TEMPERATURE AND MAGNETIC FIELD DEPENDENCE OF THE
SINGLE CRYSTAL ELASTIC CONSTANTS OF NICKEL

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INTRODUCTION

Purpose of the Investigation

The purpose of this investigation was to apply 'state-of-the-art' techniques to determine the single crystal elastic constants of a ferromagnetic material, specifically nickel, to obtain expertise in working with such materials. Supplemental to this was the up-grading of a pulsed ultrasonic apparatus to determine sound velocities; the details of the apparatus can be found in Appendix A.

The data that were desired were the temperature dependence of the demagnetized elastic constants and to measure, if possible, the ΔE effect on single crystal elastic constants quantitatively. The ΔE effect is the change in an elastic modulus from the demagnetized state to the magnetically saturated state. The effect has been thoroughly investigated in polycrystalline samples.

Nickel was chosen for this investigation because of a large ΔE effect, it has been reported to be as large as 30% for polycrystalline samples (1,2), and because the existing data on nickel are incomplete and contradictory.

Review of the Problem and Literature Survey

The unique feature of bulk ferromagnetic bodies is the presence of domains of differing direction of the magnetization vector in the demagnetized state. These domains are separated by magnetic domain walls of finite width (3) which

can be directly observed by several techniques, such as the Bitter technique or electron microscopy (4,5).

It is precisely the presence of domain walls that creates difficulties in using ultrasonic techniques to determine the single crystal elastic constants. The domain walls interact with the ultrasonic stress waves because the domain walls are not static (3). The domain walls can move quite readily under application of stress or magnetic field. In the past the theory was that the domain walls would attempt to oscillate sinusoidally with the same frequency as the applied oscillatory stress or magnetic field (1,6,7). As long as the frequency of the applied force is low enough the domain walls can oscillate in unison with the signal, which produces a strong attenuation effect in the signal due to energy losses as the signal propagates through successive walls. At sufficiently high frequencies, the domain walls can no longer follow the period of the applied signal and the attenuation becomes less severe.

Very recent work by Bostanjoglo (8) with thin film specimens of nickel, using direct observation in an electron microscope, has indicated that, contrary to the existing theories, the domain walls do not appear to be completely coupled to ultrasonic excitations. He finds that as the frequency of the excitation increases, parts of a domain wall begin to vibrate with an amplitude about equal to the wall width with no larger amplitudes being observed. At higher frequencies

large wall portions jumped to neighboring stable positions and back, but that the motion was not sinusoidal. He also noted that the positions that the walls jumped to were the same as the ones reached under an applied static magnetic field. At sufficiently high frequencies either the domain configurations were changed or the domain magnetization vectors were changed. However, the gross effects upon an ultrasonic stress wave propagating through an unsaturated ferromagnetic sample would appear to be the same with regards to attenuation and transit time changes as a function of frequency.

Nickel also exhibits a marked frequency dependence of the sound velocity in the demagnetized state in the range 2-20 MHz (9). The sound velocity increases with stress wave carrier frequency until a plateau at about 15 MHz is reached. In this investigation all measurements were made at a carrier frequency of 10 MHz. The difference between values obtained at 15 and 10 MHz is not large, being approximately 0.1% and is not really significant in terms of the measurements made in this work. Differences in velocities measured at 15 and 10 MHz for magnetically saturated samples are so small that they cannot be measured.

Another effect in saturated nickel is the velocity dependence upon the direction of an applied magnetic field. This is due to magneto-elastic coupling. The effects are also small, being on the same order as the frequency dependence. Alers

et al. (10) and Sakurai (11) have both obtained good results on this effect for nickel and it was not felt necessary to try and re-do their work.

There has been a large amount of work done on the single crystal elastic constants of nickel (1,11-18); the great bulk of the work has been done on magnetically saturated crystals though. Few measurements of demagnetized samples have been made, due mostly to experimental difficulty in propagating a signal in an unsaturated state. It was thought appropriate to try and measure the temperature dependence of a demagnetized sample to fill the existing gap in the literature and to try and measure the single crystal ΔE effect to clear up some of the controversy in regards to the magnitude of the effect (1). Also, the value of the Debye temperature, θ_D , of the demagnetized state was desired to compare it to the saturated value calculated by Alers, Neighbors and Sato (14) to see if there was any notable difference.

EXPERIMENTAL PROCEDURE

Sample Preparation

Two single crystal boules each approximately 2 cm in diameter and 6 cm in total length were grown in a modified Bridgman furnace for this investigation. One of the boules was grown from J. T. Baker Chemical Company reagent grade nickel shot under a partial atmosphere of helium in an Al_2O_3 crucible. The other boule was grown from Jarrell-Ash nickel rod, also under a partial atmosphere of helium in an Al_2O_3 crucible.

An analysis of the two crystals was performed by the Analytical Service Group using spark mass spectrometry, vacuum fusion and wet chemical techniques. Table 1 lists the impurity content of both materials after the growing process; Table 1 also contains an analysis of a Jarrell-Ash nickel rod in the as received condition. The analyses indicate that some Al and Si were introduced into the materials during the crystal growing process. The purities of the crystals were calculated to be 99.84 at.% for the Baker nickel crystal, 99.91 at.% for the Jarrell-Ash crystal and the rod was 99.96 at.%.

Two single crystals were cut from each boule. The Baker nickel boule was oriented and cut in such a manner as to yield one crystal having two sets of parallel $\{110\}$ faces and another set of parallel $\{100\}$ faces. The second crystal had three sets of parallel $\{100\}$ faces. These crystals are referred to in the

Table 1. Impurity content in atom ppm of the materials used in this investigation

Impurity	Baker nickel	Jarrell-Ash nickel	Jarrell-Ash nickel
	Crystal	Crystal	Rod
H ^a	<1	<1	3
Li	-	-	-
Be	<0.1	<0.1	<0.1
B	5	2	0.2
Ca ^a	219	29	6
Na ^a	ND	ND	ND
O ^a	2	3	4
F	0.2	0.3	2
Ne	<10	<6	<0.6
Na	50	100	100
Mg	2	0.87	16
Al	150	200	0.2
Si	150	300	30
pa	1.4	2.3	2.4
S	10	<0.5	<7
Cl	6	7	30
Ar	<3	<30	<20
K	0.6	1	2
Ca	1	10	8
Sc	<0.02	0.05	0.03
Ti	<0.2	<0.2	<0.3
V	<0.07	0.2	<0.03
Cr	0.8	<0.1	<0.3
Mn	0.48	1.1	<0.04
Fe ^a	2.3	0.5	1.8
Co	4	<0.3	<0.3
Cu	22	2	8.3
Zn	<0.3	<0.2	0.8
Ga	0.9	4	<0.06
Ge	<0.5	<0.5	<0.6
As	0.4	0.5	0.9
Se	0.1	0.3	0.6
Br	<0.09	<0.09	0.3
Kr	<2	<2	<2
Rb	<3	<3	<4
Sr	<0.3	<0.3	<0.3
Y	<0.8	<2	<1
Zr	<2	<1	8
Nb	<7	<50	<50
Mo	<1	<1	3
Ru	<0.3	<0.3	<0.4
Rh	<0.07	<0.08	<0.09

^aWt ppm results.

Table 1. (Continued)

Impurity	Baker nickel Crystal	Jarrell-Ash nickel Crystal	Jarrell-Ash nickel Rod
Pd	<0.4	<0.4	<0.5
Ag	20	0.1	0.2
Cd	<0.06	<0.07	<0.08
In	<0.03	<0.03	<0.04
Sn	<0.4	<0.4	<0.5
Sb	<0.05	<0.05	<0.05
Te	<0.5	<0.6	<0.6
I	<0.04	<0.04	<0.04
Xe	<1	<2	<2
Cs	0.02	0.03	0.09
Ba	<0.09	0.3	0.5
Hf	<2	<2	<2
Ta	<0.3	<0.3	<0.4
W	<3	9	<3
Re	<0.5	<0.5	<0.6
Os	<2	<2	<2
Ir	<0.5	<0.5	<0.6
Pt	<0.4	<0.4	<0.5
Au	<0.09	0.09	0.3
Hg	<0.2	0.4	<0.2
Tl	<0.06	<0.06	<0.07
Pb	<0.2	<0.2	<0.2
Bi	<0.04	<0.05	<0.05
Ra	<10	<10	<10
Th	6	20	20
U	<0.3	<0.3	<0.3
La	<0.2	<0.2	<0.2
Ce	<1	<2	<2
Pr	<0.2	<0.2	<0.7
Nd	<1	<1	<1
Sm	<0.4	<0.4	<0.5
Eu	<0.1	<0.1	<0.2
Gd	<4	<6	<5
Tb	<6	<2	<4
Dy	<0.5	<0.5	<0.6
Ho	<0.6	<2	<3
Er	<0.6	<0.7	<0.7
Tm	<0.2	<0.2	<0.2
Yb	<0.5	<0.6	<0.6
Lu	<0.3	<0.3	<0.4

text as Ni-B-1 and Ni-B-2, respectively.

The other boule, of Jarrell-Ash nickel, was oriented and cut to yield a crystal with the same type of orientation as Ni-B-1; the other crystal cut from the boule had one set of parallel {111} faces with the other faces cut to give a rectangular shape to the sample without regard to their orientation. These two crystals are referred to in the text as Ni-JA-1 and Ni-JA-2, respectively. Figure 1 gives the sample shapes and dimensions.

All orientations were done using standard back-reflection Laue X-ray techniques with the boule cemented to a three circle goniometer. Each set of crystal faces used in this investigation was oriented to within $\pm 1^\circ$. The faces were cut using a Sparkatron spark erosion machine with the crystal still attached to the goniometer. After cutting, each set of surfaces was polished flat and parallel to within ± 0.0002 cm using hand-lapping techniques. After thorough chemical etchings the crystals were individually sealed in evacuated Vycor capsules and annealed at approximately 625°C for a minimum of five hours, then furnace cooled.

Powder X-ray samples were prepared directly from the as-grown single crystals by filing from the surface of each boule. In the case of the Jarrell-Ash boule, powder samples were taken from both the outer as-grown surface and from the interior by filing from a cleaned and polished spark cut sur-

Figure 1. Orientation and shapes of the samples used in this investigation, dimensions are in cm

face. The powders were sealed in evacuated Vycor capsules and annealed at 600°C for at least one and a half hours and then allowed to furnace cool.

X-ray diffraction patterns were taken using Ni-filtered copper $K_{\alpha 1}$ and $K_{\alpha 2}$ radiation in a 114 mm Debye-Scherrer camera. The lattice parameter for each material was obtained from a weighted least-squares program using the Taylor-Sinclair-Nelson-Reilly error function; the program was written by Dr. F. X. Kayser of the Ames Laboratory. Table 2 lists the lattice parameter at 25°C and the X-ray density.

Table 2. Lattice parameter and corrected density for the as-grown Baker nickel and Jarrell-Ash nickel crystals

Sample No.	a_o (Å)	ρ (gm/cm ³)	At.% Ni
Ni-B-1 & 2	3.524 ₉	8.900 ₅	99.84
Ni-JA-1 & 2 ^a	3.535 ₅	8.895 ₉	99.91
Ni-JA-1 & 2 ^b	3.525 ₁	8.898 ₉	99.91

^a Powder sample taken from the outer surface of the boule.

^b Powder sample taken from the interior of the boule.

The densities in Table 2 have been calculated by correcting the mass of the average metal atom in the crystal by using the analyses given in Table 1. The contributions due to interstitial impurities were neglected in this calculation. The value for Avagadro's number used in this calculation was 6.022045×10^{23} atoms/mole.

Acoustic Measurements

Velocity of sound measurements were made using a modified pulse-echo-overlap (PEO) system whose details are given in Appendix A. Gold plated 10 MHz x and y-cut quartz transducers were used to introduce longitudinal and shear mechanical waves into the samples. Nonaq stopcock grease was used as the bonding agent between the transducer and the sample for all temperatures and propagation modes. The sample was held in a spring loaded copper container for all measurements. Sample dimensions were measured using a micrometer and parallelism of the sample faces was checked by several measurements over the face of the sample.

Samples Ni-B-1 and Ni-B-2 were used for the zero applied field fixed point temperature data. The temperature was maintained by completely immersing the sample and sample holder in the appropriate bath. The fixed temperature points were taken at the normal boiling points of helium and nitrogen, at the normal sublimation point of dry ice and at the ice point of water. Sample Ni-JA-1 was used for the continuous temperature dependence measurements without an applied field. The sample container was non-inductively wound with a manganin resistance heater. The temperature was controlled by an Artronix 5301 temperature controller using a Minco S209 platinum resistance thermometer as the sensing element. The sample temperature was determined by taping a copper-constantan thermocouple

directly to the sample and using a Newport 2400A digital millivolt meter to read the voltage.

The usual procedure for taking temperature dependent data was to immerse the sample in liquid nitrogen. This set the transducer-to-specimen bond and permitted a data point to be taken at a well determined temperature. The sample was then placed in a glass double Dewar whose outer jacket was filled with liquid nitrogen but whose inner chamber was filled with dry helium gas. The sample was allowed to come to equilibrium at the inner chamber temperature, usually near 80 K.

Data points were then taken in 5 K intervals up to whatever temperature the signal became too small to measure, usually near 250 K. The sample was then allowed to cool back down to 80 K with spot checks taken at selected temperatures to see if the data were consistent. During the heating and cooling cycles the rate of temperature change was approximately 1 K per minute. After the sample had again reached 80 K the inner chamber of the Dewar was filled with liquid helium and a fixed point at the normal boiling point of helium was taken. The helium was slowly boiled off after equilibrating by maintaining a small current in the sample heater. After the helium was gone the sample temperature was increased at the rate of about 1 K per minute with data being taken at 5 K intervals beyond 20 K. Data were not taken between 4 K and 20 K because the sensitivity of the thermocouple was very low

in this range. Above 20 K points were taken at 5 K intervals up to 100 K to insure that the data coincided with previously obtained values.

The actual sample temperature was known to only about ± 2.0 K in the low temperature range where the sensitivity was low and to about ± 1.0 K at higher temperatures. The temperature controller held the temperature stable to approximately an order of magnitude better than the temperature was actually known.

A Harvey-Wells Magnion electromagnet with five inch diameter pole pieces with a three inch air-gap was used for the single crystal elastic constant ΔE investigation. Data were taken at room temperature (296 K) and liquid nitrogen temperature (77 K). The room temperature values were taken by holding the sample and sample holder in the desired orientation in the center of the magnet gap with styrofoam blocks so that the sample could not move. The 77 K data were obtained by placing a quartz tube containing the sample and liquid nitrogen between the pole pieces. The tube was small enough in diameter so that the sample could not move when inside it.

The magnetic field strength was measured by a Rawson rotating coil gaussmeter. The highest field attainable with this magnet was 14.4 KOe. although in all cases but one any ΔE effect observed was completed before the field reached 4.0 KOe.

RESULTS

Zero Applied Field Measurements

Figures 2, 3 and 4 are plots of data for the three independent elastic modes for the [110] propagation direction as a function of temperature. The data in these figures have not been corrected for thermal expansion. Figure 2 is a plot of the longitudinal mode, $1/2(C_{11}+C_{12}+2C_{44})$; Figure 3 is a plot of the shear mode, C_{44} ; Figure 4 is a plot of the shear mode, $1/2(C_{11}-C_{12})$. Appendix B contains a brief discussion of crystal elasticity including the possible elastic constant combinations available from specific stress wave propagation directions.

Table 3 lists the experimentally determined elastic constants with no thermal expansion corrections, also in Table 3 are the values of smoothed elastic constants that have been corrected for thermal expansion using the data of Nix and MacNair (19) for pure nickel. In Figure 3 there is an apparent jump in the data near 210 K. The jump in the data is apparently due to the fact that the sample was held at that temperature overnight and finishing the data run the next morning.

The reproducibility and internal consistency of the data were extensively tested at one temperature (77 K) by measuring all the propagation modes for all the crystals several times after thermal cycling and bond changes. Table 4 contains the

Figure 2. Nickel [110] longitudinal mode temperature dependence in zero applied magnetic field

Figure 3. Nickel [110] shear mode temperature dependence in zero applied magnetic field

Figure 4. Nickel [110] shear mode temperature dependence in zero applied magnetic field

Table 3. Values of the raw experimental data taken in zero applied field and values of the smoothed data corrected for thermal expansion, $\times 10^{12}$ dynes/cm²

Temp. °K	Experimental values			Smoothed values		
	$1/2(C_{11}+C_{12}+2C_{44})$	C_{44}	$1/2(C_{11}-C_{12})$	$1/2(C_{11}+C_{12}+2C_{44})$	C_{44}	$1/2(C_{11}-C_{12})$
0	3.371 ₁	1.309 ₇	0.532 ₅	3.365 ₇	1.307 ₇	0.531 ₇
20	3.370 ₈	1.309 ₀	0.532 ₄	3.365 ₇	1.307 ₇	0.531 ₇
40	3.369 ₅	1.308 ₉	0.532 ₁	3.365 ₀	1.307 ₂	0.531 ₄
60	3.366 ₈	1.307 ₁	0.530 ₇	3.361 ₄	1.304 ₇	0.530 ₀
80	3.359 ₈	1.302 ₃	0.528 ₄	3.354 ₇	1.300 ₃	0.527 ₅
100	3.353 ₃	1.296 ₂	0.525 ₄	3.345 ₉	1.294 ₅	0.524 ₃
120	3.340 ₃	1.289 ₃	0.521 ₄	3.335 ₇	1.287 ₈	0.520 ₆
140	3.329 ₁	1.281 ₄	0.517 ₂	3.324 ₅	1.280 ₅	0.516 ₇
160	3.316 ₅	1.273 ₇	0.513 ₀	3.312 ₈	1.272 ₉	0.512 ₆
180	3.304 ₅	1.265 ₇	0.508 ₈	3.300 ₆	1.265 ₀	0.508 ₃
200	3.290 ₅	1.258 ₆	0.504 ₂	3.288 ₁	1.256 ₉	0.503 ₉
220	3.279 ₇	1.252 ₁	0.499 ₈	3.275 ₄	1.248 ₆	0.499 ₄
240	3.265 ₄	1.245 ₇		3.262 ₅	1.240 ₃	0.494 ₉
260				3.249 ₄	1.231 ₈	0.490 ₄
280				3.236 ₂	1.223 ₃	0.485 ₈
300				3.223 ₀	1.214 ₇	0.481 ₂

Table 4. Data taken at 77 K to determine repeatability and internal consistency, zero applied magnetic field

Sample no.	Propagation direction	Elastic mode	$\times 10^{12}$ dyne/cm ²
Ni-B-1	[110]	$1/2(C_{11}+C_{12}+2C_{44})$	3.369 ₀
Ni-B-1	[1 $\bar{1}$ 0]	$1/2(C_{11}+C_{12}+2C_{44})$	3.371 ₃
Ni-JA-1	[110]	$1/2(C_{11}+C_{12}+2C_{44})$	3.361 ₄
Ni-B-1	[110];[001]	C_{44}	1.294 ₄
Ni-B-1	[1 $\bar{1}$ 0];[001]	C_{44}	1.300 ₈
Ni-B-1	[001]	C_{44}	1.296 ₂
Ni-JA-1	[110];[001]	C_{44}	1.298 ₂
Ni-JA-1	[001]	C_{44}	1.291 ₆
Ni-B-2	[001]	C_{44}	1.303 ₅
Ni-B-1	[110];[1 $\bar{1}$ 0]	$1/2(C_{11}-C_{12})$	0.528 ₃
Ni-B-1	[1 $\bar{1}$ 0];[110]	$1/2(C_{11}-C_{12})$	0.521 ₉
Ni-JA-1	[110];[1 $\bar{1}$ 0]	$1/2(C_{11}-C_{12})$	0.526 ₃
Ni-B-1	[001]	C_{11}	2.613 ₃
Ni-B-1 ^a	[110]	C_{11}	2.602 ₉
Ni-B-1 ^a	[1 $\bar{1}$ 0]	C_{11}	2.592 ₄
Ni-B-2	[001]	C_{11}	2.602 ₅
Ni-B-2	[010]	C_{11}	2.611 ₂
Ni-JA-1	[001]	C_{11}	2.592 ₃
Ni-JA-1 ^a	[110]	C_{11}	2.599 ₂
Ni-B-1 ^a	[110]	C_{12}	1.546 ₃
Ni-B-1 ^a	[1 $\bar{1}$ 0]	C_{12}	1.548 ₆
Ni-JA-1 ^a	[110]	C_{12}	1.546 ₆
Ni-JA-2	[111]	$1/3(C_{11}+2C_{12}+4C_{44})$	3.652 ₅
Ni-JA-2	[111]	$1/3(C_{11}-C_{12}+C_{44})$	0.786 ₀

^a C_{11} and C_{12} were calculated by solving the three simultaneous equations obtained from the particular [110] direction of propagation.

measured values for the various propagation modes, the crystal and the particular set of faces used. For Ni-B-1 and Ni-JA-1 there were two possible sets of different [110] directions and one [001] direction of propagation. The measured values of Ni-JA-2 are also included in this table. Not all of the faces of each crystal were used because of limited size or because the orientation was known to be skewed by more than 1° .

Field Dependent Measurements

Figures 5 thru 10 represent the room temperature magnetic field dependence of the directly measurable elastic modes. Graphs of the field dependence for waves propagating in the [111] direction are not included because the signal amplitude at all fields was too small to accurately measure. For most of the samples it was impossible to propagate any signal at all at room temperature without applying a magnetic field approaching 1 kilogauss, consequently many of the possible propagation modes for various crystals are not represented.

One of the interesting things noted in this investigation was the behavior of the shear velocity corresponding to $1/2(C_{11}-C_{12})$. It was found that the change in sound velocity was virtually over when the applied field strength reached 4.0 KOe for the other modes, not so for $1/2(C_{11}-C_{12})$. This mode showed a small field dependence out to the highest field attainable with the magnet arrangement.

Table 5 contains the saturated values of the room temperature elastic constants and the values reported by other

Figure 5. Magnetic field dependence of C_{11} at 300 K, propagation direction is $[001]$, $H \parallel [010]$

Figure 6. Magnetic field dependence of $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ at 300 K with $H \parallel [001]$

Figure 7. Magnetic field dependence of C_{44} at 300 K, propagation direction is $[001]$, $H \parallel [010]$

Figure 8. Magnetic field dependence of C_{44} at 300 K, propagation direction is $[110]$, $H \parallel [001]$

Figure 9. Magnetic field dependence of $1/2(C_{11}-C_{12})$ at 300 K, $H||[001]$

Figure 10. Magnetic field dependence of $1/2(C_{11}-C_{12})$ at 300 K showing high field dependence

Table 5. Values of the saturated elastic constants at 296 K (10 MHz signal frequency)

Worker	C_{11} $\times 10^{12}$ dyne/cm ²	C_{44} $\times 10^{12}$ dyne/cm ²	C_{12} $\times 10^{12}$ dyne/cm ²
Present investigation	2.515 ₉	1.234 ₁	1.536 ₈
Alers <u>et al.</u> (14)	2.508	1.235	1.500
Bozorth <u>et al.</u> (1)	2.53	1.22	1.58
Neighbors <u>et al.</u> (12)	2.52 ₈	1.23 ₈	1.52
Epstein and Carlson (15)	2.523	1.251	1.547
Sarma and Reddy (16)	2.503	1.224	1.511
De Klerk and Musgrave ^a (13)	2.46 ₅	1.24 ₉	1.47 ₃
Sakurai ^a (11)	2.51	1.24	1.53

^aUsed signal frequency of 5 MHz.

workers. At liquid nitrogen temperatures there was essentially no measurable single crystal ΔE effect, however, it was noted that near 1 KOe a marked change in signal amplitude occurred for all modes.

For the shear modes the magnetic field was applied parallel to the atomic motion and perpendicular to it. No measurable change in velocity was observed for C_{44} , but a 0.2% change was found in $1/2(C_{11}-C_{12})$. Due to the sample holder geometry the field could not be applied in any manner except perpendicular to the particle motion for the longitudinal velocity measurements. Levy and Truell (18) did attempt to measure a single crystal ΔE effect for a field parallel and a field perpendicular to a longitudinal particle motion, but their instrument was not sensitive enough to detect the small velocity changes expected.

DISCUSSION

Magnetic Field Dependence

The attempt to measure single crystal ΔE effects for various propagation modes was only partially successful. Since pulses could not be propagated through the samples at room temperature and zero applied field for most of the possible modes, it is difficult to say anything quantitative about the effect. Two approaches were taken to remedy the problem; for those modes where a signal could be obtained without a field at room temperature and for those modes where a reasonable estimate of the demagnetized elastic constant was possible the change was expressed as

$$\Delta = [(C^S - C_0)/C_0] \times 100 \quad (1)$$

where C^S is the particular elastic modulus at saturation and C_0 is the same elastic modulus at zero applied field.

Table 6 lists directly measured and estimated Δ 's for the crystals. The second approach was to fit the temperature dependent, zero field data to a functional form and extrapolate the demagnetized data to 300 K to calculate Δ . The data were fit to a function of the form

$$C_{ij} = C_{ij}^0 - s/(e^{t/T} - 1) \quad (2)$$

where C_{ij}^0 is the elastic constant value at zero degrees Kelvin, T is the temperature in degrees Kelvin, C_{ij} is the value of the elastic constant at any particular T and s and t are adjustable parameters. The values of s and t were found by

Table 6. The change in the elastic moduli at 300 K from zero applied field to saturation, $\times 10^{12}$ dyne/cm²

Sample	Elastic constant mode	Zero field	Saturated (12.4 KOe)	$\Delta\%$
Ni-B-1	$1/2(C_{11}+C_{12}+2C_{44})$	3.248	3.262	0.43
"	"	3.24 ^a	3.258	0.56
"	"	3.24 ^a	3.259	0.59
Ni-JA-1	"	3.20 ^a	3.254	1.69
Ni-B-2	C_{11}	2.499	2.517	0.72
Ni-JA-1	"	2.490	2.518	1.12
Ni-B-2	C_{44}	1.231	1.235	0.33
Ni-B-1	"	1.23 ^a	1.234	0.33
"	"	1.23 ^a	1.234	0.33
Ni-JA-1	"	1.21 ^a	1.234	1.98
"	$1/2(C_{11}-C_{12})$	0.49 ^a	0.499	-- ^c
Ni-B-1	"	0.48 ^a	0.489	-- ^c
Ni-JA-1	$1/2(C_{11}+C_{12}+2C_{44})$	3.223 ^b	3.260	1.15
"	C_{44}	1.215 ^b	1.234	1.56
"	$1/2(C_{11}-C_{12})$	0.481 ^b	0.490	1.87
"	C_{11}	2.487 ^b	2.516	1.17
"	C_{12}	1.524 ^b	1.537	0.85

^aEstimated values.

^bExtrapolated from zero field, temperature dependent data.

^cEffect observed, but too small to quantitatively measure.

linearizing Equation 2 and varying t in small steps until the proper value for the slope was obtained. The linearized form of the equation is;

$$\ln(C_{ij}^0 - C_{ij}) = -\ln(e^{t/T} - 1) + \ln s \quad (3)$$

Thus the correct slope was constrained to be -1.00 and the intercept of the line yielded $\ln s$. The straight lines calculated by varying t were fitted using a linear-least-squares approach to obtain the slope and intercept for each t . The data used in the computation were corrected for thermal expansion. The values of the smoothed data given in Table 3 were computed using Equation 2. The validity of Equation 2 is discussed by Varshni (20).

The fit to the experimental values obtained from Equation 2 was quite good, the difference between the measured and computed elastic constants was usually on the order of $\pm 0.0005 \times 10^{12}$ dyne/cm². The fitting parameters for the temperature dependent data are given in Table 7.

Table 7. Fitting parameters for the zero field temperature dependence of the elastic constants.

Parameter	$1/2(C_{11} + C_{12} + 2C_{44})$	C_{44}	$1/2(C_{11} - C_{12})$
$C_{ij}^0 (x10^{12} \text{ dyne/cm}^2)$	3.365 ₇	1.307 ₇	0.531 ₇
$s (x10^{12} \text{ dyne/cm}^2)$	0.1484	0.0934	0.0486
$t (^{\circ}\text{K})$	213.80	208.70	202.20

In Table 6 is also the ΔE effect change calculated from the zero field data extrapolated to 300 K and the directly measured saturation values at 300 K. The values for Δ obtained from the extrapolation tend to be larger for a particular mode than the estimated or directly measured Δ .

The magnitude of the single crystal ΔE effect for the extrapolated cases agrees fairly well with the data of Bozorth et al. (1), except that they find that the changes in the shear constants are significantly larger than that of the longitudinal constant. They find that the changes in the shear values are between three and four times as large as the change in the longitudinal mode they measured. However, one must take into account that the domain configuration for a given sample shape may be quite different from that of another (3), so that only approximations may be made for the relative change between propagation modes of different samples.

No attempt was made to calculate demagnetizing factors for the sample geometries used in this investigation as the problem is very complex. Therefore, the actual field seen by an atom in the crystal is not known. However, the agreement between other work, which used disk shaped samples (1), and the present work using roughly cubic samples regarding the field at which the ΔE effect was completed is quite good. Generally the field at which the elastic constant appeared to stop changing was near 1.5 KOe. For $1/2(C_{11}-C_{12})$ the elastic

constant showed a rapid change, as did all the other measured modes, up to near 1.5 KOe but then instead of remaining a virtual constant there was a small field dependence out to the highest field attainable. The significance of this is not known.

An attempt was also made to measure the ΔE effect at liquid nitrogen temperature. The magnitude of the change was very small for a given sample. As mentioned in the previous section a marked amplitude change occurred at this temperature near 1.0 KOe for all propagation modes but there were virtually no velocity changes. The values of the saturated elastic constants at 77 K are listed in Table 8.

Table 8. Elastic constants of nickel at 77 K in a saturating magnetic field, $\times 10^{12}$ dyne/cm²

Investigator	$1/2(C_{11}+C_{12}+2C_{44})$	C_{44}	$1/2(C_{11}-C_{12})$
Present work	3.381 ₀	1.304 ₆	0.525 ₀
Alers <u>et al.</u> (14)	3.362	1.310	0.547
Sarma and Reddy (17)	3.354 ₀	1.293 ₅	0.540 ₄
Present work (demagnetized)	3.363 ₄	1.297 ₅	0.525 ₅

The values of the present work in Table 8 represent averages of all the measurements from all of the samples for both the saturated and demagnetized data. As can be seen from the average values an apparent measurable ΔE effect does exist at

77 K but the effect for any particular measurement was small. The uncertainty for the average values of the elastic constant combinations is roughly $\pm 0.004 \times 10^{12}$ dyne/cm², with the largest uncertainty in $1/2(C_{11}-C_{12})$ and the smallest uncertainty in C_{44} .

Zero Field Temperature Dependence

The most striking difference between the present investigation and the temperature dependence of the magnetically saturated elastic constants done by Alers, Neighbors and Sato (14) is the difference in C_{12} . Even making allowances for the ΔE effect the difference at all temperatures is large, being on the order of 1.5 to 2%. The overall accuracy of the elastic constants measured in this investigation is estimated to be $\pm 0.5\%$ and probably better than that at the fixed temperature points. The temperature dependent values of C_{11} , C_{44} and C_{12} found in this investigation were extrapolated to the Curie temperature (631 K) with the results being 2.332×10^{12} dyne/cm², 1.069×10^{12} dyne/cm² and 1.525×10^{12} dyne/cm², respectively. The differences between the extrapolated and measured values of Alers et al. (14) are 1.30%, -3.26% and 3.11%, respectively, which is adequate considering the length of the extrapolation.

As was mentioned in the previous section there was an apparent "annealing" phenomenon observed in the absence of a magnetic field. The effect was most prominent in C_{44} , see Figure 3 near 210 K. The effect was first noticed when the

sample was held at the same temperature for a few hours or more and then completing the data run. If the sample was then cooled back down from the break in the data, the line of new data was displaced roughly parallel to that observed previously. The effect was looked for and found in the other shear mode and the longitudinal mode. The magnitude of the effect was much smaller in the latter cases. The effect did show the same characteristics upon cooling and heating as did C_{44} . In Figure 2 near 200 K and in Figure 4 near 165 K small jumps in the data can be seen due to holding the sample at a constant temperature for a period of time. The data used in the fitting function, especially for C_{44} , was chosen to minimize this effect.

One possible explanation is a slow rearrangement of the domain configuration. This is proposed because the PEO continued to input stress waves into the sample throughout the time the sample was being held at temperature. However, the changes in velocity are quite small, being almost within the estimated experimental error.

The bulk modulus and Debye temperature were calculated for the demagnetized case. The bulk modulus at 300 K was calculated for the demagnetized state using the extrapolated elastic constants while the saturated state bulk modulus was calculated from the averaged values of the saturated measurements. The demagnetized bulk modulus at 300 K is $1.847_9 \times 10^{12}$.

dyne/cm², while that for the saturated case is $1.863_3 \times 10^{12}$ dyne/cm².

The Debye temperature was calculated from the demagnetized constants using the 4.2 K values as being good approximations of the zero Kelvin values. The Debye temperature was calculated using the method of Overton and Schuch (21). The calculated temperature was found to be 471.6 K for the demagnetized state as compared to 476 calculated by Alers et al. (14) from their saturated measurements.

SUMMARY

A series of nickel single crystals of different starting material and orientation were prepared to measure the magnetic field dependence of the single crystal elastic constants and to measure the temperature dependence of the elastic constants in the demagnetized state. The measurements were performed using a pulsed ultrasonic method of determining sound wave velocities in solids.

Three things of interest found in this investigation were; (1) the apparent magnetic field dependence of $1/2(C_{11} - C_{12})$ at high magnetic fields; (2) the large difference between the previously considered "best" value of C_{12} and the value obtained in this investigation; (3) the apparent "annealing" effect of the elastic constants in the demagnetized state. Measurements of quantitative values for the single crystal ΔE effect were only partially successful due to signal attenuation at zero applied magnetic field. Extrapolation of the demagnetized data using Varshni's functional form (20) was used to estimate the single crystal ΔE effect and to calculate the room temperature zero applied field elastic constants and bulk modulus.

The Debye temperature was calculated from the low temperature demagnetized data and compared to the value calculated by Alers et al. (14) from saturated data and no significant difference was found.

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APPENDIX A

Pulse-Echo-Overlap System

It is generally accepted that the easiest and most accurate way to determine the adiabatic single crystal elastic constants is by measuring the velocity of sound in the sample. Various electronic schemes have been devised to introduce sound waves in samples and to measure their velocity (22).

The ease in using the pulse-echo-overlap system (PEO) outlined by May (23) and developed by others (24,25,26) and the elimination of an empirical determination of the transit time error produced by the transducer-to-specimen bond thickness made the PEO the most promising for this work.

Figure A1 is a block diagram of the PEO ultrasonic system that was constructed at this laboratory. The components of the system are: a General Radio 1330-A bridge oscillator; a Computer Measurements Company 726C Counter; a General Radio 1217-B pulse generator to serve as the pulse shaper; a Hewlett-Packard 222A pulse-delay generator; a Hewlett-Packard 180D oscilloscope with 1820C and 1801A plug-in modules; an Arenberg attenuator; a frequency divider and pulsed oscillator constructed by the Ames Laboratory Instrumentation Group. Figures A2 and A3 show the circuit diagrams of the frequency divider and pulsed oscillator, respectively.

The system functions by using the bridge oscillator frequency as a relative time base to synchronize all the com-

Figure A1. PEO block diagram

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ponents to the same repetition rate. The frequency of the sine-wave generated by the bridge oscillator is divided by 10, 100 or 1000 by the frequency divider; the pulsed oscillator and pulse-delay generator are then synchronized together by a -4 V spike output from the divider.

When measuring the transit time the oscilloscope is triggered externally by the bridge oscillator and the appropriate portion of the oscilloscope trace is intensified by the pulse-delay generator. To get an overlap, the horizontal time base of the oscilloscope is adjusted and the final overlap is accomplished by adjusting the bridge oscillator frequency until there is a one-to-one cycle correspondence in each echo packet.

Generally, there is not a precise one-to-one cycle correspondence even in adjacent echoes due to dispersion of the signal by orientation errors (27), dislocations and other imperfections in the sample. This difficulty is taken care of by overlapping a large number of echoes in one group and using an average transit time which gives the group the best cycle correspondence rather than using the transit time obtained from overlapping only two adjacent echoes.

The estimated accuracy of the system is one part in ten thousand with respect to the transit time. However, due to uncertainties in the sample dimensions, orientation errors, etc., the total accuracy of the measured sound velocities is estimated to be on the order of 0.25%.

APPENDIX B

Crystal Elasticity and Wave Propagation

For sufficiently small strains the stress is directly proportional to the strain. This behavior is expressed by Hooke's law (28);

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl} \quad (1A)$$

Where the σ_{ij} 's are the tensor stress components, the ϵ_{kl} 's are the tensor strain components and the C_{ijkl} 's are the elastic constants. Due to constraints placed upon the crystal we have the condition

$$C_{ijkl} = C_{ijlk} = C_{jikl} \quad (2A)$$

This reduces the number of possible independent elastic constants from 81 to 36. The notation can be condensed to a matrix form,

$$\sigma_i = C_{ij} \epsilon_j \quad (3A)$$

It can be further shown that $C_{ij} = C_{ji}$. This leaves only 21 possible independent constants for the lowest symmetry crystal.

Nye (29) and Kittel (30) have shown that for a cubic crystal there are only three independent elastic constants, labeled C_{11} , C_{12} and C_{44} . The equations of motion of a stress wave in a cubic crystal for various orientations have been treated by Kittel. He shows that the following combinations of the elastic constants can be obtained from velocity of

sound measurements if the density of the sample is known.

For a wave propagating in the $[110]$ direction there are three possible solutions, for a longitudinal wave

$$\rho v_L^2 = 1/2(C_{11} + C_{12} + 2C_{44}) = C_L \quad (4A)$$

for a transverse wave polarized in the $[001]$ direction

$$\rho v_{T_1}^2 = C_{44} \quad (5A)$$

for a transverse wave polarized in the $[1\bar{1}0]$ direction

$$\rho v_{T_2}^2 = 1/2(C_{11} - C_{12}) = C' \quad (6A)$$

Propagation in the $[100]$ or $[111]$ direction only allows measurements of two combinations of elastic constants because only one transverse mode is possible. For waves propagating down $[100]$ the equations are

$$\rho v_L^2 = C_{11} \quad (7A)$$

$$\rho v_T^2 = C_{44} \quad (8A)$$

where v_L and v_T are the longitudinal and transverse velocities, respectively. For waves propagating down $[111]$ the equations are

$$\rho v_L^2 = 1/3(C_{11} + 2C_{12} + 4C_{44}) \quad (9A)$$

$$\rho v_T^2 = 1/3(C_{11} - C_{12} + C_{44}) \quad (10A)$$

where v_L and v_T are, again, the longitudinal and transverse velocities, respectively and ρ is the crystal density in all the equations.

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