriction is several orders magnitude larger than that found in iron group elements. A closely related phenomenon is the anomalous temperature

dependence of the elastic constants of Dy, especially C_{11} and C_{33} .⁶ The expected behavior of the elastic constants would be a monotonic decrease with increasing temperature. The longitudinal elastic constants of Dy, C_{11} and C_{33} , have very pronounced dips at the Neel and Curie temperatures,⁶ indicating an anomalous "softening" of the crystal at these temperatures. This behavior is explained by the work of Clark *et al.*⁵ in which the zero field magnetostrictions of Dy were measured. Their data indicate that, at the transition temperatures, Dy experiences a dilation, thus reducing the interatomic distance and the elastic constants.

This thesis investigates another aspect of these magnetoelastic interactions, the dependence on magnitude and direction of applied magnetic field of the elastic constants of C_{11} and C_{33} of Dy in the paramagnetic region.

In the paramagnetic region, i.e., above 179K, Dy has a hexagonal close-packed crystal structure with a c/a ratio of 1.574, slightly smaller than the ideal $c/a = 1.633$.⁷ The independent elastic constants for Dy are therefore C_{11} , C_{33} , C_{44} , C_{12} , and C_{13} .⁸ The work reported here involved only C_{11} and C_{33} , both of which can be obtained from the relation $C = \rho v^2$ where ρ is the mass density, and v is the velocity of a longitudinal acoustic wave propagating perpendicular and parallel to the c -axis, respectively.

Data taken by Moran and Luthi⁹ on C_{33} in Dy, with H perpendicular to the c-axis show, empirically, that for a given temperature in the paramagnetic region, $\frac{\Delta v}{v} \propto H^2$. Neglecting magnetostriction then $\frac{\Delta c}{c} = \frac{2\Delta v}{v} \propto H^2$. Moran and Luthi⁹ suggest that terms in the internal energy which are quadratically dependent on the strain would account for $\frac{\Delta c}{c}$, but they carry the analysis no further. Southern and Goodings¹ have proposed a theory which introduces terms in the internal energy quadratic in the strains by requiring rotational invariance of the Hamiltonian. They give the expressions:

$$\Delta C_{33} = [(A + 2B) P_2(\cos \theta) + C + D] \left[\frac{\chi_\theta(T) H}{M_0} \right]^2$$

$$\Delta C_{11} = [(A - B) P_2(\cos \theta) + C - D \pm E \sin^2 \theta \cos 2\phi] \times \left[\frac{\chi_\theta(T) H}{M_0} \right]^2$$

for heavy rare earths in the paramagnetic region, where M_0 is the saturation magnetization, $\chi_\theta(T)$ is the directional magnetic susceptibility, H is the magnitude of the applied magnetic field, and θ and ϕ give the orientation of H relative to the crystallographic c- and a-axes, respectively. A, B, C, D, E are combinations of the one and two ion magnetoelastic coupling constants and the plus sign in ΔC_{11} is for propagation along the b-axis. The values of the five magnetoelastic constants are, for the most part, unknown and one of the goals of this work is their experimental determination. Assuming

all other quantities in the equations are known, five independent equations for a given temperature are required to determine these constants at that temperature. These five equations can be obtained from the five experimental measurements: ΔC_{33} with H parallel to a-axis, ΔC_{33} with H parallel to c-axis, ΔC_{11} with H parallel to a-axis, ΔC_{11} with H parallel to b-axis, ΔC_{11} with H parallel to c-axis. To obtain only five equations at each temperature, the magnetic field dependence must be removed from the equations. This can be done by measuring ΔC as a function of H. Assuming ΔC is a linear function of H^2 , as it was in Moran and Luthi's work,⁹ $\Delta C/H^2$ is then a function only of temperature.

Experimentally, the problem then is to measure $\frac{\Delta C}{H^2}(T)$. The standard procedure in measuring elastic constants is to measure the appropriate acoustic wave velocity and use an expression such as $C = \rho v^2$. Neglecting magnetostriction again $\frac{\Delta C}{H^2} = C(T) \frac{2\Delta v}{v}(T)/H^2$. $C_{11}(T)$ and $C_{33}(T)$ are known, so the experimental problem is now reduced to measuring $\frac{\Delta v}{v}(T)/H^2$. The pulse superposition technique¹⁰ allows a very accurate measurement of this quantity and thus calculation of the magneto-elastic coupling constants.

PULSE SUPERPOSITION METHOD

The pulse superposition method of measuring ultrasonic velocities in solids was developed by McSkimin.¹⁰

A description, omitting the details of the equipment involved, follows. One must first obtain a solid with 2 flat faces parallel to each other and perpendicular to the axis along which the waves are to be propagated. A piezoelectric transducer is then attached to one face of the solid, and driven by variable repetition rate radio frequency pulses, such that the radio frequency is the resonant frequency of the transducer and the repetition rate is to be related to the acoustic wave velocity. These pulses travel through the solid and are reflected from the face opposite the one where they were produced. When the echoes reach the original face, part of each one is reflected and the remaining part piezoelectrically couples to the transducer, producing an outgoing rf pulse. The echoes are displayed on an oscilloscope, and the repetition rate adjusted until the maximum echo amplitude is obtained. The acoustic wave velocity is then $v = 2lf_{\max}$ where $f_{\max}$ is the repetition rate of the pulses at maximum echo amplitude, and l is the distance between the parallel faces.

The trace seen on the oscilloscope screen is really the superposition of several single pulse echo trains. The repetition rate giving maximum echo amplitude is easily seen to be that repetition rate where the first echo from the last pulse is superimposed with the second echo from the next-to-last pulse and the third echo from

the second-to-last pulse, etc. Since the time delay between application of a pulse and arrival of an echo is the same for every pulse, the maximal superposition of pulses at $f_{\max}$ implies that the time delay between pulses is equal to the time delay between echoes, $1/f_{\max} = 2l/v$ or $v = 2lf_{\max}$.

The repetition rate is controlled by a signal generator whose output frequency can be accurately adjusted and measured. With the sample and equipment used in this work, changes in v on the order of a few parts in 10^5 were consistently measurable.

II. Sample and Apparatus

SAMPLE

The single crystal Dy sample used in this investigation was cut from a larger single crystal purchased from Metals Research Ltd. in December, 1970. The crystal was grown from 99.999% pure stock by the floating-zone-refining method. Dr. Kamel Salama spark cut the sample from the larger crystal and at the same time, located the crystallographic axes by photographing Laue back scattered X-rays. Two flat, parallel faces were spark planed perpendicular to both the b- and c-axes. The orientation of the normals to the faces was within 1.5° of the actual crystallographic axes, and the corresponding faces were parallel to within 1.5° . Experimental difficulties, discussed in Chapter IV, encountered when the acoustic waves were propagated along the b-axis were attributed to non-parallelism of the faces which was caused, perhaps, by rough handling. One face perpendicular to the b-axis was replaned to achieve the required parallelism.

APPARATUS

As discussed in the introduction, the experimental quantities to be measured were $\frac{\Delta v}{v}(\vec{H}, T)$ for longitudinal acoustic waves propagating along the b- and c-axes. A block diagram of the necessary apparatus is given in Figure II-1. Discussion of the apparatus used to perform

Figure II-1. Sample Holder and Block Diagram

these measurements can be conveniently divided into five parts:

1. the electronics needed to generate the pulse modulated rf and to amplify the resulting echoes.
2. a transducer to convert the electrical pulses into acoustic waves in the sample, and to convert the acoustic echoes back into electrical pulses.
3. visual display of the electrical pulses corresponding to the acoustic echoes to allow maximization of the echo amplitudes (pulse superposition method).¹⁰
4. cryogenic dewar and temperature controller to allow the sample to be held at a constant temperature anywhere in the region from the Neel point at 179K to room temperature.
5. magnet and power supply providing a homogeneous magnetic field in which sample is held.

A complete discussion of each section of the apparatus is given in the following five sections.

1. A P.M. Custom Electronics Sine Burst Generator provides the 20 V. peak to peak rf pulses to the transducer. The repetition rate of the rf pulses is controlled externally by the sine wave output of a Hewlett-Packard Model 606A Signal Generator. Adjustments for the rf pulse width, and binary divider are found on the front panel of the sine burst generator. Although all work reported in this

thesis was done at 20 MHz, the rf is continuously variable from 10 to 74 MHz. At 20 MHz, the pulse width is variable from 400 to 850 nsec. The minimum pulse width giving reasonably sized echoes was used, because larger pulse widths tend to give broader maxima, making measurements more difficult. The binary divider allowed selection of the repetition rate from the possibilities $f/2^n$ $n = 0, 1, 2, \dots, 10$ where f is frequency of the input from signal generator. Also located on the front panel are three BNC connectors, rf output ($Z_{out} = 50 \Omega$), trigger output, and gate input. Internally generated rf pulses appear at the rf output and are transmitted to the transducer via coaxial cable (coax). The pulses from the trigger output are transmitted, also by coax, to the trigger input of the oscilloscope. When a square wave (amplitude approximately +30 V) is applied to the gate input, the sine burst generator will cease production of rf pulses for the duration of the square wave. This feature was necessary, because when the echo amplitudes are maximized, the time between pulses is equal to the time between echoes. As a result, the large pulses and the relatively small echoes overlap, making maximization of the echo amplitude impossible. By having the proper time delay between the trigger pulse and the gate square wave, the echoes are displayed on the oscilloscope while no pulses are being produced. A BNC connector is provided on the rear panel of the sine burst

generator for input of the sine wave from the signal generator.

The front panel of the signal generator contains manual controls for frequency (coarse and vernier), amplitude (variable from $1\mu\text{V}$ -20 V peak to peak), and modulation selector (cw only in this work). The two BNC connectors on the front panel were the sine wave output ($Z_{\text{out}} = 50 \Omega$), and modulation input which wasn't used.

Inefficiencies inherent in the piezoelectric transducer cause the returning echoes to be much smaller in amplitude than the applied pulse. Amplification of the echoes is provided by a Hewlett-Packard 426A amplifier. The front panel selector allows the choice of 20 or 40 decibels gain. Two BNC connectors are provided for input and for output ($Z_{\text{in}} = Z_{\text{out}} = 50 \Omega$). The input of the amplifier is connected by coax to the transducer, and the output of the amplifier is transmitted by coax to the Y-axis of the scope.

Impedance matching is necessary because the transducer is a high impedance capacitive load driven by the rf pulses from the sine burst generator. Maximum transfer of power to the transducer requires that the high impedance of the transducer be matched to the low output impedance of the sine burst generator. Similarly, the low output impedance of the H.P. amplifier must be matched to the

high input impedance of the Y-axis amplifiers in the oscilloscope. Several impedance matching units were tried, but the best results (maximum echo amplitude with least distortion) were obtained by trying different lengths and types of coaxial cables until a good match was obtained.

2. The transducer is composed of three parts: the sample holder in which the rf electric fields are set up, the quartz crystal placed in this field which piezoelectrically couples to the electric field producing time-varying rf strains in the quartz, and the bond which couples the quartz to the sample thus producing elastic waves in the solid. When detecting acoustic wave echoes, the process is reversed and an electric field set up in the sample holder when the acoustic wave echoes couple to the quartz.

The sample holder used for fields applied perpendicular to the direction of propagation is shown in Figure II-1. The shield is a brass cylinder with a notch cut in each side to allow access to the inside. The bottom half of the inner surface of the shield is threaded, so a plastic cylinder, threaded on the outside, can be moved into or out of the shield. The copper plate, on which the sample is placed, rests itself on this plastic cylinder. The 20 Ω heater and temperature sensing diode are mounted on this lower plate to insure good thermal contact with the sample and to keep temperature gradients small.

A BNC connector is mounted atop the shield. The center conductor is connected to another copper plate which is mounted on a spring. Moving the plastic cylinder into the shield brings the quartz transducer into contact with the spring-loaded upper plate, thus making the pressure on the quartz transducer variable. This is desirable for three reasons. First, the pressure will hold the transducer closer to the sample, making the bond thinner and more efficient. Second, the mechanical force helps hold the sample stationary when a magnetic field is applied. Third, the spring allows thermal and magnetostrictive changes in sample dimensions. The outer conductor of the BNC is connected to the lower copper plate, so, electrically, the two plates look essentially like a capacitor.

Fields applied parallel to the direction of wave propagation required use of the sample holder pictured in Figure II-2. This holder was built by Chuck Melcher to fit into the larger sample holder. It is a 1" x .7" x .5" block of Plexiglas with a 1" x .3" x .3" section removed. Removable brass plates cover the ends having the .3" x .3" openings. The sample is held in place on one side by a small brass plate attached to a spring which is connected to the end plate. The small plate on the other side of the sample is held in place by an 8-32 brass screw which is in a threaded hole in the second end plate.

PLASTIC SAMPLE HOLDER

Figure II-2. Plastic Sample Holder

Electrical contact to the upper conductor of the brass sample holder is made via spring, end plate (insulated from copper base plate) and silver paste which runs from the brass end onto the top of the plastic holder. Contact to the bottom copper plate is made via the screw and the end plate which rests directly on the copper base. Again, the configuration is like that of a capacitor.

Use of this plastic holder caused the sample to be thermally isolated from the diode. The temperature gradients were only a few degrees, but were bothersome nevertheless. Some modifications made to alleviate this problem will be discussed in a later chapter.

The electric field near the center of the plates in either holder will be approximately perpendicular to the plates. Since longitudinal acoustic waves were desired, this electric field configuration dictated the use of X-cut quartz. The 20 MHz fine ground transducers used were purchased from Valpey-Fisher Corp. Although not optimally sized for this frequency, 1/8" diameter transducers were used because of sample size restrictions.

The transducer was bonded to the sample with Nonaq stopcock grease. There are several criteria by which a bonding material is judged: convenience, strength, efficiency, and thickness. Nonaq was used in this work primarily because it is easy to use. The demands placed on it were not severe, so its shortcomings in areas other than convenience were not critical.

The Nonaq bond can be tested immediately to see if it is usable. Other bonding materials generally require longer waits before testing. Nonaq is also easy to remove from the sample and transducer, while others, such as epoxy are virtually impossible to remove. All work here was done in the paramagnetic region, so strength was not as important as it would have been had it been necessary to take measurements over a temperature range including the magnetic phase transitions. Maintaining bond integrity at those transitions is difficult, because of the discontinuous volume changes encountered.

Although Nonaq is not very efficient, sufficient electrical amplification was available to get reasonably sized echoes. Thickness becomes a problem when measuring absolute elastic constants. Only relative changes were measured in this work so bond thickness was not crucial.

3. A Tektronix type 547 oscilloscope (dual time base) with a Type M plug-in unit was used for visual display of the echoes. During the first few months of this investigation, the oscilloscope was also used to supply the square wave to the gate input of the sine burst generator. One time base was used to display the echoes while the other determined the width of the square wave, and the delay time between the trigger pulse and the leading edge of square wave was set with a potentiometer built into the scope. Approximately midway through the work reported here,

weak circuitry caused the amplitude of the square wave to become too small to gate the sine burst generator. A Chronetics Model PG-11 pulse generator externally triggered by the delayed trigger output of the scope was used in the remaining measurements. This replacement changed none of the results, but did require extra care in that one had to insure that the width of the square wave was not larger than the width of the ramp voltage which sweeps the electron beam.

4. The Andonian metal dewar has a narrow tail section which rests between the poles of the magnet. The sample and holder are held between the poles of the magnet by the dewar insert. The important parts of the dewar are the liquid nitrogen (LN_2) jacket, the reservoir, the vacuum jacket, the port for access to the sample area, and the throttle valve. When pumped down to approximately 5×10^{-6} torr, the vacuum jacket essentially eliminates all conduction of heat from the outside by convection. The LN_2 jacket shields the reservoir from radiated heat.

For temperatures below 77K, the reservoir is filled with liquid helium. This work was done at 175K or above, so the reservoir was also filled with LN_2 . The vacuum jacket was evacuated using a Consolidated Vacuum Corp. Type PMCS 2C oil diffusion pump in conjunction with a Duo Seal Model 1402 mechanical vacuum pump. Pressures down to 10^{-3} torr were measured with a National Research

Corporation (NRC) Type 501 Thermocouple gauge. Pressures below 10^{-3} torr were measurable using a NRC Model 507 Ionization Gauge Tube.

The throttle valve stem opens the throttle valve and allows the cryogenic liquid in the reservoir to flow through the capillary tube to the bottom of the tail where it vaporizes and flows past the sample.

The dewar insert consists, principally, of a thin walled stainless steel tube with a BNC connector at each end. The tube passes through a brass disc, which sits on top of the dewar, and holds the tube in place. The male BNC connector on top is joined to a piece of coax which runs through the stainless steel tube to the female BNC at the bottom which attaches to the sample holder. Wires, external to the tube, run from the diode and heater through the top plate (brass disc) of the insert. All connections and joints at the top of the insert are air-tight, so the sample chamber can be pumped out.

The sample temperature was set and held steady with a Princeton Applied Research Model 152 Cryogenic Temperature Controller and a calibrated Lake Shore Cryotronics TG-100 temperature sensing GaAs diode.

Operation of the temperature controller is fairly simple. The front panel controls are as follows: the range switch and vernier for choosing the set point corresponding to the desired temperature, an offset meter which

indicates the deviation of the actual temperature from the set point, toggle switch for selection of automatic or manual heater control, meter for indicating heater current, manual heater current adjustment, and adjustable loop parameters for automatic heater control.

The temperature controller provides a constant $10\mu\text{A}$ current to the diode. When the temperature changes, the voltage across the diode changes, thus this voltage can be used to measure temperature. In the automatic mode, the difference between the measured voltage and the set point voltage is amplified and used to drive the heater. Other circuitry damps any oscillation in this difference voltage and forces it toward zero, and in so doing, regulates the temperature. When the adjustment of the loop parameters is optimized, the temperature is stable to within $.01\text{K}$ and reproducible to $.1\text{K}$. In manual mode, the heater current is regulated manually and the deviation from the set point is indicated on the offset meter. All other circuitry is disabled.

The GaAs diode used in this investigation was calibrated with a copper-constantan thermocouple from 4.2 to 240K , and extrapolated linearly to higher temperatures.

5. The Harvey Wells L-128 magnet and HS-1050 magnet power supply provide a maximum field of 17.65 KOe with a two inch gap between pole pieces. The magnet is mounted so that it can be rotated 180° in either direction from 0° ,

and it can be oriented within $1/2^\circ$. The magnitude of the field was measured with a Systron Donner Model 3102 Digital Hall Effect Gaussmeter, which when properly calibrated is accurate to within 1%. Compensation for nonlinearities in the probe allows the field to be measured accurate to within .2%, but no such compensation was necessary in this work.

III. Procedure

PREPARATION

Evacuation of the vacuum jacket of the dewar is begun at least 24 hours before the LN_2 jacket is to be filled. The vacuum-space pump-out valve on the dewar remains closed unless the vacuum jacket is being evacuated. If the lines leading to the pump-out valve are at atmospheric pressure, the mechanical pump is used to bring their pressure down to approximately 10^{-2} - 10^{-3} torr before opening the valve. This reduces pumping time by avoiding exposing the dessicant in the vacuum jacket to the atmosphere. After the valve is opened and the pressure is about 10^{-3} torr, the diffusion pump is used to reduce the pressure to approximately 5×10^{-6} torr.

Bonding the quartz transducer to the sample and aligning the sample in the sample holder were very important, in that a high quality bond (or equivalently a large amplitude, undistorted echo pattern) permitted more precise measurements of the wave velocity.

All grease and dirt were first removed from transducer and sample with acetone. A small drop of Nonaq stopcock grease was then placed on the appropriate face of the crystal. The drop was small enough to avoid having any excess squeezed out when pressure was applied to the transducer (as in the sample holder). Any excess

inevitably found its way to the top of the transducer where it caused distorted waveforms. The transducer was then placed on the drop, care being taken to locate it so that the generated acoustic waves had an unobstructed path to the opposite face. Failure to provide a direct path resulted in multipath reflections and again, a distorted waveform. Optimal bonding was observed when there was sufficient grease to completely cover the area between transducer and sample with a thin layer.

The characteristics of the bond were observed by placing the crystal in the sample holder, and observing the resulting echo pattern at room temperature. The test was performed by first setting the binary divider to 1 (implying the repetition rate of the pulses was equal to the frequency of the signal generator output). The signal generator was then adjusted to give maximum echo amplitude. Gross bond problems, as manifested by small echo amplitudes, spurious echoes and generally malformed waveforms, would be obvious at this time. Lack of success at this point did not necessarily mean that the bond was bad, however. Repositioning the sample in the holder often improved the quality of the echo pattern. This alignment of the sample in the holder was the most critical step in the preparation. The upper and lower copper plates, between which the sample was held, were not quite parallel, so arbitrary placement of the sample in the holder led to nonuniform

pressures on the transducer, thus also to distortions in the echo pattern. By careful variation of the position and orientation of the sample, it was possible to obtain a fairly uniform pressure on the transducer, and clean waveforms.

Adjustment of spring pressure in the holder was another critical part of the bonding procedure. Recall that this is the spring on which the upper copper plate is mounted. The force it exerts on the sample and transducer determines the thickness of the bond, to some extent, and provides the major part of the mechanical force which holds the sample stationary in the applied magnetic field. Ideally, maximum possible spring pressure would be used to hold the sample in the 18 KOe fields. In actuality, however, it was observed that for most bonds, increasing the spring pressure to the maximum caused considerable deterioration of the bond.

If no improvement in the quality of the bond was obtained by repositioning the sample or by varying the spring pressure, the transducer and sample were separated, cleaned, and the procedure started anew.

The second and most sensitive test of the bond was performed with the binary divider set to 1024. The time between pulses was then 1024 times larger than the time between echoes, implying that the first echo displayed after the pulse was the superposition of the first echo

from the displayed pulse and the 1025th echo of the previous pulse. In other words, the displayed echoes were due, essentially, to the displayed pulse, and any superposition of echoes was negligible. Ideally, a single-pulse echo train should consist of a series of echoes, equally spaced, such that their amplitudes decay exponentially. In practice, some reasonable approximation to this ideal was acceptable. Spurious echoes were not uncommon, and were generally attributed to multipath reflections and excitation of shear waves with velocities different from the longitudinal waves. In bonds deemed usable, these spurious echoes were small, but not always negligible. The problem of two closely spaced ($\Delta f \sim 50$ Hz) pulse amplitude maxima, to be discussed in the section on measurement, was blamed on these unwanted echoes.

Exponential envelopes were the exception rather than the rule. The most common problem was a sinusoidal modulation of the exponential envelope caused by nonparallelism of the faces. None of the work reported here involved any measurements of attenuation; so the exact shape of the echo amplitude envelope was not important.

In the first measurements attempted, the sample was moved when placed in a high field, especially when the temperature was near the Neel point. It was thus necessary to augment the mechanical force of the spring on the sample by gluing the sample to the lower plate. When a

good bond had been made, it was necessary to remove the sample, apply glue to the plate, and return the sample to the holder, hopefully in the same position as before removal. Plastic cement was first used to hold the sample down, and was found to possess adequate strength even at low temperatures. Plastic cement was not used in later runs, because it thermally isolated the sample from the GaAs diode. E-Kote 3030 silver conductive paint was used and found to have sufficient mechanical strength while greatly reducing the thermal gradient.

For the next couple of hours, the sample remained in the holder at room temperature, allowing time for the paint or glue to dry, and also allowing assessment of bond deterioration with time. If the properties of bond, particularly its efficiency, were still tolerable, the sample was ready. A good bond was usually obtained only after repeated failures.

After noting the approximate alignment of the crystal, the dewar insert was placed in the dewar and connections made from the BNC connector to the sine burst generator, and from the heater and diode to the temperature controller. The reservoir and sample chamber were then flushed several times with dry Helium to remove any water vapor which might have frozen and disabled the throttle valve when the LN_2 jacket and reservoir were filled. LN_2 was transferred from the roll-around dewar into the LN_2 jacket and the reservoir,

while the sample chamber was held at a slight overpressure to avoid sucking moist air into the sample chamber when the He in it cooled and contracted. The reservoir vents were plugged to raise the pressure so that when the throttle valve was opened, a stream of LN_2 flowed through the capillary tube, vaporized, and flowed past the sample, cooling it. The gaseous N_2 escaping from the sample chamber was bubbled through water so its rate of flow could be monitored. Being careful not to open the throttle valve too far and flood the sample chamber with LN_2 , a reasonable flow rate was set. The temperature controller was put in the automatic mode, and the set point for the temperature placed at 180K. No measurements were made until the temperature stabilized at 180K.

It was necessary to know the orientation of crystallographic axes of the sample, because each of the five measurements (described in the introduction) to be done required the field to be applied along a particular axis. A measurement at 180K of $\frac{\Delta f}{f}(\theta)$ as the constant (magnitude) magnetic field was rotated through 180° showed a maximum and a minimum separated by 90° . An examination of the angular dependence of Southern and Goodings'¹ expressions for ΔC , given in the introduction, allowed identification of the two axes. Knowledge of the approximate orientation of the sample when placed in the dewar allowed a consistency check with the experimentally determined axes. The nominal axes were within 2° of the actual axes in all cases.

At this point, the throttle valve was closed, stopping the gas flow past the sample. Hopefully, this procedure reduced the temperature gradient between sample and diode, caused by the gas flowing past the sample which could not reach the completely enclosed diode.

MEASUREMENT

For each temperature, 180, 185, 190, 195, 200, 210, 220, ..., 300 (K), the ultrasonic velocity was measured along both orthogonal axes for magnetic fields from 0 to 17.65 KOe. The size of the magnetic field increments between data points varied with temperature. Near the Neel point, one would expect the largest deviation from the H^2 dependence of $\Delta f/f$. Salama, Melcher, and Donoho¹¹ in analogous measurements on Tb found large deviations from linearity as much as 20° above the Neel point. The experimental data presented in the next section show that, except for the case of the velocity parallel to the b-axis and the field parallel to the c-axis, the relation $\Delta f/f \propto H^2$ holds fairly well at 190K, only 10K from the Neel point. The exceptional case is not due to nonlinearities, but to difficulties encountered in measurement. When H is applied along the magnetically hard c-axis, the H^2 dependence is expected to hold very well. The very small changes in velocity found in this case were difficult to measure and these difficulties are responsible for the nonlinear behavior. Typically, measurements were taken at

0, 7, 10, 12, 14, 16, 17.65 KOe, giving the almost linear scale 0, 49, 100, 144, 196, 256, 310 (KOe)².

The actual process of measuring the frequency (or velocity, since $v = 2lf_{\max}$) is simple enough in principle. Given an echo amplitude maximum that is sharp, i.e., frequency changes of few Hz cause an observable change in echo amplitude, one has only to adjust the frequency of the signal generator to maximize the echo-superposition, and consult the digital readout of the frequency meter to obtain all the pertinent information.

Of course, nothing is ever quite as it should be, so the remainder of this chapter discusses problems encountered in measurement, and how they were dealt with in this work.

It was observed early in this experiment that even under the best conditions, there is a tendency to stop short of the maximum. For example, assume that the maximum is being approached from below. For frequencies far from the maximum of echo amplitude, the amplitude changes rapidly with frequency. As the maximum is approached, the amplitude changes much less over the same frequency interval, so the changes are less discernible. The inclination, of this experimenter at least, is to increase the frequency until no further changes are evident, and because of the broadness of the maximum, this point is usually not exactly the maximum. Fortunately, this error can be corrected by measuring the apparent maximum,

approaching from higher and lower frequencies an equal number of times, and averaging.

Most often, the problem encountered was an ambiguity in the location of the maximum. By varying the sweep rate of the scope, it was possible to display 1 to 30 or 40 echoes. Occasionally, some anomaly in the bond would cause some echoes to maximize at different frequencies than others. When faced with this dilemma, the best course of action was to check the single pulse echo pattern for obvious causes. The first echo would often be distorted, thus ignored. Unfortunately, an easy explanation was not always available. In such cases, the largest undistorted echo was used consistently in all measurements.

The problem of two closely spaced maxima ($\Delta f \sim 50$ Hz) was mentioned in the previous section in connection with small spurious echoes. It was necessary to decide which maximum was to be used, because the 50 Hz difference was large enough to obscure all but the largest of the magnetic field effects. Compounding the difficulties was the fact that this double maxima appeared for only certain values of the applied field, so one could not arbitrarily choose one of the maxima and use it consistently. Generally, the maximum was chosen which yielded results most consistent with those obtained under more ideal conditions.

Equipmental inadequacies were ordinarily a problem only at high temperatures. A small amount of noise originating in one of the amplifiers was enough to obscure the small variations in echo amplitude whose detection allowed the small changes in ultrasonic velocity to be measured. Patience, only, was required, while waiting for the noise to disappear as mysteriously as it appeared.

Probably, the accuracy of measurements at high temperatures was most severely restricted by lack of a sufficiently sensitive frequency adjustment on the signal generator. The smallest value of $\Delta v/v$ which could be measured accurately was, as stated in the introduction, about two parts in 10^5 . For repetition rates used in this work (200-300 KHz), this change in $\frac{\Delta v}{v}$ corresponds to a frequency change of approximately 5 Hz, which in turn corresponds to a .0025" displacement of a point on the perimeter of the vernier knob. Obviously, a very steady hand was required for measurements of these small frequency changes.

In situations where the relative velocity change was small even at high fields, temperature drift was a problem. A temperature drift changes the zero field velocity (or equivalently the elastic constant) and can completely obscure any field dependent velocity change if the magnitude of the drift is a significant fraction of the field induced velocity change. Use of the plastic sample holder

aggravated this problem, because its insulating effect made the sample come to equilibrium slowly. The temperature of the sample would not be constant even several hours after changing the temperature. Allowance was made for this drift by assuming, first, that over the short times (20-30 minutes) required to measure the field dependence, the temperature changed linearly with time. The zero field frequency was measured before and after the applied field measurements, and in the analysis of the data, the zero field frequency was linearly interpolated between the two measured frequencies to approximate the zero field frequency at the time each applied field measurement was made.

CONSISTENT DATA

An attempt was made to obtain a consistent set of data for each orientation of the crystal and magnetic field. A consistent set of data is defined here as one in which $|\Delta f/f/H^2|$ decreases monotonically with increasing temperature. When possible, data just taken would be quickly averaged and $\Delta f/f$ versus H^2 fit to a least-squares straight line while the temperature of the sample was being changed. This procedure allowed an immediate check of the consistency of the new and old data. When deviations from the expected behavior were encountered, measurements were repeated at the appropriate temperatures. Eventually, almost all inconsistencies were removed, and most of those remain-

ing were at high temperatures where measurements are inherently more difficult.

IV. Data

This chapter presents the subset of the experimentally obtained data which remained after discarding the data judged to be unreliable. Most discrepancies and inconsistencies were due to easily identifiable systematic errors such as slight sample misalignments and temperature gradients due to use of the plastic sample holder. Large random errors were eliminated by requiring consistency in the data where possible. (See last section of Chapter III.)

In addition to the raw data, presented in the order obtained, information concerning the four separate times measurements were taken will be given. Changes in apparatus constitute the bulk of the latter part.

The four separate measurements mentioned above are: ΔC_{33} with H parallel to the a- or b-axis, ΔC_{33} with H parallel to the c- or b-axis, ΔC_{11} with H parallel to the a- or c-axis, and ΔC_{11} with H parallel to the b- or c-axis. Of course, the experimental quantity measured in each case was $\Delta f/f(H,T)$, which can be written $\Delta f/f(x,y)$, where x is the propagation axis, y is the axis along which the field is applied, and the dependence on temperature and magnetic field is understood. In this notation, the measurements taken were: $\Delta f/f(c,a)$, $\Delta f/f(c,b)$ twice, $\Delta f/f(c,c)$, $\Delta f/f(b,a)$, $\Delta f/f(b,b)$, and $\Delta f/f(b,c)$ twice. The repeated measurements were intended to provide some

information about the temperature gradient introduced by the plastic sample holder. The error due to sample misalignment was sometimes larger than the error due to thermal gradients, so the repeated measurements were not always as useful as they could have been.

The first measurement made was of $\Delta f/f(c,a)$ and $\Delta f/f(c,b)$. Since the velocity of propagation was perpendicular to the applied field, the plastic sample holder was not needed. Bond deterioration occurred while trying to orient the sample at 190K, because the sample was tilted by the applied field. The dewar insert was removed, warmed to room temperature, and the sample glued to the lower copper plate with plastic cement. After cooling to 190K, the frequency of maximum amplitude was measured as a function of θ . In the paramagnetic region, the difference between the a- and b-axes is small, so $\frac{\Delta f}{f}(\theta)$ could not be measured accurately enough to identify the axes.

Figure IV-1 shows $\frac{\Delta f}{f}(\theta)$ for $H = 16 \text{ kOe}$ and sample temperature of 185K. The angular dependence is typical of that found for other sample configurations and is shown here because this measurement was done in more detail than the rest. The temperature was lowered to 175K and $\frac{\Delta f}{f}$ taken at 2° intervals near the maximum and minimum to locate them more precisely ($\pm 2^\circ$).

Although Southern and Goodings' theory¹ neglects the basal plane anisotropy in the paramagnetic region, the

Figure IV-1. $-\frac{\Delta v}{v}$ versus Angle of Applied Magnetic Field

difference between the a- and b-axes was measurable. The difference was small, however, so only $\Delta f/f(c,a)$ was used in subsequent data analysis. The temperature and magnetic field dependence of $\Delta f/f(c,a)$ is shown in Figure IV-2. Moran and Luthi⁶ have made essentially the same measurements, thus some check on the experimental procedure was possible. A rigorous comparison was not made, because Moran and Luthi⁶ used different temperatures, but the data reported here are at least consistent with theirs.

The second measurement made was of $\Delta f/f(c,b)$ and $\Delta f/f(c,c)$. This sample orientation required use of the plastic sample holder, so the temperature stability was less than in the first sample configuration. $\Delta f/f(c,c)$, given in Figure IV-3, had to be used in the data analysis because it could only be measured using the plastic holder. The values of $\Delta f/f(c,b)$ were not used because the equivalent data $\Delta f/f(c,a)$ were taken without the plastic sample holder. In addition to the fact that the sample holder was made of plastic, the temperature gradient was large because the brass plate which made electrical contact with the copper base was oversized and prevented the bottom of the holder from resting on the copper plate. Thus, the bulk of the holder was not touching the plate, and the only thermal path from sample to diode was through the end plate, screw, and small brass plate. As a result, the temperature of the sample is not as reliably indicated by the

Figure IV-2. Variation of $\frac{\Delta F}{F}$ (c,a)

Figure IV-3. Variation of $\frac{\Delta F}{F}$ (c,c).

diode as it was in the previous orientation (H parallel to the a- or b-axis). The sample was colder when in the plastic sample holder because there was little thermal contact with the heater. Comparison of the calculated values of $\frac{\Delta f}{f}/H^2$ indicate the sample was approximately 3K colder when in the plastic sample holder. In addition, the time required to reach equilibrium temperature was much greater. Even after having several hours to reach equilibrium, the change in zero field frequency, due to temperature drift, often obscured the magnetic field effects, especially at high temperatures. The method used to account for this drift is discussed in Chapter III.

Near the end of the measurements taken with this sample configuration, the heater circuit in the temperature controller shorted. The fuse did not blow, so some of the circuitry was damaged. Luckily, an identical temperature controller was available, so a quick check was made to ascertain whether the second temperature controller would maintain the same sample temperature as the first, given the same set points. Using the second temperature controller, in the automatic mode, the sample temperature was brought to equilibrium. After noting the equilibrium heater current, No. 2 was switched to manual mode, and the heater current manually set to its previous value, so the sample temperature would remain constant. The leads to the diode were removed from No. 2 and connected to No. 1. With

the set points on both controllers the same, and assuming the sample temperature did not change appreciably in the 1 or 2 minutes required, the offset meter on temperature controller No. 1 indicated the difference in the set point temperatures. At 180K and 250K, the deviation was less than .5K, which is negligible considering the other perturbations on the temperature.

After completing the measurement of ΔC_{33} , it was necessary to replane one of the faces perpendicular to the b-axis. Before replaning, the attenuation was large, and the spurious echoes were big enough to cause problems in measurement. Even after replaning, the echo patterns were not as good as those obtained with the velocity parallel to the c-axis, but they were usable.

The first measurements taken with v parallel to the b-axis were of $\Delta f/f(b,a)$ and $\Delta f/f(b,c)$, so the plastic sample holder was not required. The data taken are shown in Figures IV-4 and IV-5. Midway through the measurements taken in this configuration, the magnet power supply became unstable. The two mercury batteries which supply the reference voltage were replaced with a D.C. power supply, and the stability was regained.

The measurements of $\Delta f/f(b,b)$ and $\Delta f/f(b,c)$ were made only after modifying the plastic sample holder to reduce the sample-diode temperature gradient. Holes were drilled in both sides and the bottom of the sample holder to reduce

Figure IV-4. Variation of $\frac{\Delta F}{F}$ (b,a)

Figure IV-5. Variation of $\frac{\Delta F}{F}$ (b,c)

its insulating efficiency. In addition, in order to make better thermal contact between the bottom of the holder, and the lower copper plate, an aluminum plate was placed under the holder. The sample could then be heated by radiation (from the aluminum plate) passing through the holes and, similarly, by convection. It was concluded that this method of heating was much more efficient, since the sample reached equilibrium much faster. Electrical contact to the base plate was maintained by careful placement of the aluminum, which made it part of the conducting path.

The measurement of $\Delta f/f(b,c)$ was done twice, once with and once without the plastic sample holder, in hopes of gaining some information about the relative temperature gradient. Unfortunately, the plastic sample holder constrained only one axis to be in the plane of the magnetic field, the b-axis in this case. Due to sample misalignment, when the projection of the field on the c-axis was a maximum, the projection of the field on the a-axis was non-zero. $\Delta C_{11} \propto \chi_0^2$, and χ_0 is much greater for fields in the basal plane than for fields along the c-axis, so a small misorientation of the c-axis caused a large error in $\frac{\Delta f}{f}(b,c)$. Due to this error, no meaningful comparison of temperatures could be made. The usable data taken in this configuration are shown in Figure IV-6.

Figure IV-6. Variation of $\frac{\Delta F}{F}$ (b,b)

V. Theory

This chapter develops the theory necessary to calculate the magnetoelastic constants from the experimental results presented in the last chapter. The analysis will begin with an explanation of the Hamiltonian density (often referred to as the Hamiltonian) derived in the small strain approximation, and applicable to hexagonal symmetry. Reference will then be made to experimental evidence showing the inadequacy of the small-strain approximation. Following Southern and Goodings,¹ finite strain theory will be applied to the Hamiltonian which will in turn be used to calculate ΔC_{11} and ΔC_{33} in the paramagnetic region. Using these expressions, the magnetoelastic coupling constants will be calculated, and discussed in light of those obtained in other similar work.

The Hamiltonian of the solid can be written

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_m + \mathcal{H}_{me}$$

where $\mathcal{H}_e$ is the classical elastic energy density, $\mathcal{H}_m$ includes the magnetic interactions, and $\mathcal{H}_{me}$, the magnetoelastic interactions.

The elastic energy density can be written

$$\mathcal{H}_e = \frac{1}{2} C_{\alpha\beta\gamma\delta} \epsilon_{\alpha\beta} \epsilon_{\gamma\delta}$$

$$\alpha, \beta, \gamma, \delta = x, y, \text{ or } z$$

where $C_{\alpha\beta\gamma\delta}$ is the usual elastic constant and $\epsilon_{\alpha\beta}$ is the infinitesimal strain

$$\epsilon_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_{\alpha}}{\partial x_{\beta}} + \frac{\partial u_{\beta}}{\partial x_{\alpha}} \right)$$

and can be written more conveniently

$$\mathcal{H}_e = \frac{1}{2} C_{ij} \epsilon_i \epsilon_j$$

using the engineering notation to label the strains. The two conventions will be used interchangeably throughout the remainder of the text. If the only quadratic strain dependence in the Hamiltonian occurs in $\mathcal{H}_e$, then

$$\begin{aligned} C_{ij} &= \frac{\partial^2 U}{\partial \epsilon_i \partial \epsilon_j} \quad (U = \langle \mathcal{H} \rangle) \\ &= \frac{\partial^2 \mathcal{H}_e}{\partial \epsilon_i \partial \epsilon_j} \end{aligned}$$

where U is the internal energy, and $\langle \mathcal{H}_e \rangle = \mathcal{H}_e$, since $\mathcal{H}_e$ is a classical expression. More generally, the effective elastic constant C_{ij}^* can be defined by the expression

$$C_{ij}^* = \frac{\partial^2 U}{\partial \epsilon_i \partial \epsilon_j}$$

The work reported in this thesis is only concerned with changes in the elastic constants

$$\begin{aligned} \Delta C_{ij} &= C_{ij}^* - C_{ij} = \frac{\partial^2 U}{\partial \epsilon_i \partial \epsilon_j} - \frac{\partial^2 \mathcal{H}_e}{\partial \epsilon_i \partial \epsilon_j} \\ &= \frac{\partial^2 \langle \mathcal{H} - \mathcal{H}_e \rangle}{\partial \epsilon_i \partial \epsilon_j} \end{aligned}$$

so only the magnetic and magnetoelastic Hamiltonians will be considered hereafter.

The magnetic Hamiltonian $\mathcal{H}_m$ consists of three parts,

$$\mathcal{H}_m = \mathcal{H}_{ex} + \mathcal{H}_{ze} + \mathcal{H}_a$$

where $\mathcal{H}_{ex}$ and $\mathcal{H}_{ze}$ are due to the exchange and Zeeman interactions, respectively, and $\mathcal{H}_a$ incorporates the effect of the crystal field anisotropy. Since the 4f electrons are tightly bound, the wavefunctions of the 4f electrons on even neighboring ions have negligible overlap. The exchange is therefore not due to direct, Heisenberg exchange, but is due to some indirect mechanism. This indirect exchange is of the Ruderman-Kittel type in which the interaction between ions occurs via the conduction electrons near the Fermi surface which are polarized by the nearby 4f electrons.¹² This polarization is communicated via the conduction electrons to 4f electrons on other ions. Using a free electron model for the conduction electrons, the indirect exchange takes form

$$\mathcal{H}_{ex} = \sum_{i < j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

where J_{ij} is an oscillatory function (period = $1/2 k_f$) which depends on the distance between the ions i and j . The Zeeman interaction term is the usual one due to interactions between the applied magnetic field and the angular momentum of each ion,

$$\mathcal{H}_{ze} = g \mu_B \sum_i \vec{S}_i \cdot \vec{H}$$

The crystal field anisotropy energy is due to the electrostatic interaction of the charge distribution of the 4f electrons on a particular ion with the crystalline electric field due to the other rare earth ions in the lattice. The electrical potential near a particular ion can be written as a sum of the contributions of every other ion,

$$V(r, \theta, \phi) = \sum_i \frac{e_i}{|\vec{r} - \vec{r}_i|} \quad (\vec{r} = (r, \theta, \phi))$$

Expanding $\frac{1}{|\vec{r} - \vec{r}_i|}$ in spherical harmonics,¹³

$$V(r, \theta, \phi) = 4\pi \sum_i e_i \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{1}{2\ell+1} \frac{r_i^{\ell}}{r^{\ell+1}} Y_{\ell m}^*(\theta_i, \phi_i) Y_{\ell m}(\theta, \phi)$$

or in a simpler more phenomenological form¹⁴

$$V(r, \theta, \phi) = \sum_{\ell, m} B_{\ell}^m r^{\ell} Y_{\ell}^m(\theta, \phi)$$

where

$$B_{\ell}^m = 4\pi \sum_i e_i \frac{1}{2\ell+1} \frac{r_i^{\ell}}{r^{\ell+1}} Y_{\ell m}^*(\theta_i, \phi_i)$$

can be calculated roughly, but is usually measured experimentally. The crystal field energy density will then be

$$U_{cr} = N_v \langle V(r, \theta, \phi) \rangle$$

where N_v is the number of ions per unit volume, and $\langle \tilde{O} \rangle$ is the expectation value of $\tilde{O}$. The wavefunctions used in taking this expectation value can be written in the central

field approximation as $\psi = f(r) |L S J M_J\rangle$. The radial function $f(r)$ will have to be numerically calculated, and the $|L S J M_J\rangle$ will be a linear combination of Slater determinants for the particular $4f^n$ configuration desired. Neither problem is easily done, so Stevens¹⁵ developed an alternative method of evaluating these matrix elements by using angular momentum operator equivalents.

Using the properties of the spherical harmonics, it is possible to show that for f electrons, all contributions to $V(r, \theta, \phi)$ from spherical harmonics of order greater than 6 will be zero¹⁶, so V can be written

$$V(r, \theta, \phi) = \sum_{\ell=1}^6 r^{\ell} \sum_{m=-\ell}^{\ell} B_{\ell}^m Y_{\ell}^m(\theta, \phi)$$

It can also be shown¹⁷ that for axial symmetry, the only non-zero B 's are B_2^0 , B_4^0 , B_6^0 , and that reducing the symmetry to hexagonal introduces only $B_6^{\pm 6}$. Now, V can be written

$$V(r, \theta, \phi) = r^2 B_2^0 Y_2^0 + r^4 B_4^0 Y_4^0 + r^6 B_6^0 Y_6^0 + r^6 B_6^6 (Y_6^6 + Y_6^{-6})$$

Using the Wigner-Eckhart theorem,

$$\langle j_1 m_1 | Y_{\ell}^m | j_2 m_2 \rangle \propto \langle j_1 m_1 | T_{\ell}^m | j_2 m_2 \rangle$$

(where T_{ℓ}^m is any irreducible tensor operator), Stevens¹⁵ showed that the spherical harmonics Y_{ℓ}^m could be assumed proportional to the irreducible tensor operator $\tilde{O}_{\ell m}(\vec{J})$. The $\tilde{O}_{\ell m}$'s are formed from the angular momentum operators

S_x, S_y, S_z , so evaluation of their expectation values is straightforward.¹⁸ An operator equivalent for the crystal field can thus be defined

$$V(r, \theta, \phi) = \langle r^2 \rangle \alpha_2 \beta_2^0 \tilde{O}_{20}(\vec{s}) + \langle r^4 \rangle \alpha_4 \beta_4^0 \tilde{O}_{40}(\vec{s}) \\ + \langle r^4 \rangle \alpha_4 [\beta_6^0 \tilde{O}_{60}(\vec{s}) + \beta_6^4 (\tilde{O}_{64}(\vec{s}) + \tilde{O}_{6-4}(\vec{s}))]$$

where the expectation value $\langle r^n \rangle$ is taken using only the radial part of the wavefunction $f(r)$, and α_l is the proportionality constant between the matrix elements of Y_l^m and $\tilde{O}_{lm}$. The expectation value of $V(r, \theta, \phi)$ is now taken between the angular functions $|L S J M_J\rangle$, the radial dependence having been accounted for. Absorbing all constants into the B's, $\mathcal{H}_a$ can be written¹

$$\mathcal{H}_a = \tilde{B}_2^0 \sum_i \tilde{O}_{20}(\vec{s}_i) + \tilde{B}_4^0 \sum_i \tilde{O}_{40}(\vec{s}_i) + \\ \tilde{B}_6^0 \sum_i \tilde{O}_{60}(\vec{s}_i) + \tilde{B}_6^4 \sum_i [\tilde{O}_{64}(\vec{s}_i) + \tilde{O}_{6-4}(\vec{s}_i)]$$

summing over the ions in one unit volume of the solid.

The magnetoelastic Hamiltonian $\mathcal{H}_{me}$ is the sum of two parts, $\mathcal{H}_{me}^I$ and $\mathcal{H}_{me}^{II}$, due to one and two-ion magnetoelastic interactions, respectively. Physically, the single-ion magnetoelastic interaction is due to modulation of the crystal field by the strain. A strain will change the positions of the remaining ions relative to the

position of the ion under consideration, thus the crystal field will change. To lowest order, the single ion magnetoelastic interaction term can be written

$$\mathcal{H}_{me}^I = M_{ijk\ell} S_i S_j \epsilon_{k\ell}$$

where M is the magnetoelastic constant, S_i and S_j are components of the angular momentum of the ion and ϵ_{kl} is the usual infinitesimal strain. This form is not very useful, because it is difficult to apply symmetry to restrict the number of independent magnetoelastic constants. Callen and Callen¹⁹ have derived the single ion Hamiltonian by using the hexagonal symmetry to restrict the form of the Hamiltonian. The six strains ϵ_{xx} , ϵ_{yy} , ϵ_{zz} , ϵ_{zy} , ϵ_{zx} , ϵ_{xy} , transform into each other under the operations of the point group of the ion. The six-dimensional representation they form is reducible into 2 one-dimensional and 2 two-dimensional irreducible representations. The linear combinations of Cartesian strains which form basis functions for the representations are¹⁹

$$\epsilon^{a,1} = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}, \quad \epsilon^{a,2} = \epsilon_{zz} - \frac{1}{3} \epsilon^{a,1}$$

$$\epsilon_1^y = \frac{1}{2} (\epsilon_{xx} - \epsilon_{yy}), \quad \epsilon_2^y = \epsilon_{xy}$$

$$\epsilon_1^e = \epsilon_{yz}, \quad \epsilon_2^e = \epsilon_{xz}$$

where $\epsilon_i^{\Gamma,j}$ ($i = 1, \dots, n$) form the basis for the n -dimensional representation Γ , and $j = 1, 2$ distinguishes between the two possible different sets which may form a basis for the same representation.

The six spin functions for $l = 0, 2$ can also be used as basis functions for these representations. The explicit forms of $\tilde{O}_{00}$ and $\tilde{O}_{2m}$ and details of how they transform among themselves can be found in Appendix 1. From this point on, only coupling between the strains and the spin operators $\tilde{O}_{2m}$ will be considered. The trivial case of coupling to the constant $\tilde{O}_{00}$ is not considered. Likewise, coupling of strains to spin operators O_{lm} $l > 2$ is not considered, because the thermal averages of these higher order operators are very small in the paramagnetic region. This point will be more fully discussed in a later section.

Callen and Callen¹⁹ used group theoretical considerations at this point to determine which strain modes and spin operators are allowed to couple to each other. Generally, χ_{me}^I is given by the expression¹⁹

$$\chi_{me}^I = - \sum_f \sum_{\Gamma} \sum_{j,j'} B_{jj'}^{\Gamma}(f) \sum_i \epsilon_i^{\Gamma,j} S_i^{\Gamma,j'}(f)$$

where f is the position of the ion under consideration, and

$$S_i^{\Gamma,j}(f) \quad (i = 1, \dots, n)$$

are the spin functions forming a basis for the irreducible

representation Γ . Eliminating the terms which are zero (couplings that are now allowed), Callen and Callen¹⁹

obtain

$$\begin{aligned} \mathcal{H}_{me}^I(f) = & - \tilde{B}_{12} \epsilon^{d,1} \int^{d,2}(f) - \tilde{B}_{22} \epsilon^{d,2} \int^{d,2}(f) - \\ & \tilde{B}^{\delta} [\epsilon_1^{\delta} S_1^{\delta}(f) + \epsilon_2^{\delta} S_2^{\delta}(f)] - \\ & \tilde{B}^{\epsilon} [\epsilon_1^{\epsilon} S_1^{\epsilon}(f) + \epsilon_2^{\epsilon} S_2^{\epsilon}(f)] \end{aligned}$$

In Southern and Goodings'¹ notation,

$$\begin{aligned} \mathcal{H}_{me}^I(j) = & - M_{20}^{d,1} \epsilon^{d,1} \tilde{O}_{20}(\vec{s}_j) - \\ & M_{20}^{d,2} \epsilon^{d,2} \tilde{O}_{20}(\vec{s}_j) - \\ & M_{21}^{\epsilon} [\epsilon_1^{\epsilon} i \tilde{O}_{21}^{+}(\vec{s}_j) + \epsilon_2^{\epsilon} (-i) \tilde{O}_{21}^{-}(\vec{s}_j)] - \\ & M_{22}^{\delta} [\epsilon_1^{\delta} \tilde{O}_{22}^{+}(\vec{s}_j) + \epsilon_2^{\delta} \tilde{O}_{22}^{-}(\vec{s}_j)] \end{aligned}$$

where

$$M_{20}^{d,1} = \sqrt{1/3} \tilde{B}_{12}^d \quad M_{20}^{d,2} = \sqrt{1/3} \tilde{B}_{22}^d$$

$$M_{21}^{\epsilon} = \sqrt{2/3} \tilde{B}^{\epsilon} \quad M_{22}^{\delta} = \sqrt{1/3} \tilde{B}^{\delta}$$

and

$$\tilde{O}_{\ell m}^{+} = 1/2 (\tilde{O}_{\ell m} + \tilde{O}_{\ell -m})$$

$$\tilde{O}_{\ell m}^{-} = 1/2 (\tilde{O}_{\ell m} - \tilde{O}_{\ell -m})$$

As might be expected, since the strain deforms the lattice, the symmetry of the crystal field is no longer axial, but also includes terms in $\tilde{O}_{21}$ and $\tilde{O}_{22}$.

The two-ion magnetoelastic coupling is due to modulation of the exchange interaction by the applied strain. An applied strain will change the distance between ions i and j , thus changing J_{ij} and the exchange interaction between the two ions. To lowest order, the two-ion Hamiltonian can be written

$$\mathcal{H}_{me}^{\text{II}}(i, j) = D_{ijkl} \epsilon_{kl} \vec{S}_i \cdot \vec{S}_j$$

where $\vec{S}_i$ and $\vec{S}_j$ are the angular momentum of the ions i and j , and D_{ijkl} is the two-ion magnetoelastic coupling constant. Again allowing the basis strains to couple to $l = 2$ spin functions and applying group theory, $\mathcal{H}_{me}^{\text{II}}$ can be written¹

$$\begin{aligned} \mathcal{H}_{me}^{\text{II}}(i, j) = & -\tilde{D}_{11ij}^a \epsilon^{a,1} \vec{S}_i \cdot \vec{S}_j - \tilde{D}_{21ij}^a \epsilon^{a,2} \vec{S}_i \cdot \vec{S}_j \\ & - \tilde{D}_{12ij}^a \epsilon^{a,1} \sqrt{3}/2 (S_{iz} S_{jz} - 1/3 \vec{S}_i \cdot \vec{S}_j) \\ & - \tilde{D}_{22ij}^a \epsilon^{a,2} \sqrt{3}/2 (S_{iz} S_{jz} - 1/3 \vec{S}_i \cdot \vec{S}_j) \\ & - \tilde{D}_{ij}^x \left[\epsilon_1^x 1/2 (S_{ix} S_{jx} - S_{iy} S_{jy}) + \epsilon_2^x 1/2 (S_{ix} S_{jy} + S_{iy} S_{jx}) \right] \\ & - \tilde{D}_{ij}^y \left[\epsilon_1^y 1/2 (S_{iy} S_{jz} + S_{iz} S_{jy}) + \epsilon_2^y 1/2 (S_{ix} S_{jz} - S_{iz} S_{jx}) \right]. \end{aligned}$$

Notice that in the two-ion Hamiltonian there are terms present, representing coupling of $\tilde{O}_{00}$ to the strains,

which were not present in the one-ion Hamiltonian. These extra terms result from the fact that $\tilde{O}_{oo}(i,i) = \vec{S}_i^2 = S_i(S_i+1)$, is a constant, while $\tilde{O}_{oo}(i,j) = \vec{S}_i \cdot \vec{S}_j$ which is not a constant if $i \neq j$. The discussion of the Hamiltonian, derived in the small strain approximation, is now complete. The next section will discuss finite strain theory, and apply it to this Hamiltonian.

Eastman,²⁰ while measuring the magnetoelastic constants of yttrium iron garnet, and Melcher,²¹ while measuring the elastic constants of antiferromagnetic MnF_2 , obtained experimental results which disagreed with small strain theory, as applied in their particular problems. They found, however, that their results were consistent with the predictions of finite strain theory. The disagreement between small strain theory and experiment, which they found, was due to the fact that small strain theory neglects infinitesimal rotations

$$\omega_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial x_\beta} - \frac{\partial u_\beta}{\partial x_\alpha} \right)$$

which occur in a pure shear strain

$$\frac{\partial u_\alpha}{\partial x_\beta} = \epsilon_{\alpha\beta} + \omega_{\alpha\beta}$$

Small strain theory assumes that the internal energy of a coupled elastic and magnetic system can be expressed in terms of the ϵ 's and $\vec{M}$, the magnetization,

$$U = U_m(\vec{M}) + U_e(\epsilon_{ij}) + U_{me}(\vec{M}, \epsilon_{ij})$$

Equivalently, the Hamiltonian can be expressed in terms of the classical ϵ 's and the spin functions, whose thermal averages are related to the magnetization. Small strain Hamiltonians are generally not rotationally invariant, and therefore do not conserve angular momentum. Finite strain theory insures the rotational invariance of the Hamiltonian by expressing the Hamiltonian in terms of a different set of quantities. Southern and Goodings¹ use the same set of quantities used by Brown²² and Melcher²³:

$$S_{i\mu}^* = R_{\mu\nu} S_i \quad H_\mu^* = R_{\mu\nu} H_\nu$$

$$E_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) + \frac{1}{2} \frac{\partial u_\alpha}{\partial x_\alpha} \frac{\partial u_\beta}{\partial x_\beta}$$

where $R_{\mu\nu}$ is an orthogonal matrix describing a finite rotation of the medium, and $E_{\alpha\beta}$ is the finite strain matrix. This set is particularly useful because it conserves the angular momentum commutation relations. The rotationally invariant finite strain Hamiltonian is obtained by making the substitutions

$$E_{\alpha\beta} \rightarrow \epsilon_{\alpha\beta} \quad \vec{S}^* \rightarrow \vec{S} \quad \vec{H}^* \rightarrow \vec{H}$$

into the small strain Hamiltonian. The first order terms can now be obtained by using the approximations

$$E_{\alpha\beta} = \epsilon_{\alpha\beta} \quad R_{\alpha\beta} = 1 + \omega_{\alpha\beta}$$

The terms which now appear are all those in the small strain Hamiltonian plus, terms linear in $w_{\mu\nu}$ which were not present in the small strain Hamiltonian. These terms, neglected in small strain theory, are responsible for the disagreement of the predictions of small strain theory with experiment found by Melcher²¹ and Eastman.²⁰

This thesis reports only on work done with longitudinal waves, for which $w_{\mu\nu} = 0$ ($\mu = \nu$), so the rotational effects are not important. What is important, however, is that the finite strains $E_{\mu\mu}$ contain second order terms in $\epsilon_{\mu\mu}$, $E_{\mu\mu} \approx \epsilon_{\mu\mu} + \frac{1}{2} \epsilon_{\mu\mu}^2$. Expressions for ΔC_{11} and ΔC_{33} are desired, so the important terms in the Hamiltonian are those proportional to E_{11} and E_{33} , since $\Delta C_{ij} = \frac{\partial^2 U}{\partial \epsilon_i \partial \epsilon_j}$.

Only contributions from the single-ion Hamiltonian will be treated in detail, since the two-ion contribution can be obtained analogously. The terms containing E_{11} and E_{33} are

$$\begin{aligned} \mathcal{H}_E^I = & - M_{20}^{d,1} \sum_i (E_{11} + E_{33}) \tilde{O}_{20}(\vec{s}_i) \\ & - M_{20}^{d,2} \sum_i (\frac{2}{3} E_{33} - \frac{1}{3} E_{11}) \tilde{O}_{20}(\vec{s}_i) \\ & - M_{22}^{\gamma} \sum_i (E_{11} - E_{22}) \tilde{O}_{22}^+(\vec{s}_i) \end{aligned}$$

where E_{22} is included in the last term because E_{11} and E_{22} are not equivalent in it, as they are everywhere else.

Using the approximation

$$E_{\mu\mu} = E_{\mu\mu} + \frac{1}{2} E_{\mu\mu}^2 \quad (\text{no sum on } \mu)$$

and keeping only the terms proportional to $e_{\mu\mu}^2$,

$$\begin{aligned} \mathcal{H}_{e^2}^I = & -M_{20}^{d,1} \sum_i \frac{1}{2} (e_{11}^2 + e_{33}^2) \tilde{O}_{20}(\vec{S}_i) \\ & - M_{20}^{d,2} \sum_i \frac{1}{2} (2/3 e_{33}^2 - 1/3 e_{11}^2) \tilde{O}_{20}(\vec{S}_i) \\ & - M_{22}^{\gamma} \sum_i \frac{1}{2} (e_{11}^2 - e_{22}^2) \tilde{O}_{22}^+(\vec{S}_i) \end{aligned}$$

is obtained. Now it is necessary to calculate the expectation value of $\mathcal{H}$, $U = \langle \mathcal{H} \rangle$, which will involve taking the expectation value of the spin operators. At a finite temperature, the angular momenta of the ions will be precessing around the field with a distribution of orientations. Since the orientation of the angular momentum affects its energy, this fact should be included in the analysis. Callen and Callen²⁴ have derived an expression which can be used to calculate the thermal averages of the spin operators. Their method is to take a weighted average of the possible orientations of the angular momenta, where the Boltzmann factor is used to weight each orientation. This weighted average will be a sum of $2S + 1$ terms where S is the angular momentum of each ion. For large S (as in rare earths) Callen and Callen²⁴ assume this sum can be approximated by an integral over continuous orientations. The integral has a closed form which they give as

$$\langle Y_l^m(\theta, \phi) \rangle_T = \hat{I}_{l+1/2}(\mathcal{J}^{-1}(\sigma)) Y_l^m(\theta, \phi)$$

where (θ, ϕ) specifies the orientation of the field relative to the crystallographic axes. $\hat{I}_{l+\frac{1}{2}}(x) = \frac{I_{l+\frac{1}{2}}(x)}{I_{\frac{1}{2}}(x)}$ where $I_{l+\frac{1}{2}}(x)$ is the modified Bessel function of half-odd integral order, σ is the reduced magnetization $\frac{M}{M_0}$, and $\mathcal{L}^{-1}(x)$ is the inverse Langevin function ($\mathcal{L}(x) = \hat{I}_{3/2}(x) = \text{ctnh}(x) - \frac{1}{x}$).

The only spin operators appearing in $\langle U \rangle$, are $\langle \tilde{O}_{20} \rangle_T$ and $\langle O_{22}^+ \rangle_T$, where $\langle \rangle_T$ signifies thermal average. $\langle \tilde{O}_{20} \rangle_T$ will be worked out in detail. $\tilde{O}_{20} = \frac{1}{2} (3S_z^2 - S(S+1))$, so one would expect that at zero temperature with a small field along the z-axis that $\langle \tilde{O}_{20} \rangle_T = \frac{1}{2} (3S^2 - S(S+1)) = S(S-\frac{1}{2})$. In the paramagnetic region, however, $\langle \tilde{O}_{20} \rangle_T$ will generally be much less than this, because of thermal randomization of the ionic moments. An expression of the form

$$\langle \tilde{O}_{20} \rangle_T = S(S-\frac{1}{2}) f(T) g(\theta, \phi)$$

would be expected, where $f(0) = 1$, and f decreases monotonically with temperature and $g(\theta, \phi)$ accounts for the fact that $\langle \tilde{O}_{20} \rangle_T$ will change as the direction of the applied field is rotated away from the z-axis. Callen and Callen's²⁴ expression for the thermal average allows f and g to be found explicitly. Inspection of the expression

$$\tilde{O}_{20} = \frac{1}{2} (3S_z^2 - S(S+1))$$

gives the angular factor

$$g(\theta, \phi) = P_2^0(\cos \theta) = \frac{1}{2} (3 \cos^2 \theta - 1)$$

The temperature dependence $f(T) = \hat{I}_{5/2}(\mathcal{L}^{-1}(\sigma(T)))$ is easily obtained. The reduced magnetization σ is obtained in the paramagnetic region from a solution of the equation

$$\sigma = \mathcal{L}(y) \quad y = \frac{S g \mu_B H}{k T}$$

For laboratory fields and temperatures in the paramagnetic region, y is small so $\mathcal{L}(y)$ can be expanded in a Taylor series near $y = 0$. The expansion gives to lowest order

$$\mathcal{L}(y) = \frac{1}{3} y, \text{ so } \mathcal{L}^{-1}(\sigma) = 3\sigma. \quad \hat{I}_{5/2}(3\sigma)$$

can now be expanded in a Taylor series

$$\hat{I}_{\ell+1/2}(3\sigma) \approx \frac{1}{(2\ell+1)!!} (3\sigma)^\ell$$

where only the first term is kept because σ is small in the paramagnetic region. It is now possible to justify the neglect of all terms containing the spin operators of order $\ell > 2$. In the paramagnetic region, σ is small (~ 0), so $\langle \tilde{O}_{\ell m} \rangle_T \propto \sigma^\ell$ and only the lowest order operators ($\ell = 0, 2$) will contribute. Now,

$$f(T) = \hat{I}_{5/2}(\mathcal{L}^{-1}(\sigma)) = \frac{3}{5} \sigma^2$$

and

$$\langle \tilde{O}_{20} \rangle_T = \frac{3}{5} \sigma^2 S(S-1/2) P_2^0(\cos \theta)$$

$\langle \tilde{O}_{22}^+ \rangle_T$ is obtained in analogous fashion, with only the angular function being different.

$$\langle \tilde{O}_{22}^+ \rangle_T = \frac{3}{5} \sigma^2 S(S-1/2) \sin^2 \theta \cos 2\phi$$

$U_{\epsilon^2}^I$ can now be written

$$\begin{aligned} U_{\epsilon^2}^I = & -M_{20}^{d,1} \frac{1}{2} (\epsilon_{11}^2 + \epsilon_{33}^2) N_V \frac{3}{5} \sigma^2 S(S-1/2) P_2^0(\cos \theta) \\ & - M_{20}^{d,2} \frac{1}{2} (2/3 \epsilon_{33}^2 - 1/3 \epsilon_{11}^2) N_V \frac{3}{5} \sigma^2 S(S-1/2) P_2^0(\cos \theta) \\ & - M_{22}^{\gamma} \frac{1}{4} (\epsilon_{11}^2 - \epsilon_{22}^2) N_V \frac{3}{5} \sigma^2 \sqrt{6/4} S(S-1/2) \sin^2 \theta \cos 2\phi \end{aligned}$$

or using Southern and Goodings¹ notation

$$\begin{aligned} U_{\epsilon}^I = & -b_1^d \frac{1}{2} (\epsilon_{11}^2 + \epsilon_{33}^2) \frac{3}{5} \sigma^2 P_2^0(\cos \theta) \\ & - b_2^d \frac{1}{2} (2/3 \epsilon_{33}^2 - 1/3 \epsilon_{11}^2) \frac{3}{5} \sigma^2 P_2^0(\cos \theta) \\ & - b_2^{\gamma} \frac{1}{8} (\epsilon_{11}^2 - \epsilon_{22}^2) \sin^2 \theta \cos 2\phi \frac{3}{5} \sigma^2 \end{aligned}$$

where

$$b_1^d = N_V M_{20}^{d,1} S(S-1/2) \quad b_2^d = N_V M_{20}^{d,2} S(S-1/2)$$

$$b_2^{\gamma} = N_V \sqrt{3/2} M_{22}^{\gamma} S(S-1/2)$$

The contributions to ΔC_{11} and ΔC_{33} from the single-ion Hamiltonian can be obtained by differentiating $U_{\epsilon^2}^I$ with respect to the ϵ 's, giving

$$\Delta C_{33}^I = -b_1^{\alpha} \frac{3}{5} \sigma^2 P_2^0(\cos \theta) - b_2^{\alpha} \frac{2}{3} \frac{3}{5} \sigma^2 P_2^0(\cos \theta)$$

$$\Delta C_{11}^I = -b_1^{\alpha} \frac{3}{5} \sigma^2 P_2^0(\cos \theta) + b_2^{\alpha} \frac{1}{3} \frac{3}{5} \sigma^2 P_2^0(\cos \theta)$$

$$+ \frac{1}{4} b_2^{\gamma} \frac{3}{5} \sigma^2 \sin^2(\theta) \cos 2\phi$$

χ_{e2}^{II} can be obtained similarly, from χ_{me}^{II} . The only major difference is that the spin functions appearing in χ_{me}^{II} are two-ion spin correlation functions such as $\langle \vec{S}_i \cdot \vec{S}_j \rangle_T$ or $\langle S_{iz} S_{jz} - 1/3 \vec{S}_i \cdot \vec{S}_j \rangle_T$. These can be evaluated easily, by assuming no spin correlation in the paramagnetic region, and evaluating the thermal average of each ion's angular momentum separately.

Including two-ion contributions, the complete expressions for ΔC_{11} and ΔC_{33} are¹

$$\Delta C_{33} = \left\{ -\left(\frac{3}{5} b_1^{\alpha} + d_{12}^{\alpha}\right) P_2^0(\cos \theta) - \frac{2}{3} \left(\frac{3}{5} b_2^{\alpha} + d_{22}^{\alpha}\right) P_2^0(\cos \theta) - d_{11}^{\alpha} - \frac{2}{3} d_{21}^{\alpha} \right\} \sigma^2$$

$$\Delta C_{11} = \left\{ -\left(\frac{3}{5} b_1^{\alpha} + d_{12}^{\alpha}\right) P_2^0(\cos \theta) + \frac{1}{3} \left(\frac{3}{5} b_2^{\alpha} + d_{22}^{\alpha}\right) P_2^0(\cos \theta) - d_{11}^{\alpha} + \frac{1}{3} d_{21}^{\alpha} + \frac{1}{4} \left(\frac{3}{5} b_2^{\gamma} + d^{\gamma}\right) \sin^2 \theta \cos 2\phi \right\} \sigma^2$$

where

$$d_{11}^{\alpha} = N_v S^2 \frac{1}{2} \sum_j \tilde{D}_{11}^{\alpha}{}_{ij}$$

$$d_{21}^{\alpha} = N_v S^2 \frac{1}{2} \sum_j \tilde{D}_{21}^{\alpha}{}_{ij}$$

$$d_{12}^{\alpha} = N_v S^2 \frac{1}{2} \sum_j \tilde{D}_{12}^{\alpha}{}_{ij}$$

$$d_{22}^{\alpha} = N_v S^2 \frac{1}{2} \sum_j \tilde{D}_{22}^{\alpha}{}_{ij}$$

$$d^{\gamma} = N_v S^2 \frac{1}{2} \sum_j \tilde{D}^{\gamma}{}_{ij}$$

$$\sigma = \frac{M}{M_0} = \frac{\pi_0 H}{M_0}$$

and the upper sign in ΔC_{11} is for propagation along the a-axis. The one and two-ion magnetoelastic constants are grouped in the expression above according to which strain and spin mode coupling they characterize. b_1^α and d_{12}^α , for example, correspond to coupling between $\epsilon^{\alpha,1}$ and $\tilde{O}_{20}$. In the interest of keeping the subsequent equations simple, it is convenient to relabel the magnetoelastic constants

$$\begin{aligned} A &= -3/5 b_1^\alpha - d_{12}^\alpha & B &= -1/5 b_2^\alpha - 1/3 d_{22}^\alpha \\ C &= -d_{11}^\alpha & D &= -1/3 d_{21}^\alpha & E &= 1/4 (3/5 b^\alpha + d^\alpha) \end{aligned} \quad "$$

Application of the equations for ΔC_{11} and ΔC_{33} to calculations of the magnetoelastic constants at a given temperature requires that $\Delta C_{\mu\mu}$ be expressed in terms of $\Delta f/f/H^2$. Using the relations $C_{\mu\mu} = \rho v^2$, $v = 2\ell f$ then $\Delta C_{\mu\mu}$ can be written

$$\Delta C_{\mu\mu} = C_{\mu\mu} \left(\frac{\Delta \rho}{\rho} + \frac{2\Delta v}{v} \right) = C_{\mu\mu} \left(\frac{\Delta \rho}{\rho} + \frac{2\Delta \ell}{\ell} + \frac{2\Delta f}{f} \right).$$

ρ is the mass density M/volume, so for a given mass,

$$\frac{\Delta \rho}{\rho} = - \frac{\Delta \text{volume}}{\text{volume}} = - \frac{\Delta \ell_a}{\ell_a} - \frac{\Delta \ell_b}{\ell_b} - \frac{\Delta \ell_c}{\ell_c}$$

where $\frac{\Delta \ell_a}{\ell_a}$ is the relative change in length along the a-axis of the crystal. The complete expression for $\Delta C_{\mu\mu}$ is then

$$\Delta C_{\mu\mu} = C_{\mu\mu} \left(\frac{2\Delta\ell_x}{\ell_x} + \frac{2\Delta f}{f} - \frac{\Delta\ell_a}{\ell_a} - \frac{\Delta\ell_b}{\ell_b} - \frac{\Delta\ell_c}{\ell_c} \right)$$

where $x = a$ or b is the axis along which the longitudinal wave propagates. For a constant temperature, the $\frac{\Delta\ell}{\ell}$'s are of magnetostrictive origin, and will depend on the orientation of the field. Clark, DeSavage, and Bozorth⁵ have measured these magnetostrictions in single crystal Dy. Following their notation, let $\lambda(x,y) = \frac{\Delta\ell_x}{\ell_x}$ when the field is applied along y-axis. Using strain gauge techniques, Clark et al. measured $\lambda(c,c)$, $\lambda(c,a)$, $\lambda(a,b)$, $\lambda(a,a)$ and $\lambda(a,c)$. In the paramagnetic region, all directions in the basal plane are assumed equivalent, so $\lambda(c,b) = \lambda(c,a)$, $\lambda(b,c) = \lambda(a,c)$, $\lambda(b,b) = \lambda(a,a)$, $\lambda(b,a) = \lambda(a,b)$. Applying these to the five equations for ΔC_{11} and ΔC_{33} in terms of $\Delta f/f$ and the magnetostrictions, the following equations are obtained

$$\Delta C_{33} (H \parallel a\text{-axis}) = C_{33} \left(\frac{2\Delta f}{f} (c,a) + \lambda(c,a) - \lambda(a,a) - \lambda(a,b) \right)$$

$$\Delta C_{33} (H \parallel c\text{-axis}) = C_{33} \left(\frac{2\Delta f}{f} (c,c) + \lambda(c,c) - 2\lambda(a,c) \right)$$

$$\Delta C_{11} (H \parallel a\text{-axis}) = C_{11} \left(\frac{2\Delta f}{f} (b,a) + \lambda(a,b) - \lambda(a,a) - \lambda(c,a) \right)$$

$$\Delta C_{11} (H \parallel b\text{-axis}) = C_{11} \left(\frac{2\Delta f}{f} (b,b) + \lambda(a,a) - \lambda(a,b) - \lambda(c,a) \right)$$

$$\Delta C_{11} (H \parallel c\text{-axis}) = C_{11} \left(\frac{2\Delta f}{f} (b,c) - \lambda(c,c) \right)$$

where the $\frac{\Delta f}{f}$ (c,a) notation is analogous to that used for the λ 's. Figures V-1 and V-2 give the $\frac{\Delta c}{c}$'s for all give cases.

The work of Clark et al.⁵ shows that the λ 's also have an H^2 dependence in the paramagnetic region. This dependence is not surprising, because the static magnetostriction has the same physical origin as the magnetic field dependence of the elastic constants C_{11} and C_{33} . The major contribution to each is the coupling of the $\tilde{\sigma}_{lm}$'s to the strain modes, implying that the field dependence of each is that of $\langle \tilde{\sigma}_{2m} \rangle_T \propto \sigma^2 \propto H^2$ (in the paramagnetic region). Using the fact that $\Delta f/f/H^2$ and λ/H^2 are constants, the magnetoelastic constants can be calculated from the five equations

$$\begin{aligned} [-1/2 A - B + C + 2D] &= \frac{M_0^2 C_{33}}{\chi_{\perp}^2} \left[\frac{2\Delta f}{f} (c,a)/H^2 + \frac{\lambda(c,a)}{H^2} \right. \\ &\quad \left. - \frac{\lambda(a,a)}{H^2} - \frac{\lambda(a,b)}{H^2} \right] \\ [A + 2B + C + 2D] &= \frac{M_0^2 C_{33}}{\chi_{\parallel}^2} \left[\frac{2\Delta f}{f} (c,c)/H^2 + \frac{\lambda(c,c)}{H^2} - \frac{2\lambda(a,c)}{H^2} \right] \\ [-1/2 A + 1/2 B + C - D + E] &= \frac{M_0^2 C_{11}}{\chi_{\perp}^2} \left[\frac{2\Delta f}{f} (b,a)/H^2 + \frac{\lambda(a,b)}{H^2} \right. \\ &\quad \left. - \frac{\lambda(a,a)}{H^2} - \frac{\lambda(c,a)}{H^2} \right] \\ [-1/2 A + 1/2 B + C - D - E] &= \frac{M_0^2 C_{11}}{\chi_{\perp}^2} \left[\frac{2\Delta f}{f} (b,b)/H^2 + \frac{\lambda(a,a)}{H^2} \right. \\ &\quad \left. - \frac{\lambda(a,b)}{H^2} - \frac{\lambda(c,a)}{H^2} \right] \\ [A - B + C - D] &= \frac{M_0^2 C_{11}}{\chi_{\parallel}^2} \left[\frac{2\Delta f}{f} (b,c)/H^2 - \frac{\lambda(c,c)}{H^2} \right] \end{aligned}$$

Figure V-1. Variation of $\frac{\Delta C_{33}}{C_{33}} / H^2$ with Temperature

Figure V-2. Variation of $\frac{\Delta C_{11}}{C_{11}} / H^2$ with Temperature

where $\chi_{\parallel}$ and $\chi_{\perp}$ are the paramagnetic susceptibilities of Dy for fields parallel and perpendicular to the c-axis respectively. $C_{11}(T)$, $C_{33}(T)$, $\chi_{\parallel}(T)$, $\chi_{\perp}(T)$, M_0 and the λ 's were taken from the literature: C_{11} and C_{33} from Rosen and Klimker,⁶ $\chi_{\parallel}$, $\chi_{\perp}$, and M_0 from Behrendt, Levgold and Spedding,⁴ and the λ 's from Clark et al.⁵

The data were analyzed first fitting, at each temperature and for each sample orientation, the $\Delta f/f$ versus H^2 data to a straight line (least squares fit). Since the linearity does not hold as well near the Neel point, the first five points (those taken for the lowest magnitudes of the field) of the $\Delta f/f(c,a)$ and the first four points of the $\Delta f/f(b,a)$ data were used in calculating the slope of the line. These slopes ($\Delta f/f/H^2$), given in Table I, and the data taken from the literature were necessary to specify the magnetoelastic constants. The five equations given above were then inverted at each temperature to find the magnetoelastic constants at that temperature. Figures V-3 and V-4 show these magnetoelastic constants graphed versus temperature, and Table V-2 gives their numerical values. Although the magnetoelastic constants were calculated at temperatures of 180, 185, 190, 195, 200, 210, 220, ..., 300 (K), the inconsistencies in the data above 260K no doubt are reflected in the magnetoelastic constants themselves, reducing their reliability at these higher temperatures. Also, the

Figure V-3. Temperature Dependence of $\frac{3}{5} b_1^\alpha + d_{12}^\alpha$ and $\frac{3}{5} b_2^\alpha + d_{22}^\alpha$ with Corrections for Magnetostriction

MAGNETOELASTIC CONSTANT (10^{11} ergs/cm³)
corrected for magnetostriction

Figure V-4. Temperature Dependence of d_{11}^{α} , d_{21}^{α} , and $3/5 b^{\gamma} + d^{\gamma}$ with corrections for magnetostriction.

Table V-I

Temp. (K)	in units of $10^{-12} [0_e]^{-2}$				
	$-\frac{\Delta f}{f}(c,a)/H^2$	$-\frac{\Delta f}{f}(c,c)/H^2$	$-\frac{\Delta f}{f}(b,a)/H^2$	$\frac{\Delta f}{f}(b,b)/H^2$	$-\frac{\Delta f}{f}(b,c)/H^2$
180	132	4.52	28.9	1.02	.405
185	96.9	8.12	15.4	8.67	.743
190	68.2	7.50	9.45	5.11	.627
195	47.3	6.80	6.06	3.60	.509
200	32.8	6.10	3.98	2.76	.553
210	17.9	4.98	1.82	1.56	.521
220	11.0	4.04	.981	1.40	.310
230	7.18	3.11	.480	.944	.251
240	4.86	2.50	.182	.779	.256
250	3.49	2.04	.147	.510	.145
260	2.56	1.89	.128	.442	.124
270	1.96	1.43	- .0518	.250	.101
280	1.74	1.39	- .00852	.245	.0921
290	1.29	1.07	- .0228	.206	.122
300	1.14	.800	.000525	.143	.0135

Table II

T	$3/5 \ b_1^{\alpha} + d_{12}^{\alpha}$	$3/5 \ b_2^{\alpha} + d_{22}^{\alpha}$	d_{11}^{α}	d_{21}^{α}	$3/5 \ b^{\gamma} + d^{\gamma}$
(K)	$10^{11} \text{ ergs/cm}^3$				
180	-.0977	.0172	4.75	4.75	-2.45
185	.481	.563	5.99	5.99	-3.00
190	.415	.402	5.88	5.88	-2.56
195	.472	.568	5.51	5.51	-2.25
200	.636	.768	5.22	5.22	-2.08
210	.767	.961	4.56	4.56	-1.62
220	.714	.911	4.53	4.53	-1.82
230	.722	.902	3.94	3.94	-1.43
240	.784	.870	3.55	3.55	-1.27
250	.673	.877	3.39	3.39	-1.17
260	.791	1.20	3.38	3.38	-1.28
270	.721	.960	3.11	3.11	- .617
280	.729	1.10	3.33	3.33	- .808
290	.765	.750	2.92	2.92	- .768
300	.394	.529	2.82	2.82	- .712

critical attenuation of ultrasonic waves which occurs near the Neel point²⁵ made the measurements at 180K difficult, so little significance should be attached to the measured values of the magnetoelastic constants there.

If Southern and Goodings'¹ theory takes into account all the physical processes contributing to the magnetoelastic coupling, then, away from the Neel point, the magnetoelastic constants should be independent of the temperature. Near the Neel point, of course, some temperature dependence would be expected due to short range ordering of the moments. The agreement with theory found in this work is fairly good, in that the temperature dependence is small, the worst case being reduced in magnitude by a factor of only 3 over the region of reliable data. Salama et al.¹¹ found much more temperature dependence in the magnetoelastic constants of Tb which they measured by the same method used here. It is likely, however, that at least part of the temperature dependence they found is due to their neglecting magnetostrictive corrections. Figures V-5 and V-6 show the magnetoelastic constants obtained from the data on Dy with no corrections being made for magnetostriction. d_{11}^{α} , d_{21}^{α} , $3/5 b^{\gamma} + d^{\gamma}$ are only slightly affected, but the temperature dependence of $3/4 b_1^{\alpha} + d_{12}^{\alpha}$ and $3/4 b_2^{\alpha} + d_{22}^{\alpha}$ is greatly enhanced near the Neel point, indicating that, at least in Dy, the magnetostrictive corrections are important.

Figure V-5. Temperature Dependence of $\frac{3}{5} b_1^\alpha + d_{12}^\alpha$ and $\frac{3}{5} b_2^\alpha + d_{22}^\alpha$ with no Corrections for Magnetostriction.

Figure V-6. Temperature Dependence of $d_{||}^{\alpha}$, d_{21}^{α} , and $3/5 b^{\gamma} + d^{\gamma}$ with no Corrections for Magnetostriction

Table II gives the calculated values of the magnetoelastic constants in Dy after corrections have been made for magnetostrictions. For the sake of comparison, the magnetoelastic constants for Tb, reported by Salama et al.¹¹ are given in Table III. Although the temperature range was smaller for the measurements made on Tb, the variation of the magnetoelastic constants is larger than that for Dy. Also, there is little correlation in the magnitudes of the corresponding magnetoelastic constants for Dy and Tb. One would, of course, like to check the consistency of these results with those obtained by other methods. Callen and Callen¹⁹ give expressions relating the magnetoelastic constants to the λ 's measured by Clark et al.⁵ Inversion of the equations would allow comparison of the static and dynamic magnetoelastic constants. Unfortunately, the expressions are rather complicated ones involving the elastic constants, thermal averages of the one and two-ion spin functions, and the magnetoelastic constants themselves. In addition, Callen and Callen's expressions are in terms of different magnetoelastic constants (D 's rather than d 's), and their definitions of the strain modes and spin functions differ in normalization from the ones used here. Although a comparison of the static and dynamic cases will be done later, sufficient time was not available to allow the results to be included in this thesis.

Table III

T	$3/5 \text{ } b_1^{\alpha} + d_{12}^{\alpha}$	$3/5 \text{ } b_2^{\alpha} + d_{22}^{\alpha}$	d_{11}^{α}	d_{21}^{α}	$3/5 \text{ } b^{\gamma} + d^{\gamma}$
(K)	$10^{11} \text{ ergs/cm}^3$				
240	-8.87	6.09	.34	20.58	- .40
250	-5.38	3.54	.22	13.13	.22
260	-2.82	4.22	-.38	7.65	.22
270	-1.82	3.83	-.34	6.25	.30
280	-1.32	4.12	-.19	5.76	- .21
290	- .78	2.60	-.01	4.76	- .23
300	- .37	1.84	.17	4.04	.37

In conclusion it can be said that although the evidence is not conclusive, theory and experiment appear to agree fairly well for Dy. The temperature dependence of the magnetoelastic constants, while not negligible, is less pronounced than that found in Tb, probably because of the corrections for magnetostriction which were applied to Dy but not to Tb. The last chapter outlines the plans for future work and for improvement of the results presented here.

VI. Conclusion

There are several ways the results presented here can be improved. Most important, perhaps, is redesign of the sample holders, particularly the plastic one. Temperature control could be improved by mounting the diode closer to the sample. Only a small amount of redesigning of the brass sample holder need be done to accomplish this. Ideally the brass holder should be built to completely enclose the sample with metal when in the dewar, so that the sample would not be excessively chilled by the cold gas which fills the sample chamber. Also, a holder built to hold the sample stationary while in a magnetic field would eliminate the need to use glue or paint to secure the sample, thus removing another thermal barrier. The plastic sample holder should be completely rebuilt from some high thermal conductivity material, and although electrical insulation would be a problem, careful design should allow a great improvement over the present system.

More precise control of the signal generator output frequency would allow increased accuracy in determining small changes in the ultrasonic wave velocity. A suitable voltage controlled oscillator would be an improvement over the present mechanical control.

Procedural as well as mechanical improvements are possible. Slightly distorted waveforms are a difficulty apparently inherent in ultrasonic work done in magnetic fields. These relatively small effects can render the pulse superposition method virtually useless. Measurements made using the pulse overlap method should be little affected by these small effects. The pulse overlap method is similar to the pulse superposition method in that both methods relate the easily and accurately measurable output frequency of a signal generator to the pulse transit time. The two methods are different in that, while in the pulse superposition method the signal generator controls the repetition rate of the applied pulses whose echoes are summed before being displayed, the pulse overlap method uses the signal generator to control the repetition rate of the trigger pulses to the oscilloscope and the echoes are displayed separately and unsummed. The fine adjustment of the frequency is done by aligning the zero crossings of the corresponding rf cycles in each echo, so spurious echoes and other small defects in the waveform should be less critical using the pulse overlap method.

More conclusive proof of the agreement of experiment and theory can be obtained by taking measurements further out in the paramagnetic region, where the theory is expected to be most valid. The decrease in the magneto-elastic coupling with increased temperature requires that

a larger magnetic field be used. Using a superconducting magnet with a maximum field of 50 kOe, would increase the effect of the coupling by a factor of about 9 over that obtained using a 17.65 kOe maximum field. It is anticipated that the measurements above 250K reported in this thesis will be repeated at higher fields and that measurements at higher temperatures will be made in the future.

An improvement in the calculation of the magnetoelastic constants would be the use of values of $\chi_{\perp}$, $\chi_{\parallel}$, C_{11} , C_{33} , and the λ 's which were measured for the same sample whose magnetoelastic constants are being measured, since small amounts of impurities can have a large affect on these quantities.

Finally, a critical examination of Southern and Goodings'¹ theory is planned to insure that all terms quadratic in the ϵ 's are being included. Although finite strain theory has been quite successful in explaining the rotational effects found in shear waves,^{20,21} it is not clear at this point whether it works as well for longitudinal waves. For example, terms quadratic in the finite strains include terms quadratic in the infinitesimal strains which are not included in Southern and Goodings' theory. Since quadratic coupling of the finite strains will involve a different coupling coefficient, it is possible that these additional terms are negligible. It seems however that a more thorough investigation of such terms is desirable.

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Appendix I

Spin Functions

$$\tilde{O}_{20} = \frac{1}{2} [3 S_z^2 - S(S+1)]$$

$$\tilde{O}_{2\pm 1} = \mp \frac{\sqrt{6}}{4} [S_z S_{\pm} + S_{\pm} S_z]$$

$$\tilde{O}_{2\pm 2} = \frac{\sqrt{6}}{4} S_{\pm}^2$$

Spin Basis Functions

Irr. Rep.

$S_i^{\Gamma, j}$

$$\Gamma^{d,1} \quad 1 = \tilde{O}_{00}$$

$$\Gamma^{d,2} \quad \frac{\sqrt{3}}{2} [S_z^2 - \frac{1}{3} S(S+1)] = \frac{1}{\sqrt{3}} \tilde{O}_{20}$$

$$\Gamma^x \quad \frac{1}{2} [S_x^2 - S_y^2] = \frac{1}{\sqrt{6}} [\tilde{O}_{22} + \tilde{O}_{2-2}]$$

$$\frac{1}{2} [S_x S_y + S_y S_x] = \frac{i}{\sqrt{6}} [\tilde{O}_{22} - \tilde{O}_{2-2}]$$

$$\Gamma^e \quad \frac{1}{2} [S_y S_z + S_z S_y] = \frac{i}{\sqrt{6}} [\tilde{O}_{21} + \tilde{O}_{2-1}]$$

$$\frac{1}{2} [S_x S_z + S_z S_x] = \frac{-i}{\sqrt{6}} [\tilde{O}_{21} - \tilde{O}_{2-1}]$$