ULTRASONIC ATTENUATION IN SUPERCONDUCTING MOLYBDENUM

by

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A DISSERTATION

IN

PHYSICS

Submitted to the Graduate Faculty
of Texas Tech University in
Partial Fulfillment of
the Requirements for
the Degree of

DOCTOR OF PHILOSOPHY

Approved

Accepted

December, 1972

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CHAPTER I

INTRODUCTION

Properties and Theory of Superconductors

Since the discovery of superconductivity in 1911,¹ the unique characteristics of superconductors have fostered a wide range of both theoretical and experimental inquiries. Of these characteristics, the most notable are the apparent infinite conductivity and perfect diamagnetism (Meissner Effect) exhibited by superconducting metals.^{2,3} These effects occur in all superconductors at temperatures below a characteristic transition temperature (T_c) which varies from one superconductor to the next.

It is also evident, however, that superconductors still exhibit a degree of normal metal properties below the transition temperature. Evidence of this is found in studies of the temperature dependence of the critical magnetic field, specific heat, and thermal conductivity of superconductors. These studies, among others, have suggested that superconductivity is primarily a property of the conduction electrons in metals at low temperatures. These studies also suggest that the normal state characteristics of superconductors are most strongly evident near T_c and completely vanish as the superconductors' temperatures approach absolute zero.⁴

This combination of two different kinds of effects,

normal metal characteristics and the special superconducting effects, led to phenomenological models such as that of Gorter and Casimir.^{5,6} These investigators were attempting to explain the exponential decrease in the electronic contribution to the specific heat of superconductors. Their model envisioned a superconductor as containing two separate electron seas. The first of these seas consisted of normal state electrons which in every way behaved as if no superconducting effects were present in the metal. The second sea consisted entirely of electrons responsible for the effects associated with superconductivity. It was assumed that as the temperature decreased, the number of "superconducting electrons" increased at the expense of the number of "normal electrons." This temperature dependent population would cause the superconductor to be devoid of normal metal effects at absolute zero. The Gorter and Casimir model was not entirely quantitatively successful in explaining all the phenomena associated with superconductivity. However, the model did offer a reasonable qualitative picture of superconductivity.

Two developments led to an improved, quantum mechanical model for superconductivity. The first of these developments was a growing awareness that some sort of energy gap must exist between the energies of the normal state and superconducting state electrons. The exponential decrease with temperature of the electronic specific heat has already

been mentioned. Such a decrease could suggest a two-level energy system with an exponential type probability of occupation.⁷ In addition, measurements of high frequency resistivity indicated that infrared photons could destroy the superconducting state below the transition temperature.⁸ The second important development was the discovery of the isotope effect. It was discovered that T_c depended on m , the isotopic mass, and that T_c varied as $m^{-1/2}$.^{9,10} This discovery strongly suggested that superconductivity occurred because of some interaction between electrons and crystal lattice vibrations (phonons).

The above considerations led to a microscopic theory of superconductivity as proposed by Bardeen, Cooper, and Schrieffer (hereafter referred to as BCS).¹¹ Details of this theory and analyses of it are presented elsewhere and will not be presented here. However, it should be profitable to discuss some of the principal features of the theory which have reference to ultrasonic attenuation in superconductors.

The BCS theory suggests that superconductivity occurs because of a fundamental type of electron-phonon interaction. In a metal, the nearly-free conduction electrons repel each other because of coulombic interactions. These electrons also interact with the crystal lattice. Since the lattice in a metal consists of the positive metal ion cores, the movements of the conduction electrons can produce charge

density fluctuations in the lattice. Electrons in a metal obey Fermi-Dirac statistics. These statistics imply that the most likely elementary excitations which take place involving electrons in a metal will involve only electrons with energies within $k_B T$ order of the Fermi energy in that metal. The constant k_B is Boltzmann's constant and T is the absolute temperature. At high temperatures $k_B T$ is of the same order as thermal phonon energies, and electrons can excite these normal lattice vibrational modes by scattering events with the lattice of ion cores. At temperatures where superconducting effects take place (1.0 to 10.0 Kelvin), however, $k_B T$ is about two orders of magnitude less than thermal phonon energies. However, because of the Heisenberg uncertainty relationship

$$\Delta E \Delta t \sim h, \quad (1)$$

electron interactions with the lattice can momentarily produce a "virtual" phonon. The BCS theory envisions that one electron in a momentum state $\vec{k}_1$ emits a virtual phonon of wavevector $\vec{q}$. This electron is thus scattered to a state

$$\vec{k}_1' = \vec{k}_1 - \vec{q} \quad (2)$$

A second electron of wavevector $\vec{k}_2$ absorbs this phonon

according to

$$\vec{k}_2' = \vec{k}_2 + \vec{q} \quad . \quad (3)$$

So in the entire process, momentum is conserved.

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_1' + \vec{k}_2' \quad (4)$$

This process may be visualized as the transmission of a lattice charge density fluctuation from the vicinity of one electron to the vicinity of the other. BCS envisions that this type of process can lead to screening of the electron charges by the lattice. The net result is that the electron pair (called a Cooper pair) can form a bound state with a lower overall energy than for the separate electrons. For the special type BCS process to occur

$$\vec{k}_1 = -\vec{k}_2$$

$$\vec{k}_1' = -\vec{k}_2' \quad (5)$$

Also, the paired electrons will most likely have opposite spins. The quantum mechanical wave function associated with the paired electrons has a spatial extent of the order of 10^{-4} centimeters. This not only indicates that the pairing is a long range effect, but it also suggests that there is considerable overlap between different pairs.¹²

It may in fact be best to regard the superconducting state as a collective state of paired electrons in which each pair continually scatters according to Eq.(4) and Eq.(5).

These arguments quite naturally lead to the concept of an energy gap in the electronic density of states function of a superconductor. In a normal metal, the excitation of electrons from the Fermi sea into quasi-particle states is governed by the Fermi-Dirac statistics. Thus, an electron may be excited from a momentum state $\vec{k}_1$ to a momentum state $\vec{k}_2$ if the state $\vec{k}_2$ is unoccupied. This process then leaves the state $\vec{k}_1$ open for another electron. In the superconducting state, when an electron pair is excited from the Cooper pair state $(\vec{k}_1, -\vec{k}_1)$ a certain amount of energy must be first provided to break up this pair. This energy must be provided since the transferral of either the electron in $\vec{k}_1$ or the electron in $-\vec{k}_1$ to another momentum state precludes the existence of an electron pair in the state $(\vec{k}_1, -\vec{k}_1)$. Also, since this reduces the total number of states which superconducting electron pairs have available for scattering into, the total collective energy of the pair is reduced.¹³

The energy necessary to destroy a superconducting electron pair is of the order of 10^{-7} electron-volts. This energy can be provided from outside the superconductor, hence the previously mentioned destruction of the superconducting state by high frequency radiation. But there

is also an available source of energy inside the superconductor which destroys pairs. This energy is the energy associated with thermal phonons. At the temperatures at which superconductivity takes place, these energies can be calculated from the Debye theory.¹⁴ This theory also predicts that the dominant phonon mode in a low temperature solid will shift to lower energies as the temperature decreases. This suggests that fewer electron pairs will be destroyed by thermal phonons as the temperature of the superconductor decreases. This picture agrees with the fact, widely confirmed experimentally, that the energy gap in the electron density of states increases as the temperature decreases.

Ultrasonic Attenuation in Superconductors

One of the principal sources of ultrasonic attenuation in metals at low temperatures is the interaction between ultrasound and conduction electrons. In the normal state of a metal, Pippard¹⁵ has shown that the ultrasonic attenuation depends on the ultrasonic frequency and the electron mean free path. At low temperatures in pure metals, the mean free path is limited by electron-thermal-phonon interactions and electron-impurity interactions. Electron-thermal-phonon interactions decrease in probability as the temperature decreases. Thus the mean free path will eventually be limited by impurities and will be, therefore, independent of tempera-

ture. The normal state attenuation will then depend only on the frequency and this dependence will be determined by the ratio of the electron mean free path to the dominant phonon wavelength associated with the ultrasound.

In the superconducting state, the ultrasonic attenuation will again depend on the interaction of sound waves with normal electrons. If the frequency of ultrasound is sufficiently high (10^{10} hertz), the ultrasound will not only interact with normal electrons, but also will destroy superconducting electron pairs. For lower frequencies, however, the ultrasonic attenuation will depend only on those normal state electrons already present in the superconductor. If the energies associated with the ultrasonic phonon are much less than the energy required to bind two electrons into a Cooper pair, then the ratio of the superconducting to normal state ultrasonic attenuation is given by:¹⁶

$$\frac{\alpha_s}{\alpha_n} = \frac{\alpha}{\exp[\Delta(T)/k_B T] + 1} \quad (6)$$

where $\Delta(T)$ is the temperature dependent energy gap. The expression Eq.(6) was originally derived for the case of electron mean free paths longer than the ultrasound phonon wavelength. Tsuneto,¹⁷ however, has shown that Eq.(6) is equally valid for the opposite case.

Superconductivity in Molybdenum

Superconductivity was discovered in molybdenum by Geballe et.al.¹⁸ in 1962. The consensus of work since that time indicates that this superconductor has a transition temperature of about 0.92 Kelvin.¹⁹⁻²³ The critical field at zero Kelvin for molybdenum has been found to be between 95 and 114 gauss.²³

One of the most important measurable quantities characterizing a superconductor is the value of the energy gap at zero Kelvin, $\Delta(0)$. This important quantity is predicted by BCS to be

$$\Delta(0) = 1.76 k_B T_c \quad (7)$$

It should be noted that Eq.(7) as well as Eq.(6) were developed for an ideal superconductor with an isotropic Fermi surface and an isotropic crystal structure. Such oversimplification is no doubt not the case in a real metal with a complicated electronic structure such as molybdenum. In general, it would be expected that the energy gap in molybdenum would be anisotropic.^{22,24,25} In addition, it is possible that molybdenum has two or more different energy gaps associated with superconductivity.²⁴

Only a few attempts have been made to measure the zero Kelvin energy gap in superconducting molybdenum.¹⁹⁻²³ Agreement between various investigators has been only fair.

All investigators do obtain values which are below the value predicted by Eq.(7). Using ultrasonic methods, Jones and Rayne have found anisotropy in the energy gap.²⁰ Unfortunately, however, the values which these authors obtain for $\Delta(0)$ for various crystallographic orientations do not agree with values obtained for these same orientations by other investigators using similar techniques.^{19,21} No experimental results have been offered by any investigator for multiple gaps in molybdenum.

Confronted with the interesting possibilities of energy gap anisotropy and multiple gaps in superconducting molybdenum, it was decided to make a detailed study of the ultrasonic attenuation in normal and superconducting molybdenum. Thus far ultrasonic studies in molybdenum by other investigators have been confined to frequencies above about 200 megahertz. The probable reason for this is the relatively small value of the electronic attenuation in molybdenum at low ultrasonic frequencies.²⁶ It was felt that an improved ultrasonic experiment could be constructed which would circumvent this problem. This experiment is described in detail in Chapter II.

To be specific, an investigation has been made of the ultrasonic attenuation in normal and superconducting molybdenum at temperatures of 1.2 Kelvin and less. In expectation of anisotropic effects, the ultrasonic attenuation has been measured for ultrasound propagated in each of

three crystallographic directions: $[100]$, $[110]$, and $[111]$. From these measurements, a characteristic effective energy gap has been found for each orientation. These gaps have been determined by fitting the ultrasonic attenuation data to an equation of the form of Eq.(6). In making this fit an attempt has been made to include the possibilities of multiple energy gaps for each orientation. Since Eq.(6) indicates that the energy gap should be frequency independent, measurements were made so as to detect any anomalous frequency dependence of the energy gap.

CHAPTER II

EXPERIMENTAL APPARATUS

Introduction

The function of the experimental apparatus to be described is to measure the temperature dependence of the ultrasonic attenuation in normal and superconducting molybdenum. Molybdenum exists in the superconducting state only for temperatures of less than about 0.92 degrees Kelvin (K). Thus the experiment must consist of an electronic system capable of accurately measuring ultrasonic attenuation in molybdenum single crystals at these temperatures, a cryostat capable of reaching these temperatures, and accurate thermometry capable of monitoring these temperatures. These requirements quite naturally divide a discussion of the experimental apparatus into three parts. First, a discussion will be made of the ultrasonic technique and the electronic equipment used to measure the ultrasonic attenuation. Second, the He^3 refrigerator-cryostat and its associated apparatus will be considered. Third, the discussion will center on the thermometers and the method of their calibration.

Ultrasonic Method

The experimental technique used to determine the amount of ultrasonic attenuation in superconducting molybdenum was the pulse-echo method. This technique was developed during and shortly after the Second World War as an aid to the study

of the mechanical properties of matter. It was quickly recognized that the ultrasonic pulse-echo method would be a valuable experimental tool for the physicists studying basic mechanisms in solid single crystals.²⁷ In their pioneering work, Bommel²⁸ and Mackennon²⁹ showed that the method was sensitive enough to detect electron-phonon interactions in metals at low temperatures and ultrasonic frequencies of 10 megahertz (MHz) and greater. Since that time the technique has been widely applied to low temperature studies of metals in both the normal and superconducting state.

The core of the pulse-echo ultrasonic method is illustrated by Figure 1. The figure is a schematic representation of the single crystal specimen to be studied, the ultrasonic transducer, and the mechanical bond between them. The transducers to be considered here are of the piezoelectric type³⁰ and are plated on both ends but not plated on the sides. A radio frequency (r.f.) pulse of about two microseconds duration is impressed onto the plated transducer. The piezoelectric effect in the transducer converts this pulse into a mechanical strain at the same frequency. This strain is transmitted as an ultrasonic pulse through the bond and into the specimen. After traveling through the specimen, the pulse is reflected from the far end of the specimen and returns to the transducer as an echo. At the transducer, the piezoelectric effect works in reverse, and the echo produces an r.f. signal which can be sampled and detected. The remainder

FIGURE 1
SPECIMEN, BOND, AND TRANSDUCER

FIGURE 2
ULTRASONIC ECHO TRAIN DISPLAY

of the energy in the first echo is transmitted back out into the specimen to produce yet another echo. After many such repetitions of this process, an amplified oscilloscope display is obtained as in Figure 2. This display shows the initial pulse and accompanying echo train as a function of the time. The time from one echo to the echo immediately following is the round-trip time for an ultrasonic pulse through the specimen. This suggests that specimen length must be a major consideration in the preparation of single crystal samples for ultrasonic studies. Echoes produced in too short a specimen can superimpose, making the interpretation of the echo pattern difficult if not impossible.

Definition of the Attenuation Coefficient

In Figure 2, the voltage height of each echo is an amplified representation of the amplitude of the ultrasonic echoes at the transducer. A quantitative description will now be obtained for the decrease in amplitude of the initial ultrasonic pulse as a function of the distance this pulse travels through the specimen. It is assumed that this pulse is a monochromatic plane wave passing through a homogeneous specimen. The decrease in pulse amplitude over a distance dx is given by

$$d\sigma(x) = -\alpha\sigma(x)dx \quad (8)$$

where $\sigma(x)$ is the pulse amplitude and α is defined as the

attenuation coefficient. This coefficient characterizes all the energy loss mechanisms in the specimen and is independent of x by the assumption of homogeneity. The amplitude of the ultrasonic pulse is then given by solving Eq.(8):

$$\sigma(x) = \sigma_0 e^{-\alpha x} \quad (9)$$

where σ_0 is the initial amplitude of the ultrasonic pulse. This is the envelope function of the echo train shown in Figure 2. This expression may be also written

$$\ln_e \sigma(x) = \ln_e \sigma_0 - \alpha x \quad (10)$$

Then, for two different points x_1 and x_2 where $x_1 < x_2$, the attenuation coefficient can be expressed as the difference of two equations of the type Eq.(10).

$$\alpha = \frac{1}{x_2 - x_1} \ln_e \left[\frac{\sigma(x_1)}{\sigma(x_2)} \right] \quad (11)$$

where α is expressed in the units of nepers per unit length. It is more customary to change the logarithmic base and to write

$$\alpha = \frac{20}{x_2 - x_1} \log_{10} \left[\frac{\sigma(x_1)}{\sigma(x_2)} \right] \quad (12)$$

where α is now expressed in decibels (db) per unit length.³¹

As the voltage on the transducer is a measure of $\sigma(x)$ (each time the pulse reaches the transducer) the α can be readily obtained from a display as in Figure 2. If V_0 is the voltage corresponding to the initial generation of the ultrasonic pulse, and V_j is the voltage corresponding to the arrival of the j th echo at the transducer, then

$$\alpha = \frac{1}{2(jL)} 20 \log_{10} \left(\frac{V_0}{V_j} \right) \quad (13)$$

where L is the length of the specimen.

In the experiment to be discussed, the intention was to study α as a function of the temperature T . During the course of each measurement, the value of V_0 was held constant. It was assumed that the value of the attenuation coefficient was known at some reference temperature, T_{ref} . Then at any other temperature, T , the attenuation coefficient is, from Eq.(13)

$$\alpha(T) = \alpha_{ref}(T_{ref}) + \frac{10}{jL} \log_{10} \left[\frac{V_j(T_{ref})}{V_j(T)} \right] \quad (14)$$

The voltages $V_j(T_{ref})$ and $V_j(T)$ represent the amplified transducer voltage for the j th echo at temperatures T_{ref} and T respectively. Clearly, if measurements can be made on echo heights as a function of temperature from a display such as Figure 2, then the attenuation as a function of temperature can be calculated from Eq.(14).

Electronic Equipment

There are a number of time-tested techniques for making ultrasonic attenuation measurements.³² The equipment to be described is in most respects similar to that which is in standard usage. However, it was foreseen that the attenuation changes in superconducting molybdenum might be quite small at low frequencies. It was felt that the usual electronics might not be sufficiently sensitive to measure these changes with an acceptably low experimental error. For this reason some improvements were made over the conventional techniques. These improvements are modeled after the ultrasonic apparatus of Hemphill,³³ with the principal difference being that his system was designed to operate at frequencies above 200 MHz.

A block diagram of the electronic apparatus is shown in Figure 3. The Roman numerals on this diagram at various locations around the circuit have reference to the illustrations of Figure 4.

Despite the complexity of Figure 3, the philosophy behind this equipment arrangement is straightforward. It was designed to detect small changes in an ultrasonic echo height as a function of the molybdenum specimen's temperature. It was anticipated that these changes would be so small that random electronic noise in the data could become a significant problem. To circumvent this noise problem, the ultrasonic sending and receiving circuits were electronically chopped at a fixed reference frequency. Echoes were then detected

FIGURE 3
ELECTRONIC EQUIPMENT

ILLUSTRATION I, PULSE GENERATOR ONE OUTPUT

ILLUSTRATION II, REFERENCE SIGNAL

ILLUSTRATION III, AND GATE OUTPUT

ILLUSTRATION IV, DISPLAY SCANNER OUTPUT

FIGURE 4

SELECTED WAVEFORMS FROM

ELECTRONIC EQUIPMENT CIRCUIT

at the chopping frequency, and all other frequencies were discriminated against. This allowed for selective amplification of the changes in the echo heights without corresponding amplification of noise.

In the course of operation, the first Hewlett-Packard model 212 pulse generator operated in an internally triggered mode at a frequency of 800 Hz. This generator simultaneously sent a trigger signal to the Hewlett-Packard model 175A oscilloscope and produced a pulse of about ten microseconds duration. The output of this pulse generator is Illustration I of Figure 4. The period $\tau_1 = 1/800$ second. This signal was sent to the binary counter and the AND gate (see Appendix A). The four-stage binary counter divided the 800 Hz signal to produce a 50 Hz square wave shown in Illustration II of Figure 4. The period $\tau_2 = 1/50$ second. This 50 Hz square wave was sent to the Princeton Applied Research model 121 lock-in amplifier to serve as a reference chopping frequency. The square wave was also sent from the binary counter to the AND gate. The AND gate allowed pulses to be sent from the first pulse generator to the second pulse generator during only one-half of the period τ_2 . So the input trigger to the second Hewlett-Packard model 212 pulse generator was as shown in Illustration III, Figure 4. This second pulse generator triggered the Arenberg pulsed oscillator, producing r.f. pulses of about two microseconds duration (adjustable). The voltage amplitude of these r.f. pulses was adjustable from

about one volt to several hundred volts peak to peak. These pulses were sent through an electrical "tee" into the cryostat where each pulse produced an ultrasonic echo train, as previously described. The electronic signal corresponding to this echo train returned from the cryostat to the Arenberg model PA-620SN pre-amplifier. This pre-amplifier had tuning circuits which could be used to match the impedance of the cryostat to the 93 ohm impedance of the Arenberg receiver system. The pre-amplifier also clipped the r.f. pulse from the oscillator to approximately one volt in order to prevent saturation of the pre-amplifier circuits. The output from the pre-amplifier was sent directly to an Arenberg model WA-600-D wide-band amplifier. This amplifier was a combination r.f. amplifier and video amplifier. The output of the video amplifier was sent to the vertical input of the oscilloscope where the display was as in Figure 2. The oscilloscope had a Hewlett-Packard model 1782A display scanner plug-in which made it possible to manually sample the amplitude of the oscilloscope trace at any point along the trace. During an experiment, this point was selected to coincide with the peak of one given echo. The output from the display scanner then approximated a 50 Hz square wave whose amplitude was proportional to the amplitude of the echo. This output is shown as Illustration IV, Figure 4. This last signal was fed to the lock-in amplifier where all noise having frequency components different from 50 Hz was filtered from the signal. From this

signal the lock-in amplifier put out a D.C. signal which was proportional to the amplitude of the echo being sampled. This output was displayed on the vertical axis of a model 2X2A Moseley X-Y recorder.

Cryogenic Apparatus

In order to study the ultrasonic attenuation in superconducting molybdenum, it was necessary to utilize a He^3 refrigerator modified for ultrasonic applications. This type of refrigerator is capable of reaching temperatures in the vicinity of 0.3 K and sustaining these temperatures for a period of many hours. The instrument is most useful between temperatures of about 0.3 K and 1.5 K. Within this range, it is an easy task to regulate and stabilize the refrigerator's temperature to any chosen value. The He^3 refrigerator is thus ideal for the study of superconductors having transition temperatures in the neighborhood of 1.0 K.

The He^3 refrigerator to be discussed was based on the design of Robbins and Marshall.³⁴ Their instrument attained temperatures of 0.3 K and was capable of sustained operations for a period of about three hours. This time limitation was due to the rate at which liquid He^4 surrounding the refrigerator's cryostat boiled away. This cryostat was constructed for use in specific heat and magnetic susceptibility experiments. Large induction coils associated with the magnetic susceptibility experiment made the cryostat physically too large to be deeply immersed in the He^4 bath. Recharges of liquid He^4

at two to three hour intervals were required in order to keep the entire cryostat continually covered with liquid He^4 .

To extend the operating time, a new cryostat was constructed for the ultrasonic experiments. It was possible to retain all of the original refrigerator's apparatus external to the cryostat. The cryostat was constructed minus the susceptibility coils and it rested deeply in the He^4 bath when in operation. Although the new cryostat could conceivably be used for other types of experiments, it was specifically designed for ultrasonic measurements. A schematic representation of the refrigerator is shown in Figure 5. Although principal structural parts are indicated in this figure, electrical wiring has been omitted in the interest of clarity.

In operation, the cryostat was situated in a glass double dewar system. The outer dewar was filled with liquid nitrogen at 77.4 K. The inner dewar was filled with liquid He^4 . By sealing the inner dewar and pumping on the He^4 , the boiling point of this liquid could be lowered to about 1.5 K. If gaseous He^3 was now admitted from the storage tank into the He^3 pumping line, it began to condense and fall into the evaporation can. At first, the liquid He^3 immediately evaporated upon reaching the relatively warm He^3 can. This carried heat away from the can and the specimen. Through a cyclic process of condensation and evaporation (the so-called

FIGURE 5
REFRIGERATOR-CRYOSTAT

reflux stage) the He^3 can was eventually cold enough so that the condensing liquid He^3 collected in the can. By pumping on the liquid He^3 , it was possible to lower the temperature of the boiling He^3 , the He^3 can, and the specimen. Temperature control was obtained by regulating the vapor pressure above the liquid He^3 . This regulation was obtained by means of a controlled leakage of He^3 gas from the storage tank back into the pumping line. The rate of this leakage determined the pumping rate of the He^3 pump, and hence, the temperature of the He^3 liquid.

The lowest temperature could be obtained from the refrigerator by minimizing the heat leaks into the He^3 can and maximizing the pumping rate through the He^3 pumping line. The length of time that the refrigerator could operate depended on the total amount of He^3 gas in the system, the efficiency with which this gas could be condensed, and the heat leak. Optimum performance from the refrigerator represented a compromise on the above considerations.

By far the most important single factor affecting the performance of the refrigerator was the He^3 pumping line. This line represented one of the principal paths for heat leaks into the high vacuum can. And its physical dimensions of length and diameter affected the pumping rate directly. Robbins and Marshall decided on an inside diameter of 0.5 inches (in.) for this line. This decision represented a

compromise between a small diameter line with its accompanying small heat leak and low pumping rate, and a large diameter line with a relatively larger heat leak and relatively higher pumping rate. The pumping line on the ultrasonic cryostat was constructed in accord with this decision, but with one important change. As mentioned earlier, it was desired to lengthen the time interval that the refrigerator operated at low temperatures. With this in mind, the high vacuum can of the ultrasonics cryostat was located approximately 28.2 centimeters (cm) deeper into the He^4 dewar than the can of the earlier cryostat. It was expected that this would leave the high-vacuum can submerged in the liquid He^4 for an appreciably longer time. This meant that the pumping line had to be lengthened by 28.2 cm. This lengthening did reduce the heat leak into the high vacuum can somewhat, but it also lowered the effective pumping rate through the line.

The pumping line was constructed of 0.010 in. wall thickness type 304 stainless steel tubing. This material was advantageous for the construction of the pumping line for two reasons. First, the steel tubing is sufficiently strong that very thin walls can be used so as to reduce the rate of heat flow along the length of the pumping line. Second, the 304 stainless steel has a relatively low thermal conductivity at temperatures near 1.0 K.³⁵ It should be noted that since the pumping line passed through the He^4

bath, it was effectively thermally grounded at 1.5 K. This means that the heat leak along the pump line wall represented only heat flowing from the pumped He^4 bath into the He^3 can.

In order to thermally ground radiation heat leaks down the He^4 pumping line, a radiation trap was installed. This trap was modeled after the design used by Wheatly³⁶ and was fitted directly into the pumping line. The trap was epoxied into the line using Stycast 2850FT low temperature epoxy. The trap was located in the pumping line at the position where the line passed through the lid of the high-vacuum can. This location insured that the trap would serve as a thermal ground for as long as the liquid He^4 bath covered the high vacuum can. In addition to reducing the heat leak due to radiation down the pumping line, it also helped to reduce conduction of heat via the low pressure He^3 gas remaining in the line. Unfortunately, but unavoidably, the trap also reduced the pumping rate through the line.

Convection would not be expected to occur in the He^3 gas in the pumping line. There is a continuously decreasing temperature drop down the length of the pipe. This means that the He^3 gas is most dense at the lowest part of the pumping line: the He^3 can.

The high-vacuum pumping line was constructed according to the same principles as those used in the construction of the He^3 pumping line. It was found, however, that the

radiation trap in this line broke loose from the side walls of the line during an experiment. The cause of this break seemed to be the difference between the low temperature expansion coefficients of the stycast and the 304 stainless. Although the trap was again epoxied into place and gave no subsequent difficulties, it was decided to install a second radiation trap as a precaution. This trap was epoxied to the underside of the high vacuum can lid directly under the location where the pumping line entered the lid. Since the Stycast and the copper lid were known to have similar expansion coefficients,^{37,38} no difficulties were expected from the second trap.

The high vacuum line was connected externally to an oil diffusion pump. This pump reduced the pressure in the high vacuum can and pumping line to below 10^{-5} torr before the refrigerator was ever placed into operation. Garfunkel and Wexler³⁹ have suggested that the pressure inside the can and pumping line falls to about 10^{-10} torr once a He^3 cryostat is placed in liquid He^4 . It was found that the pressure inside the ultrasonic cryostat did drop below 10^{-6} torr after the He^3 can and sample had reached liquid He^4 temperatures. It became a matter of practice to isolate the high vacuum in the cryostat from the diffusion pump once this cryo-pumping had begun. This should have allowed the pressure in the cryostat to drop to the 10^{-10} torr value suggested by Garfunkel and Wexler. At these low pressures, conduction heat leaks

via the gas remaining in the high-vacuum can and pumping line were very small.

Another of the principal differences between the Robbins and Marshall cryostat and the cryostat being described was the installation of an electrical transmission line. As in the case of the pumping lines, it was necessary to minimize heat leaks down the transmission line into the sample and He³ can. In addition, the electrical impedance of the transmission line had to be compatible with the impedance characteristics of the electronic equipment previously described. All of the Arenberg ultrasonic equipment previously described was designed with input and output impedances of 93 ohms. And the co-axial cables connecting the Arenberg equipment to the cryostat transmission line also had a characteristic impedance of 93 ohms. Using available materials, the transmission line was constructed according to standard principles.⁴⁰ The outer conductor was constructed of 0.25 inch inner diameter type 304 stainless steel tubing of 0.010 inch wall thickness. The inner conductor was 0.040 inch outside diameter cupro-nickel (70-30) tubing of 0.002 inch wall thickness. The inner and outer conductors were separated by 0.1 inch thick 0.25 inch diameter teflon spacers placed approximately 3.0 inches apart down the length of the transmission line. Constructed with these dimensions and including the effect of the teflon spacers, the transmission line had a nominal impedance of approximately 105 ohms. At the room temperature

end of the transmission line, the annular region between the conductors was filled with Stycast. A female type BNC 93 ohm cable connector was then soldered to the top of the assembled line. A stycast plug was inserted into the inner conductor where the transmission line entered the can lid. Here also the annular region between the conductors was filled with Stycast. These two stycast seals served both as radiation traps and as a thermal ground for the inner conductor.

Some difficulties were encountered with electrical breakdown in the Stycast seal between the conductors at the can lid. The dielectric constant of the Stycast was thought to have been sufficiently high that this should not have been a problem. Interestingly, although the electrical properties of the epoxy changed after several temperature cycles, the seal appeared to remain mechanically sound. As no substitute was found for the Stycast, it was necessary to replace the transmission line on two separate occasions.

At the bottom of the transmission line a 0.25 inch long number 00-90 screw was soldered onto the end of the inner conductor. A spring loaded ultrasonic plunger was threaded onto this screw. This plunger was used to make electrical contact with the top, plated surface of the ultrasonic transducer. Recall Figure 1. Electrical signals were then sent down the inner conductor to the transducer. The bottom plated surface of the transducer was grounded through the binder, metal crystal, and cryostat to the outer conductor.

The height of the plunger could be adjusted by moving the plunger up or down the 00-90 screw.

The electrical leads were another major source of conduction heat leaks into the high vacuum can. These leads were used to monitor the resistance of carbon thermometers (see section of this chapter on thermometry), provide current to the sample heater, and provide current to the superconducting solenoid. This solenoid was situated around the sample while the experiment was in progress. The solenoid was used to force the sample into the normal state by exceeding the critical field of molybdenum.⁴¹

The top section of all of the leads was made of American Wire Gauge (AWG) #36 copper wire. This wire comes originally coated with an insulating varnish. This section of the leads extended from the room temperature terminals through the He⁴ bath to terminals near the top of the high-vacuum can. Since the He⁴ bath was under a vacuum, the room temperature terminals were made to ceramic Kovar vacuum seals. At the low temperature termination, the copper wires were each soldered to AWG #38 niobium-titanium (52-48) alloy wire. This alloy becomes a superconductor for temperatures below 10.0 K. The superconducting leads were each passed through a vacuum seal into the high-vacuum can. These vacuum seals were made by removing the insulation from each wire at the point where it passed into the can and sealing the stripped wire into the can with Stycast. The Stycast provided both a

vacuum seal for the can and electrical insulation between the wires and the can. The superconducting wires were then sent to a common thermal ground on the He^3 can. From this thermal ground, the wires separated, running to either the carbon resistors, the sample heater, or the superconducting solenoid. Superconducting leads were used because they produce no heat when a current is sent through them while they are in the superconducting state. In addition, the wires have a somewhat lower thermal conductivity in the superconducting state than in the normal state.⁴² To reduce the heat leak even further, it was subsequently decided to insert a one-inch long section of AWG #38 manganin wire into each of the superconducting leads which ran to the carbon resistors. This section of manganin was inserted between the Stycast vacuum feed-throughs on the high vacuum can and the thermal ground on the He^3 can. The alloy manganin (82Cu-15Mn-3Ni) has a very low thermal conductivity even at very low temperatures. Since it also has a high electrical resistivity, it was not possible to insert the manganin section in the leads going to the superconducting solenoid and to the sample heater. These particular leads had to be able to sustain currents as great as one ampere.

Another source of heat leak is the radiation from the high vacuum can walls shining onto the He^3 can and sample. Robbins,³⁴ however, has applied the Stefan-Boltzmann law to this very configuration. His calculation shows that the

heat leak due to this radiation is negligible even compared to the small heat leaks from other sources of the types which have been discussed here.

Mention should be made concerning thermal contact between the sample and the He^3 vacuum can. The can itself was constructed in approximately the form of a very short, large diameter circular cylinder. This configuration was used in order to obtain a maximum evaporation rate of liquid He^3 . This design also provided a very short thermal path between the sample and the can. The sample was mounted on top of a solid pure copper block soldered directly onto the He^3 can lid. The sample heater was wound around the base of this block. The heater consisted of a few turns of manganin wire. The carbon resistance thermometers were mounted securely into holes drilled in the sides of this block. The carbon resistors were sealed into their mounting holes with D-C stopcock grease. Besides being useful as an ultrasonic bond, this grease was useful as a thermal bond at low temperatures. Before placing the sample on the copper block, the top surface of the block was burnished before each experiment to remove any deposits which may have collected since the previous experiment. When the sample was in place it was surrounded with the stopcock grease in order to improve thermal contact with the table. The superconducting solenoid was then placed around the sample and also was surrounded by the grease.

The cryostat just described did not reach quite as low a temperature as was expected. Thermometry to be discussed indicated that the cryostat regularly reached a minimum temperature of 0.38 K. This was not quite as low as the 0.27 K reached by the specific heat cryostat of Robbins and Marshall. It is felt that the higher minimum temperature in the ultrasonics cryostat was due to the lengthening of the He³ pumping line by about 33%. The only other difference between the two cryostats was the use of the transmission line in the ultrasonics cryostat. To test the effect of the transmission line on the ultimate temperature of the cryostat, some experiments were run with the ultrasonic plunger suspended over the transducer instead of being placed in contact with it. Disconnecting the plunger from the transducer should have eliminated any conduction heat leaks down the transmission line. However, the ultimate low temperature attained was found to be the same with this arrangement as in the case of direct contact. This suggests that heat leaks down the transmission line were probably negligible and certainly did not limit the minimum temperature obtained.

There was some question as to whether radio frequency heating in the transducer might produce a thermal gradient between the sample and the He³ can. To examine this problem, signals of various strengths were applied to the transducer while the refrigerator was in operation at a fixed temperature. Small temperature changes were observed to occur for

moderate to strong transducer voltages. It was found, however, that it was possible to take data for transducer voltages which produced virtually no detectable temperature shifts even at the lowest temperatures.

Vacuum Systems

Figure 6 gives a schematic representation of the He^3 refrigerator vacuum system. The system may be roughly divided into two separate but interacting systems: the high vacuum system and the He^3 pumping system. In order to see how these two systems are used, it is probably best to consider the operational procedure for the cryostat.

When the refrigerator was not in use, the He^3 pump cut-off valve, needle valve and Whitey micrometer needle valve were closed. This sealed the He^3 gas into the pump and storage tank. The He^3 pump itself is a specially sealed, five cubic feet per minute capacity Welch Duo-Seal mechanical vacuum-pump, model 1402. The He^3 gas was stored at a pressure of just less than one atmosphere so that any leaks which might develop would result in only a minimal loss of He^3 gas. Any air which leaked into the He^3 pump and storage tank would condense once the refrigerator would start operating at low temperatures.

To prepare the refrigerator for operation, the connecting valve and high vacuum isolation valve were opened to the high vacuum pumping line. A mechanical pump was used to reduce

FIGURE 6
VACUUM SYSTEMS

the pressure to about 10^{-3} torr. The connecting valve was then closed and a six-inch oil diffusion pump was connected to the high vacuum pumping line. This pump reduced the pressure to about 10^{-5} torr. This pressure was monitored with the aid of a Consolidated Vacuum Corporation cold cathode discharge gauge located in this line. Once the cryostat had been cooled to liquid nitrogen temperatures (78 K), He^4 liquid was transferred into the dewar surrounding the cryostat. But because of the vacuum in the high-vacuum can, the sample and He^3 can remained at 78 K for some time. At this point in the experiment it became the usual practice to admit the He^3 gas through the needle valves into the He^3 pumping line. This procedure caused the He^3 can temperature to fall fairly quickly to the temperature of the pumped He^4 bath. The He^3 would condense in about one hour's time. One could judge the amount of He^3 gas which was condensed by monitoring the readings on an Ashcroft vacuum gauge connected to the He^3 gas storage tank. Once the He^3 gas was condensed, the He^3 pump was turned on and the He^3 pump cut-off valve slowly opened to its maximum open position. A bellows was installed in the He^3 pumping line between the He^3 pump and the cryostat. The purpose of this bellows was to reduce vibrations transmitted from the pump to the cryostat. The pressure in the He^3 pumping line was regulated by the rate at which He^3 leaked into the line through the needle valves. These valves could be hand regulated very

satisfactorily. The pressure in the He^3 line was monitored on a Wallace and Tiernan absolute pressure indicator, model FA160. This gauge was calibrated at the factory and later checked for calibration in the laboratory. No adjustment of the factory calibration was necessary. The gauge had a range from 20.00 torr to 0.10 torr with an absolute accuracy of 0.067 torr anywhere within the range of the gauge. For pressures below 0.10 torr, a Hastings Model T thermocouple vacuum gauge was also installed in the He^3 pumping line. These two gauges were used to determine the rate at which the pressure (and hence, the temperature) was changing while data was being taken. As will be described in the next section, the Wallace and Tiernan gauge was also used to calibrate the carbon resistance thermometers at the He^3 can.

Thermometry

Temperature of the molybdenum sample was monitored with the aid of carbon resistor thermometers. These thermometers were mounted in the solid copper table which supported the molybdenum samples. To insure good thermal contact between the resistors and the copper table, the resistors were packed in DC-11 stopcock grease. Two resistors were provided for monitoring the temperature. The first thermometer, denoted by CRT A, was a one-half watt Allen-Bradley resistor with a nominal resistance of 5.1 ohms at room temperature. The second thermometer was a one-half watt Allen-Bradley re-

sistor with a nominal resistance of 2.7 ohms at room temperature. As it developed, CRT A was an order of magnitude more sensitive than CRT B in the temperature range in which data were taken (1.2 K to 0.38 K). Thus, all data were taken with CRT A as the thermometer.

The resistance of CRT A was determined by the conventional four-terminal resistance measurement technique. A constant current power supply provided current to CRT A. This current also passed through two precision 0.05% standard resistors. The voltage drop across these standard resistors was constantly displayed on a digital voltmeter. This voltage display indicated that the current passing through CRT A was stable to at least 0.2%. This current was continuously adjustable from about 0.3 microamperes to about 100.0 microamperes. For purposes of calibration, the voltage drop across CRT A was monitored on a second digital voltmeter. For purposes of data taking, the voltage drop across CRT A was sent directly to a Leeds and Northrup model 9835-B direct current microvolt amplifier. The output of this amplifier was used to drive the x-axis of the Moseley recorder on which attenuation data was being taken.

The carbon resistors were calibrated against the vapor pressure of He^3 gas at the beginning of each experiment. This pressure was measured on the precision Wallace and Tiernan absolute pressure gauge attached to the He^3 pumping line at room temperature. Although a procedure exists for

correcting the pressure measured at room temperature to the pressure at the temperature of the He^3 can, this correction turns out to be negligible for pressures above 1.0 millimeter.⁴³ Carbon resistor temperatures were determined from the corresponding He^3 pressures with the aid of the $T_{62} \text{He}^3$ Tables prepared by Sherman, Syderick, and Roberts.⁴⁴

Because the calibration of the carbon resistors was carried out between He^3 vapor pressures of 1.0 millimeter and 20.0 millimeters, the resistors were calibrated between 1.3 K and 0.65 K. In order to interpolate between data points in this temperature range, the calibration data was fit to the Clement-Quinnell Equation:⁴⁵

$$\frac{1}{T} = A(\log_{10} R + \frac{B}{\log_{10} R}) + C$$

where R is the resistance of the carbon resistor, T is the temperature corresponding to this resistance, and A , B , and C are experimental constants. The data was fit to this equation by the method of least squares. The fit was found on every occasion to be much better than 1.0%. It was also found that the calibration of CRT A repeated itself to better than 1.0% from one experiment to the next. Resistance versus temperature data from 0.65 K to 0.38 K was obtained by extrapolation of the fitted data with the aid of the Clement-Quinnell Equation. It was found that for the extreme low temperature case of 0.38 K, the extrapolation repeated itself to better than 3.0% from one experiment to the next.

CHAPTER III

SAMPLE PREPARATION

Introduction

This chapter is concerned with a discussion of the preparation of samples for the ultrasonic experiments. Included in this discussion will be a treatment on both the ultrasonic transducer and the binders used in this experiment, along with the method of preparation and the analysis of the purity of the molybdenum single crystal.

Ultrasonic Transducers

Transducers used in this study were thin quartz wafers obtained from Valpey Crystal Corporation.⁴⁶ These quartz transducers were cut, oriented, and polished at the factory so that they would respond to an excitation of either ten megahertz or an odd harmonic of ten megahertz. These so-called "x-cut" transducers were oriented so that they would vibrate in a longitudinal mode.

As was mentioned previously, the transducers must be plated on both top and bottom so that an electric field can be impressed across them. The transducers were plated at the factory with a layer of gold over a layer of chrome. This layering was necessary as gold will not adhere directly to quartz. Gold is an excellent plating because of its high electrical conductivity and because of its resistance to

tarnish and wear.

Binders

The binder used to make the mechanical bond between the transducer and the single crystal specimen had to satisfy a number of requirements. The primary requirement was that the bond be sufficiently rigid and relatively strain free so as to transmit ultrasonic pulses in the temperature region of interest. It was desirable to be able to prepare the bond at room temperature. Since all of these ultrasonic measurements were carried out in the vicinity of 1.0 K and below, it was necessary that the bond be compatible with the expansion coefficients of both the transducer and specimen from 300 K down to these low temperatures. It was also desirable that the bond be as thin as possible so as to minimize errors incurred as the ultrasonic pulses travel through the binder. Coupled with this requirement was the requirement that the binder produce as little ultrasonic attenuation as possible. Last, but not least, was the requirement that the binder be reasonably easy to apply in such a way that one can be confident that it will not break at low temperatures. This last consideration was particularly important since the very nature of the cryogenics employed meant a delay of several days if a binder proved faulty when low temperatures were reached.

Although several types of binders were tested, only one type was found to be satisfactory with respect to the

above requirements. This binder was Dow Corning DC-11 stopcock grease.⁴⁷ There was in fact only one minor drawback to the use of this binder. Because the binder was not very rigid at room temperatures, it was difficult to evaluate the quality of the bond at these temperatures. In practice, the bond was made and then the temperature of the specimen was lowered below the freezing point of the binder (about 210 K) before an evaluation was made. On the positive side, DC-11 was insoluble in water and in most common organic solvents. This insolubility gave assurance that the binder would be relatively free of dissolved impurities which could possibly cause the bond to break when the binder was frozen.

The technique of binder application was straightforward. First, the surface of the molybdenum specimen was gently cleaned with a damp tissue. Next, the binder was applied in a very thin film directly to the specimen. The transducer was then placed on top of the binder. While applying a slight pressure to the transducer, the transducer and bond were worked so as to remove air bubbles from the bond. The quality of the bond was then evaluated by placing the prepared specimen directly into liquid nitrogen (78 K) and attempting to transmit ultrasonic pulses through the specimen. Once a satisfactory bond was obtained, it was found that the specimen could be cycled between cryogenic and room temperatures any number of times with no detectable deterioration in the quality of the bond.

Crystal Specimens

Molybdenum samples suitable for ultrasonic work were prepared from a single crystal grown by Metals Research Limited.⁴⁸ As delivered, the molybdenum crystal was a cylinder of about 1.0 cm diameter and about 2.5 cm length. Metals Research stated that the crystal was grown from 99.995% pure materials. The crystal was grown so that the cylinder axis was oriented in approximately the [100] crystallographic direction.

It was desired to study ultrasonic attenuation in the three different crystallographic directions: [100], [110], and [111]. It was thus necessary to prepare separate samples from the original crystal cylinder in order to obtain these orientations. In addition to the orientation requirement, the samples had to meet several basic requirements as to their dimensions.

Recall the earlier discussion of the pulse-echo ultrasonic method. It was pointed out that the specimens must be of a minimum length in the direction of ultrasound propagation in order to prevent echo over-run. Measured values of the elastic constants of molybdenum⁴⁹ give for the velocity of propagation of compressional sound waves in the [100], [110], and [111] directions:⁵⁰

$$v_{[100]} = 6.62 \times 10^5 \text{ cm/sec}$$

$$\begin{aligned} v_{[110]} &= 6.52 \times 10^5 \text{ cm/sec} \\ v_{[111]} &= 6.49 \times 10^5 \text{ cm/sec} \end{aligned} \quad (16)$$

near temperatures of 1.0 K. The ultrasonic pulse is approximately 2.0 microseconds in duration. As the velocities given in Eq.(16) are about equal, it can be seen that the minimum acceptable sample length for any of the orientations is about 0.5 cm. At the same time, however, it must be remembered that too great a sample length can result in excessive ultrasonic attenuation. Thus a compromise must be effected between a minimum length and an acceptable amount of attenuation. In practice, the attenuation of ultrasound in molybdenum for temperatures in the neighborhood of 1.0 K was found to be very great at high frequencies. This meant that the samples were prepared with lengths as close to the minimum length as feasible.

Other requirements on the dimensions of the samples concern the end faces. As the transducer is to be applied to one of these end faces, these faces must be very parallel. Non-parallelism can result in obvious errors in the ultrasonic path length in the specimens. Non-parallelism can also cause reflections from side walls which in turn can make data interpretation difficult.⁵¹ These same type of errors can also be introduced if care is not taken to make the surface area of the end faces at least slightly larger than the surface area of the transducer.

All sample preparation including cutting and polishing

was performed on an Elox model TQH-31 electric discharge machine. This method of preparation assures that a minimum of strains and dislocations would be introduced into the samples. In fact, Laue x-ray photographs of the specimen surfaces suggested that damage was principally limited to within 0.1 millimeter of the surfaces or less.

It was possible to obtain all three crystallographic orientations by preparing only two samples. The first sample was a right circular cylinder with the cylinder axis oriented in the [100] direction. The length between the two end faces of the cylinder was 0.5118 cm. Molybdenum has a body centered cubic crystal structure.⁵² In such a structure, there is a [110] direction at an angle of 90° from the [100] direction.⁵³ So two parallel faces perpendicular to the [110] direction were polished into the side of the cylindrical surface of the first sample. These faces were 0.8735 cm apart. The second sample was approximately cylindrical with its end faces aligned perpendicular to the [111] direction. These faces were separated by 0.5758 cm.

Crystallographic orientation of the samples was determined using the conventional Laue back-reflection technique.^{54,55} Orientation of the sample's end faces were to within 1.0° of perpendicular to the desired crystallographic direction in each case.

Each pair of sample end faces were polished to within 0.0005 cm of parallel on the Elox electric discharge machine.

Crystal Specimen Purity

In order to obtain strong electron-phonon interactions in metals a very high specimen purity is essential. There is a decrease in the probability of electron scattering from thermal phonons as the temperature decreases. Thus electron mean free path lengths can become quite long (0.01 cm) and are limited only by impurity and dislocation scattering at the lowest temperatures. An elementary free electron treatment relates the electrical resistivity ρ to the electron mean free path, λ , by⁵⁶

$$\rho = \frac{m_e v_f}{n e^2 \lambda} \quad (17)$$

In this expression, m_e is the mass of the electron, v_f is its average Fermi velocity, n is the number of electrons per unit volume, and e is the unit electronic charge. When the mean free path becomes impurity limited, λ becomes temperature independent and the resistivity goes to the "residual resistivity". Customarily, the purity of metal single crystals is specified by stating the residual resistivity ratio. This quantity is defined as the ratio of the room temperature resistivity to the residual resistivity of the metal. Once this ratio is measured, the value of λ can be calculated from Eq.(17). Such a calculation, however, must necessarily require an estimate of the Fermi velocity.

Unless details of the Fermi surface are known for a particular metal, the estimated Fermi velocity can turn out to be only an educated guess.

It is possible to estimate the electron mean free path directly using ultrasonic methods. Deaton and Gavenda^{57,58} have proposed a technique which will give a good estimate for λ if values of $\vec{q}\lambda$ are not too high. Recall $\vec{q}$ was previously defined as the phonon wavevector. It should be realized that the Deaton and Gavenda method is based on a free electron theory, as was Eq.(17). Regrettably, molybdenum does not seem to follow the free electron theory too well.^{59,60} It is felt, however, that a determination of the average electron mean free path in molybdenum by the method of Deaton and Gavenda will be at least as accurate as a determination from residual resistivity measurements.

Based on the free electron model, Pippard⁶¹ has shown that the attenuation of longitudinal sound waves due to conduction electrons in a normal metal is given by:

$$\alpha_L(\vec{q}\lambda) = \frac{nm_e}{Dv\tau} \left[\frac{q^2\lambda^2 \tan^{-1} q\lambda}{3[q\lambda - \tan^{-1} q\lambda]} - 1 \right] \quad (18)$$

where D is the metal density, v is the sound wave velocity, τ is the electron relaxation time ($\tau = \frac{\lambda}{v_f}$), and the other symbols are as previously defined. If the metal sample is placed in a magnetic field, and sound waves are propagated in a direction perpendicular to the field, then it is found

that the longitudinal attenuation depends on the magnetic field strength, H . In fact, α_L turns out to be approximately periodic as a function of the reciprocal field strength. This property is known as the magnetoacoustic effect and has been widely used in studies of the Fermi surfaces of metals. Pippard has shown that the limiting value of the longitudinal attenuation as $H \rightarrow \infty$ should be given by:

$$\lim_{H \rightarrow \infty} \alpha_L(H) = nm_e v_f q^2 \ell / 15 D v \quad (19)$$

This limit is approached as $1/H^2$. If a sound frequency can be found so that the zero field attenuation, Eq.(18), is equal to the attenuation at infinite field, Eq.(19), then a numerical calculation shows that $q\ell = 6.8$ at that particular sound frequency.

Magnetoacoustic Cryostat

A simple cryostat designed to be placed directly into a liquid He^4 bath was constructed. This cryostat is represented schematically in Figure 7. All construction materials were either brass or copper, and the transmission line was constructed of non-magnetic type 304 stainless steel. Temperature control was obtained by varying the gas pressure in the vacuum jacket between the cryostat and the He^4 bath. A few turns of manganin wire were provided as a heater. The temperature of the molybdenum sample was monitored with the

FIGURE 7
MAGNETOACOUSTIC CRYOSTAT

aid of a Cryocal calibrated germanium resistance thermometer mounted securely in the crystal table. The transmission line and spring-loaded contact were similar, except for minor details, to those described for the He^3 cryostat in Chapter II.

Experimental Procedure

As the intention was only to make an estimate of the electron mean free path, the study of the field dependence of longitudinal ultrasonic attenuation in normal state molybdenum was limited to sound wave vectors in the [100] direction. The experimental apparatus was arranged so that the magnetic field vector could be rotated in a plane perpendicular to the sound wave vector. Thus, some information was also obtained on the anisotropy of the mean free path as a function of the magnetic field orientation with respect to the molybdenum crystallographic axes.

The magnetic field was produced by a Varian twelve inch electromagnet with ten inch diameter pole faces. These pole faces were separated by 2.5 inches. As the sample was placed as close as possible to the midpoint of the center line between the pole faces, the field was very uniform over the volume of the sample while data was being taken. The field strength was monitored with the aid of an Hall probe mounted on one pole face of the magnet. A voltage output directly proportional to the field strength was provided on the magnetic power supply by Varian. This voltage was used to

drive the x-axis of the Moseley recorder being used to display attenuation data.

Ultrasonic electronics was exactly as described in Chapter II. In the entire experiment, the Hewlett-Packard display scanner plug-in was locked onto the voltage height of the first ultrasonic echo. The display thus obtained on the Moseley recorder was of the height of this echo (in volts) as a function of field strength (in gauss).

In practice, the experiment was run with pumped liquid He^4 to obtain the lowest temperature possible. The germanium thermometer at the crystal indicated this lowest temperature to be 1.47 K. All data to be presented for the determination of the mean free path was taken at this temperature.

Experimental Results

As the magnetic field and not the temperature is the variable in the mean free path experiment, Eq.(14) can be rewritten as

$$\alpha(H) = \alpha_{\text{ref}}(H_{\text{ref}}) + \frac{10}{j\lambda} \log_{10} \left[\frac{v_j(H_{\text{ref}})}{v_j(H)} \right] \quad (20)$$

For convenience in analyzing the data, H_{ref} is chosen to be zero field and α_{ref} is arbitrarily set equal to zero. Thus $v_j(H_{\text{ref}})$ ($j=1$ for the first echo) became the amplified voltage height of the first echo at zero magnetic field strength.

Typical samples of recorder tracings illustrating the method of analysis are shown in Figures 8, 9, and 10. These

FIGURE 8
HEIGHT OF FIRST ECHO VERSUS H-FIELD FOR HII [110] AT 8.5 MHz

FIGURE 9
HEIGHT OF FIRST ECHO VERSUS H-FIELD FOR H₁ [1110] AT 29.5 MHz

FIGURE 10
HEIGHT OF FIRST ECHO VERSUS H-FIELD FOR HII [110] AT 50.5MHZ

tracings were made for ultrasonic frequencies of 8.5, 27.5, and 50.5 MHz respectively. For these tracings the magnetic field vector was oriented within 2.0° of the [011] crystallographic direction in the molybdenum sample. The figures show the voltage height of the first ultrasonic echo as a function of the applied field from zero to ten kilogauss.

Note the appearance of magnetoacoustic oscillations for field settings of one kilogauss and less. According to some authors,^{62,63} magnetoacoustic oscillations do not appear unless the value of $\vec{q}l$ is at least $\vec{q}l > 1$.

The data from these figures is reduced by calculating the attenuation as a function of field strength from two kilogauss to ten kilogauss. The attenuation is then plotted for each frequency as a function of $1/H^2$ and extrapolated to $H=\infty$. The difference between the attenuation in zero field and the extrapolated attenuation at each frequency is plotted as a function of frequency. Using the data from Figures 8, 9, and 10, the plot in Figure 11 is obtained. From this figure and the theory, it is evident that $\vec{q}l = 6.8$ at 29.9 MHz for $\vec{H}$ [011].

Data to determine the mean free path was taken as a function of field orientations in a 90° arc from $\vec{H}$ [001] to $\vec{H}$ [010]. Since the sound wave was propagated in a crystallographic direction having four-fold rotational symmetry, this data covers all possible orientations of the magnetic field in the crystal. All of this data was analyzed in the

FIGURE II
PLOT TO DETERMINE FREQUENCY
FOR WHICH $q_1 = 6.8$

manner illustrated above and the results are given in Table 1. The angle θ represents the angle between the magnetic field vector and the [001] crystallographic axis. The frequency, ν , was determined for each value of θ from a plot analogous to Figure 11. This frequency is the value of the frequency for which $\vec{q}\ell = 6.8$.

The velocity of longitudinal ultrasound in the [100] direction is given by Eq.(16). Thus the mean free path values in Table 1 can be calculated from

$$\ell = \frac{6.8v}{2\pi\nu} \quad (21)$$

Note that the electron mean free path is only slightly anisotropic. Fawcett's⁶⁰ measurements of magnetoresistance in molybdenum indicate that the electron relaxation time is isotropic to the nearest order of magnitude. This suggests that the values of ℓ in Table 1 reasonably approximate values of the mean free path for all orientations in the molybdenum crystals being studied. A simple calculation shows that this implies that $\vec{q}\ell > 1$ for these crystals for frequencies of 10 Mhz and higher.

Table 1
Values of the Electron Mean Free Path
in Molybdenum Specimens

θ	ν (Mhz)	λ (cm)
0°	32.3	0.022
10°	29.3	0.025
20°	28.5	0.025
30°	28.4	0.025
40°	29.9	0.024
50°	29.9	0.024
60°	29.2	0.025
70°	28.5	0.025
80°	32.3	0.022
90°	32.3	0.022

CHAPTER IV

RESULTS AND INTERPRETATION

Ultrasonic Attenuation Data

As described in Chapter II, the data taken in this experiment consisted of plots of the voltage height of a given ultrasonic echo as a function of the temperature. Many mechanisms can contribute to the attenuation of ultrasound in metals at low temperatures. Since not all of these mechanisms are well understood, it is difficult to interpret the echo height changes in terms of the total attenuation coefficient. Therefore it has been assumed that all mechanisms contributing to ultrasonic attenuation in metals at low temperatures are temperature independent except for those involving interactions between electrons and the crystal lattice vibrations. This assumption has been widely invoked by other investigators making similar ultrasonic attenuation studies in superconductors. Thus far the results of such experiments seem to substantiate such an assumption. With this assumption, it is possible to reduce the ultrasonic attenuation data in such a way that only temperature dependent attenuation changes will appear in the final analysis. The method by which this reduction is accomplished is now illustrated.

Figure 12 represents schematically the type of recorder trace which results when the temperature variation of a given

FIGURE 12
SCHEMATIC RECORDER TRACE

ultrasonic echo is displayed on the Moseley X-Y recorder. Let v_{j0} represent the height of the j th echo if there were no attenuation. According to the BCS theory (see Eq.(6)), there should be no ultrasonic attenuation due to electron-phonon interactions at zero Kelvin. Thus, if superconductivity is the only temperature dependent effect altering the ultrasonic attenuation, then at zero Kelvin the echo height in the superconducting state will be due to temperature independent non-electronic "residual" attenuation only. This attenuation, α_r , will be given by:

$$\alpha_r = \frac{10}{jL} \log_{10} \left(\frac{v_{j0}}{v_{js}(0)} \right) \quad (22)$$

where $v_{js}(0)$ is the j th echo voltage height at zero Kelvin in the superconducting state and the other symbols are as previously defined. This attenuation is chosen as the reference attenuation in Eq.(14), and is set equal to zero. Then the ultrasonic attenuation in the superconducting and normal states respectively will be given by:

$$\alpha_s(T) = \frac{10}{jL} \log_{10} \left(\frac{v_{js}(0)}{v_{js}(T)} \right) \quad (23)$$

and

$$\alpha_n(T) = \frac{10}{jL} \log_{10} \left(\frac{v_{js}(0)}{v_{jn}(T)} \right) \quad (24)$$

where the j th echo voltage height at a given temperature is represented in the superconducting and normal states by $v_{js}(T)$ and $v_{jn}(T)$ respectively. Then the ratio of the electronic attenuations in the superconducting and normal states,

$$\frac{\alpha_s(T)}{\alpha_n(T)} = \log_{10} \frac{v_{js}(0)}{v_{js}(T)} / \log_{10} \frac{v_{js}(0)}{v_{jn}(T)} \quad (25)$$

can be compared to the BCS prediction given in Eq.(6).

The data taken to determine the ultrasonic attenuation in the normal state of molybdenum indicated that $\alpha_n(T)$ was a constant below about 1.2 K. These data were taken with a magnetic field of about 200 gauss impressed on the molybdenum sample. This field somewhat exceeded the estimated zero Kelvin critical field²² for molybdenum and insured that the sample would remain in the normal state while attenuation measurements were being made. It was noted that the magnetic field produced a slight decrease in the normal state attenuation. This shift was nearly independent of the temperature and increased as the applied magnetic field increased. This change in the normal state attenuation was thought to be due to the presence of the parallel-field magnetoacoustic effect in molybdenum. This effect has been previously reported in cadmium and zinc.⁶⁴ An extrapolation of the normal state attenuation as a function of field strength suggested that the zero field normal state attenuation at all temperatures

below the superconducting transition temperature was equal to that above the transition temperature for temperatures at least as high as 1.2 K. So, in the analysis of data, the value of the normal state attenuation between 1.2 K and the transition temperature was assumed to represent the normal state attenuation down to zero Kelvin. Considering the purity of the molybdenum samples, it should be expected that the electron mean free path would be impurity limited and the normal state attenuation constant at all temperatures below about 2.0 K.

A complete analysis of the data taken to determine the ultrasonic attenuation in the superconducting state must allow for the possibility of other types of temperature dependent attenuation besides that due to electron-phonon interactions. Only one other type of temperature dependent attenuation has been shown with certainty to exist at these temperatures in superconductors. Love, Shaw, and Fate⁶⁵ first discovered that the attenuation in a superconductor depends on the amplitude of the ultrasound. These investigators theorized that this amplitude dependence was due to the interaction between ultrasound and dislocations in the superconductor. This interaction gives rise to an increase in the ultrasonic attenuation in the superconducting state as the temperature decreases. Since this increase directly opposes the natural tendency of the superconducting state attenuation to decrease at lower temperatures, the amplitude

effect is readily discernible in the data. The effect can be very large at high ultrasonic amplitudes but can be made insignificant by the use of low transducer voltages.

In anticipation of a possible amplitude dependent effect in molybdenum, all ultrasonic attenuation data were taken as a function of the amplitude of the voltage impressed onto the ultrasonic transducer. No obvious amplitude dependence was evident in any of the data taken. In addition, the values of the superconducting energy gaps obtained from this data were found to be independent of the ultrasonic amplitude in all cases.

It should be recalled from Chapter II in this regard that ultrasonic amplitudes were kept small in order to reduce radio frequency heating in the transducer. No data were used for calculating energy gaps which were taken for transducer voltages of greater than about fifty volts peak to peak, and most measurements were made with far smaller voltages. Because radio frequency heating apparently caused distortion of the data at very high transducer voltages, it was not possible to definitely conclude that amplitude dependence was absent in the molybdenum samples studied. It is felt, however, that if the amplitude dependent effect is present in the data, it is extremely subtle and has no effect on the values of the energy gaps to be given.

It became the procedure when taking data to fix the transducer voltage and then take at least two sets of data.

One of these sets was always taken with the temperature falling and the other with the temperature rising. In each case a temperature range from about 1.1 K to about 0.38 K was covered. Usually a time interval of fifteen to thirty minutes was required to cover this temperature range. When the data for each transducer voltage were analyzed, it became evident that there were no differences between data taken for rising or falling temperatures. This suggests that both sets of data represented a continuous succession of thermal equilibrium states.

Results and Analysis

In order to calculate the limiting effective energy gap $\Delta(0)$ from the ultrasonic attenuation ratio $\alpha_s(T)/\alpha_n(T)$, Eq.(6) was written

$$\frac{\Delta(T)}{k_B T} = \ln_e \left(\frac{2\alpha_n(T)}{\alpha_s(T)} - 1 \right) \quad (26)$$

It is customary to normalize the temperature dependence of $\Delta(T)$ by introducing the reduced temperature $t = \frac{T}{T_c}$. This temperature dependence can be expressed in terms of the limiting energy gap $\Delta(0)$ by

$$\Delta(t) = G(t) \cdot \Delta(0) \quad (27)$$

The function $G(t)$ has been tabulated from the BCS theory by

Muhlschlegel.⁶⁶ However, for purposes of calculation, it is more convenient to use an analytic form given by Clem:⁶⁷

$$G(t) = 1.7367(1-t)^{1/2} \cdot [1 - 0.4095(1-t) - 0.0626(1-t)^2] \quad (28)$$

Numerical calculation shows that Clem's formula agrees with Muhlschlegel's results within an error of 0.1% for $t > 0.4$. Substituting Eq.(27) into Eq.(26) gives

$$\Delta(0) \frac{G(t)}{t} = \ln_e \left(\frac{2\alpha_n(t)}{\alpha_s(t)} - 1 \right) \quad (29)$$

in units of $k_B T_c$. This expression implies that if the BCS theory is correct, then a plot of $\ln_e \left(\frac{2\alpha_n}{\alpha_s} - 1 \right)$ as a function of calculated values of $\frac{G(t)}{t}$ should be a straight line whose slope is the energy gap at zero Kelvin. Since it was not possible to take data on $\alpha_s(t)$ below $t = 0.45$, it was necessary to rely on Eq.(29) as a means of estimating the echo voltage height in the superconducting state at zero Kelvin, $V_s(0)$. This was accomplished by fitting each set of data separately to Eq.(29) by the method of least squares while treating $V_s(0)$ as a variable parameter to obtain the best fit. As will be shown, the data seems to fit a BCS type of equation rather well, and this would seem to justify the assumption of this method of extrapolating the superconducting state attenuation below $t \approx 0.46$.

Although it was possible to fit each set of data over the entire temperature range $1.0 > t > 0.46$, it soon became

evident that a slightly better fit could be obtained on the range $0.87 > t > 0.46$. This was particularly true at the lower ultrasonic frequencies. This finding is consistent with similar experiences by other investigators attempting similar types of fits in other superconductors.^{68,69} The type of problem which occurs at high reduced temperatures is illustrated in Figure 13 for a fit of one particular set of data for molybdenum. The figure shows the fit to Eq.(29) for a set of data for which ultrasound was propagated in the [100] direction at a frequency of 11.0 MHz. Note the tendency of the data to be lower than the fitted straight line for large values of reduced temperatures. Also note that the fitted curve has a positive y-intercept. While Figure 13 does illustrate the general problem, it does represent one of the most extreme cases. As will be noted this problem may be due to the presence of multiple energy gaps for some or all orientations in the superconductor. On the other hand the problem more likely may be associated with an error in the determination of $\alpha_n(t)$. As can be seen from Figure 12, the ultrasonic echo takes on its smallest value and hence has the smallest signal to noise ratio when the superconductor is in the normal state. This makes an error in the determination of $V_n(t)$ much more likely than a corresponding error in determining $\alpha_s(t)$. It can be shown that Eq.(29) is much less sensitive to errors in $\alpha_n(t)$ at low reduced temperatures than for values of t near the transition temperature.⁶⁸ Hence it was decided to omit the highest reduced temperatures from the fit.

FIGURE 13
 FIT TO $\text{LN}_e(2a_n/a_s - 1)$ VERSUS $G(t)/t$ FOR
 A SET OF DATA WITH $\bar{q} \parallel [100]$ AT 11.0 MHZ

Values obtained for the zero Kelvin energy gap in the manner described above are given as $\Delta_1(0)$ in Table 2. The value given for each ultrasonic frequency represents the average over several sets of data taken at different transducer voltage levels at that frequency. As previously mentioned, the energy gap was found to be independent of the transducer voltage. The error given with the values of $\Delta_1(0)$ has been estimated from the reproducibility of the determined value of the energy gap from one set of data to the next. In each determination of the energy gap from a given set of datum, that datum was fit to Eq.(29) directly from the Moseley X-Y recorder tracing obtained in the experiment. It was found necessary to slightly smooth the data below $t = 0.65$ in approximately 25% of the data. Without this smoothing in these cases, the IBM System 360 computer being used to make the fit was unable to obtain a physically acceptable value of $V_s(0)$ subject to the requirement that this value of $V_s(0)$ must give the best fit. Since the values obtained for $\Delta_1(0)$ from these smoothed sets of data were no different from those obtained from other sets of data for the same frequency and orientation, it is felt that this smoothing did not prejudice the data.

In order to examine variations of the data from a perfect fit to Eq.(29), the energy gap function $\Delta_2(t) = \frac{\Delta(t)}{G(t)}$ is introduced. From Eq.(26)

$$\Delta_2(t) = \frac{t}{G(t)} \ln_e \left(\frac{2\alpha_n(t)}{\alpha_s(t)} - 1 \right) \quad (30)$$

For an ideal superconductor in the sense of the BCS theory,

$\Delta_2(t)$ should be independent of t and have a value $\Delta(t) = 1.76$ (in units of $k_B T_c$). Included in Table 2 are values of $\Delta_2(t)$ at $t = 0.46$ and at $t = T_c$ calculated in each case from the same sets of data used to determine $\Delta_1(0)$. For each determination of $\Delta_2(t)$, the value of $V_s(0)$ obtained in fitting Eq.(29) was used to calculate $\alpha_n(t)$ and $\alpha_s(t)$ in Eq.(30).

As can be seen from Table 2, the values of $\Delta_2(t)$ at $t = 0.46$ and $t = 0.90$ suggest that an equation of the BCS type (Eq.(6)) provides a good description of the ultrasonic attenuation in the [110] and [111] directions in superconducting molybdenum. Figure 14, for instance, shows the temperature dependence of the average value of $\Delta_2(t)$ for 51.0 MHz ultrasound propagated in the [111] direction. The curve gives a virtually temperature independent value of $\Delta_2(t) = 1.51 k_B T_c$. The behavior of $\Delta_2(t)$ in this figure typifies the behavior of $\Delta_2(t)$ at all frequencies studied for the [110] and [111] orientations in molybdenum. Note, however, that while the ultrasonic attenuation data seems to fit an equation of the BCS type rather well, that the energy gaps obtained differ systematically from the value predicted by the BCS isotropic model. There is also an indication of frequency dependence of the energy gap for the [111] orientation at the lowest frequency.

By way of contrast to the straightforward behavior of data for the [110] and [111] orientations, the data for $\Delta_2(t)$ for the [100] direction suggests a temperature dependence of the energy gap. Given in Figure 15 and Figure 16

FIGURE 14
EFFECTIVE ENERGY GAP FUNCTION $\Delta_2(t)$ FOR
 $\bar{q} \parallel [110]$ AT 51.7 MHZ

FIGURE 15
EFFECTIVE ENERGY GAP FUNCTION $\Delta_2(t)$ FOR
 $\bar{q} \parallel [100]$ AT 11.0 MHZ

FIGURE 16
EFFECTIVE ENERGY GAP FUNCTION $\Delta_2(t)$ FOR
 $\bar{q}||[100]$ AT 32.6 MHZ

Table 2

Effective Energy Gaps Determined by
Ultrasonic Attenuation

Direction	Frequency	$\Delta_1(0)$	$\Delta_2(.46)$	$\Delta_2(.90)$
[100]	11.0	$1.38 \pm .10$	$1.55 \pm .10$	$1.76 \pm .10$
	32.6	$1.61 \pm .10$	$1.68 \pm .10$	$1.81 \pm .10$
	50.0	---	---	---
[110]	9.6	$1.65 \pm .15$	$1.69 \pm .10$	$1.74 \pm .10$
	32.3	$1.64 \pm .10$	$1.61 \pm .10$	$1.60 \pm .10$
	51.7	$1.71 \pm .15$	$1.66 \pm .10$	$1.64 \pm .10$
[111]	8.7	$1.19 \pm .10$	$1.22 \pm .10$	$1.21 \pm .10$
	30.7	$1.37 \pm .10$	$1.48 \pm .10$	$1.56 \pm .10$
	51.0	$1.52 \pm .15$	$1.52 \pm .10$	$1.50 \pm .10$

Table 3

Comparison of Effective Energy Gaps in Molybdenum
as Determined in Various Investigations

Authors	Method	T_c	$\Delta_1(0)/k_B T_c$ [orientation]
Horwitz and Bohm ¹⁹	ultrasonic(239 MHz)	$0.92 \pm .01$	$3.5 \pm .2[100]$
Jones and Rayne ²⁰	ultrasonic (200 MHz to 1000 MHz)	$0.92 \pm .01$	$3.3 \pm .2[100]$ $3.5 \pm .2[110]$ $3.1 \pm .2[111]$
Karfunkel et.al ²¹	hypersonic (10 GHz)	0.914	$2.5 \pm .4[111]$
Forrer et.al. ²²	specific heat	$0.913 \pm .002$	$3.5 \pm .2[\text{avg.}]$
Alaieh and Zebouni ²³	thermal conductivity critical field	0.903 0.903	$3.2 \pm .1[\text{avg.}]$ $3.4 \pm .1[\text{avg.}]$
Present work	ultrasonic (10 MHz to 50 MHz)	$0.912 \pm .010$	$3.2 \pm .2[100]$ $3.4 \pm .2[110]$ $3.0 \pm .2[111]$

are plots of $\Delta_2(t)$ as a function of t for the 11.0 and 32.6 MHz data respectively. Both of these curves suggest a high value for the energy gap from the data near the transition temperature and a tendency for the gap to decrease nearly linearly with decreasing temperature. A linear extrapolation of $\Delta_2(t)$ versus t on each of these figures gives a value of $\Delta_2(t)$ which is very close to the corresponding previously calculated value of $\Delta_1(0)$ for each frequency. This suggests that the value of $\Delta_1(0)$ obtained by fitting the data to Eq.(29) represents a limiting low temperature energy gap. Figures 15 and 16 suggest that $\Delta_2(t)$ for the [100] direction is approaching a limiting type of behavior as the frequency increases. Unfortunately the lack of 50 MHz data for the [100] direction makes it difficult to conclude whether or not Figure 16 represents this limiting behavior.

Comparison with Other Investigations

Given in Table 3 is a comparison of the results of the measurements of the superconducting ground state energy gap, $2\Delta_1(0)$, and the transition temperature, T_c , for molybdenum by various investigators. Where the energy gap has been measured by ultrasonics, the direction of propagation of ultrasound for which the measurement was made is listed. Energy gap values measured by other methods represent averages over all orientations. Values of $2\Delta_1(0)$ given from the present investigation were taken from the value of $\Delta_1(0)$

at the highest frequency at which $\Delta_1(0)$ was measured for each orientation. The given value of T_c from the present study represents the average value obtained from all data sets for all orientations. From the scatter in T_c from one data set to the next and from the repeatability of the carbon resistor thermometers, the error in T_c is estimated to be ± 0.010 K.

The results of the present work are in reasonably good agreement with previous investigations giving an average energy gap. Comparison between the gaps obtained by different ultrasonic investigations seems to offer a consistent picture regarding the sense of the anisotropy in the energy gap. There are, however, discrepancies between the results of the different investigations.

For the [110] direction, there is good agreement between the high frequency result of Jones and Rayne and the result in the present investigation. Furthermore, Table 2 suggests nothing ambiguous in the determination of this particular gap even at the lowest frequency.

For the [100] direction on the other hand, Horwitz and Bohm obtain a result somewhat higher than that of either Jones and Rayne or this investigation. To obtain their result, Horwitz and Bohm fit their data to an expression of the form of Eq.(26). Because their experiment only attained a reduced temperature of $t = 0.6$, the data fit made by these authors had to favor the high reduced temperatures. The

manner in which the non-electronic attenuation was eliminated was not stated. Figures 15 and 16 suggest that a determination of the energy gap from data near the transition temperature will in fact yield a result like that of Horwitz and Bohm. By way of contrast, Jones and Rayne attained a reduced temperature of $t = 0.44$, a temperature very comparable to that attained in the present experiment. Significantly, these authors performed an analysis and fit similar to those employed in the present work to find the energy gap, and restricted the fit to the reduced temperature range $0.44 < t < 0.60$ (see reference 70). This suggests that there should be good agreement between Jones and Rayne and the present investigation on this gap. At the same time, Figures 15 and 16 suggest that the low temperature energy gap is increasing with increasing frequency. This suggests that the results of Jones and Rayne may very well be correct at the relatively higher frequencies at which they made their determination.

The above comparison of results for the [100] direction would seem to offer a unified picture and simultaneously raise some questions. Both the results of the present investigation and those of Horwitz and Bohm at 239 MHz suggest that the energy gap near the transition temperature has a value of about $3.5 k_B T_C$. Simultaneously both the results of the present investigation and those of Jones and Rayne point to a limiting low temperature energy gap of about $3.3 k_B T_C$. The conclusion would seem to be that the energy gap for the

[100] direction in molybdenum deviates from the ideal BCS behavior much as shown in Figure 16.

In the case of the [111] direction, there does not seem to be any obvious reason for the discrepancies between the energy gap reported in this work and those given by other investigators. Garfunkel et.al. made their determination of the energy gap for phonon energies very near those required to destroy Cooper pairs. In determining the energy gap, they had to use the general expression for the attenuation ratio (of which Eq.(6) is the low frequency limit) from the BCS theory. They did find a good agreement with the BCS theory predictions for hypersonic attenuations, but they admit a rather large error on their results. The method in which Jones and Rayne obtained their result has been described. There is only fair agreement between the present work and the slightly higher value given by Jones and Rayne for this particular gap. However, in view of the value given by Garfunkel et.al. the value of the [111] energy gap obtained in this present work is certainly reasonable.

Interpretation

A proper understanding of ultrasonic attenuation in a superconductor such as molybdenum will eventually require a theory which makes allowance for very complicated multi-band Fermi surfaces in metals. As yet no detailed theory exists which may be compared with the data here. One multi-band model which is sometimes employed⁷¹ is a variation of

Eq.(6). It is assumed that the ratio α_s/α_n depends on several energy gaps $\Delta_i(t)$ such that

$$\frac{\alpha_s}{\alpha_n} = \sum_i \frac{A_i}{\exp[\Delta_i(T)/k_B T] + 1} \quad (31)$$

Each energy gap $\Delta_i(T)$ is associated with a given band and it is implicitly understood that there is no inter-band interaction. The constants A_i are chosen subject to the condition:

$$\sum_i A_i = 2 \quad (32)$$

and it is assumed that the $\Delta_i(T)$ each have the temperature dependence given by Eq.(6). This model has been employed with some success for a two gap superconductor by Perz and Dobbs.^{68,72} Since specific heat data on molybdenum²² suggests the presence of multiple gaps, the model Eq.(31) could be applied to molybdenum. There is, however, no reason to suppose that there are just two gaps contributing to the total effective gap in any direction in molybdenum. In fact, an estimate of the size of these several energy gaps from tunnelling experiments is generally required before one can proceed with confidence with Eq.(31). Unfortunately, no such experiments have been reported for molybdenum. Some general observations can still be made, however.

Recall the discussion of the temperature dependence of

$\Delta_2(t)$ for the [100] orientation in molybdenum. In particular, if it is assumed that one of those energy gaps is smaller than the others and that the values of the A_i in Eq.(31) are of the same order, then the term in Eq.(31) containing this smallest gap will dominate α_s/α_n as the reduced temperature approaches zero. This suggests from Table 2 that the smallest gap has the value given by $\Delta_1(0)=1.61 \text{ kT}_c$ at an ultrasonic frequency of 32.6 MHz. At higher temperatures, particularly near the transition temperature, the value of $\Delta_2(t)$ will be an average, all terms in Eq.(31) contributing evenly.

An extension of this type of argument to the [110] and [111] directions in molybdenum is difficult, since the effective energy gap $\Delta_2(t)$ in these directions is virtually temperature independent. It is still possible that there are several gaps, all of which are of about the same size. But until supplemental information is provided on the presence of multiple gaps, there would seem to be no reason to prefer the more complicated expression Eq.(31) to the simplicity of a single gap model such as Eq.(6).

As has been previously noted, the present study indicates a frequency dependence of the energy gaps in the [100] and [111] directions in molybdenum. In the case of the [111] direction, this frequency dependence applies to the effective energy gap regardless of the temperature. In the case of the [100] direction, the frequency dependence appears

to apply to only what has been interpreted to be the smallest of several possible energy gaps: the effective gap at zero Kelvin.

Measurements described in Chapter III indicated that the ultrasonic attenuation measurements described in this work were made in a range of ultrasonic frequencies such that $q\ell \geq 1$. When the principles of the conservation of energy and momentum are applied to the problem of electron-phonon interactions in normal metals, it is found that only a fraction of the total number of electrons contribute to ultrasonic attenuation. This fraction is determined by the requirement that the velocity component $V_f \cos \theta$ of the electrons contributing to attenuation must be equal to the sound wave velocity V and be parallel to the phonon wavevector $\vec{q}$. The angle θ is the angle between the Fermi velocity vector and the phonon wavevector.⁷¹ Leibowitz⁷³ has discussed the electronic ultrasonic attenuation for the case $q\ell \geq 1$. He finds that the fraction of the Fermi surface on which electrons contribute to ultrasonic attenuation can be expressed in terms of θ by

$$\cos \theta = \left(\frac{V}{V_f} \right) + \frac{1}{q\ell} \quad (33)$$

Thus the interaction favors electrons toward the equator of the Fermi surface perpendicular to the phonon wavevector. The expression Eq.(33) suggests that for an anisotropic

superconductor, the energy gap should be dependent on $q\lambda$ for low values of $q\lambda$. Furthermore this dependency should vanish as $q\lambda \rightarrow \infty$.

In the molybdenum samples studied the value of λ was impurity limited in the entire temperature range in which attenuation measurements were made. In light of Eq.(33) this would seem to explain the observed frequency dependence of the energy gaps in molybdenum. As expected by the above argument, the energy gap at about 10 MHz ($q\lambda \sim 1$) goes to a constant value at the higher values of 30 MHz ($q\lambda \sim 7$) and 50 MHz ($q\lambda \sim 12$). Furthermore, the values of the gaps obtained at 30 and 50 MHz appear to be equal to or approaching the limiting value of the gaps given by Jones and Rayne at high frequencies ($q\lambda \rightarrow \infty$). The fact that the energy gap in the [110] direction appears to have reached its limiting value already at 10 MHz suggests that the effective value of λ governing electron-phonon interactions for this orientation is somewhat longer than λ for the other orientation studied.

Summary

Presented in this work has been a determination of the effective energy gap in superconducting molybdenum in the [100], [110], and [111] directions. This determination has been made to complement ultrasonic determinations of the energy gap in molybdenum which have been made at much higher

frequencies. It has been found in this study that the effective energy gap in molybdenum is anisotropic and frequency dependent. This frequency dependence has been related to the q_2 values in the particular molybdenum samples studied.

It is concluded that the ultrasonic attenuation in the [110] and [111] directions in molybdenum can be described very effectively by a single gap BCS model. The value of the energy gap obtained at 50 MHz for each orientation is felt to represent the frequency independent energy gap predicted by BCS.

Measurements of the ultrasonic attenuation in the [100] direction have indicated the possible existence of multiple energy gaps in this direction. Data given for the temperature dependence of this gap at 30 MHz is felt to represent the limiting frequency independent behavior of this gap at high frequencies.

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APPENDIX A

AND Gate

The term AND gate is applied to the type of logic circuit which is used to register coincidence between events from different sources. An output is obtained from this kind of circuit only when an event is registered on all input circuits to the gate simultaneously. In order to visualize this operation, consider the simple AND gate with three inputs shown in Figure 17.

In the AND gate of Figure 17, three signal sources are each connected in series with diodes. For convenience, the circuit is arranged so that the three input signals e_1 , e_2 , and e_3 and the output signal e_0 have a common electrical ground. The value of the resistance R is chosen to be somewhat greater than either the forward resistance of any of the three diodes (normally identical) or the output resistances of the signal sources producing e_1 , e_2 , and e_3 . This means that when there are no input signals to the gate, the output terminal P is fairly close to ground potential.

As shown in the figure, a positive signal first arrives simultaneously on the first and third inputs. These signals bias diodes D_1 and D_3 off and these diodes stop conducting. However, because no simultaneous signal appears on the second input, diode D_2 holds P near ground potential and no output results. By way of contrast, the second positive signal ap-

FIGURE 17
AND GATE

pears at all three inputs. This biases all three diodes so that they stop conducting and the potential at P rises. As long as this second signal is displayed on all three inputs, there is an output signal. Finally, as in the first case, the third signal appears only on inputs one and two so that no output results.⁷⁴

In the ultrasonic electronic circuit shown in Figure 3, an AND gate having only two inputs (and hence, two diodes) was used. The input signal to terminal one of the gate was the output from the first pulse generator. This output consisted of two microsecond length pulses at a repetition rate of 800 per second. This signal was that represented as Illustration I of Figure 4. The input signal to the second terminal of the gate consisted of a 50 Hz square wave from the binary counter. This signal was that represented as Illustration II of Figure 4. Since the AND gate would output a signal only when there was a signal on both inputs, the output signal from the gate was that represented by Illustration III of Figure 4. Thus the AND gate served to modulate the 800 Hz output from the pulse generator so that it was chopped at a frequency of 50 Hz. This chopped output caused the entire experiment to be modulated at 50 Hz and this made the use of the lock-in amplifier possible.

APPENDIX B

ORIGINAL DATA

Included in this appendix are all of the data which were used to calculate the energy gaps given in Table 2 of Chapter IV. These data consist of values of the echo voltage height as a function of the reduced temperature in reduced temperature increments of $t = 0.02$. The data were taken in each case directly from the experimental recorder tracings. Some of the data has been slightly smoothed below $t = 0.70$ where noted. The data in the following tables have been grouped first according to the direction of propagation in the sequence [100], [110], and [111]. Then within each direction, the data are grouped in the order of increasing frequency in the chronological sequence in which the data were taken. In the tables, the symbol V denotes the absolute echo voltage height (in volts) and the symbol t denotes the reduced temperature. The voltage used to calculate the normal state attenuation in each case is the echo voltage height given for $t = 1.00$.

Table 4

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	2.43	.80	4.45	.60	5.22
.98	3.01	.78	4.56	.58	5.29
.96	3.29	.76	4.62	.56	5.37
.94	3.49	.74	4.72	.54	5.43
.92	3.68	.72	4.78	.52	5.50
.90	3.81	.70	4.88	.50	5.52
.88	3.97	.68	4.98	.48	5.60
.86	4.08	.66	5.07	.46	5.67
.84	4.20	.64	5.11		
.82	4.32	.62	5.18		

Table 5

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	2.78	.80	5.52	.60	6.78
.98	3.52	.78	5.69	.58	6.89
.96	3.88	.76	5.80	.56	7.00
.94	4.18	.74	5.92	.54	7.12
.92	4.40	.72	6.10	.52	7.21
.90	4.57	.70	6.19	.50	7.33
.88	4.79	.68	6.30	.48	7.40
.86	4.99	.66	6.42	.46	7.43
.84	5.18	.64	6.57	.44	
.82	5.35	.62	6.67		

Table 6

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	2.43	.78	6.10	.58	7.62
.98	3.21	.76	6.24	.56	7.77
.96	3.69	.74	6.36	.54	7.89
.94	4.00	.72	6.64	.52	8.00
.92	4.32	.70	6.73	.50	8.13
.90	4.63	.68	6.88	.48	8.22
.88	4.92	.66	7.04	.46	8.38
.86	5.22	.64	7.17		
.84	5.49	.62	7.32		
.82	5.74	.60	7.48		
.80	5.94				

Table 7

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	2.48	.80	4.49	.60	5.30
.98	3.19	.78	4.59	.58	5.39
.96	3.43	.76	4.70	.56	5.43
.94	3.61	.74	4.79	.54	5.48
.92	3.78	.72	4.87	.52	5.51
.90	3.90	.70	4.92	.50	5.59
.88	4.03	.68	5.01	.48	5.62
.86	4.18	.66	5.09	.46	5.70
.84	4.27	.64	5.19		
.82	4.38	.62	5.21		

Table 8

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	2.43	.80	4.45	.60	5.22
.98	3.01	.78	4.56	.58	5.29
.96	3.29	.76	4.62	.56	5.37
.94	3.49	.74	4.72	.54	5.43
.92	3.68	.72	4.78	.52	5.50
.90	3.81	.70	4.88	.50	5.52
.88	3.97	.68	4.98	.48	5.60
.86	4.88	.66	5.07	.46	5.67
.84	4.20	.64	5.11		
.82	4.32	.62	5.18		

Table 9

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	2.70	.78	5.85	.56	7.89
.98	3.28	.76	6.02	.54	7.79
.96	3.67	.74	6.21	.52	7.89
.94	4.00	.72	6.41	.50	8.02
.92	4.28	.70	6.60	.48	8.20
.90	4.52	.68	6.81	.46	8.31
.88	4.74	.66	7.08		
.86	4.98	.64	7.39		
.84	5.21	.62	7.41		
.82	5.42	.60	7.49		
.80	5.62	.58	7.58		

Table 10

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	2.83	.80	6.83	.60	8.72
.98	3.90	.78	7.07	.58	8.86
.96	4.41	.76	7.27	.56	8.90
.94	4.82	.74	7.49	.54	9.17
.92	5.19	.72	7.67	.52	9.31
.90	5.51	.70	7.89	.50	9.47
.88	5.81	.68	8.09	.48	9.54
.86	6.09	.66	8.27	.46	9.62
.84	6.38	.64	8.43		
.82	6.59	.62	8.61		

Table 11

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	2.20	.80	5.61	.60	7.29
.98	3.12	.78	5.81	.58	7.39
.96	3.61	.76	5.99	.56	7.52
.94	3.98	.74	6.18	.54	7.69
.92	4.28	.72	6.30	.52	7.81
.90	4.52	.70	6.51	.50	7.90
.88	4.77	.68	6.68	.48	8.03
.86	4.99	.66	6.82	.46	8.11
.84	5.21	.64	7.02		
.82	5.43	.62	7.12		

Table 12

Echo Voltage Height vs. Reduced Temperature for
q [110] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	1.50	.80	4.77	.60	6.79
.98	2.19	.78	4.99	.58	6.93
.96	2.53	.76	5.22	.56	7.10
.94	2.85	.74	5.46	.54	7.27
.92	3.10	.72	5.67	.52	7.42
.90	3.38	.70	5.87	.50	7.59
.88	3.66	.68	6.07	.48	7.70
.86	3.97	.66	6.27	.46	7.79
.84	4.23	.64	6.47		
.82	4.51	.62	6.66		

Table 13

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	1.52	.80	4.81	.60	6.79
.98	2.32	.78	5.01	.58	6.95
.96	2.70	.76	5.23	.56	7.11
.94	2.99	.74	5.48	.54	7.29
.92	3.29	.72	5.74	.52	7.42
.90	3.56	.70	5.92	.50	7.57
.88	3.82	.68	6.10	.48	7.72
.86	4.10	.66	6.28	.46	7.81
.84	4.37	.64	6.47		
.82	4.68	.62	6.60		

Table 14

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	..98	.80	3.98	.60	5.99
.98	1.69	.78	4.19	.58	6.12
.96	1.99	.76	4.39	.56	6.28
.94	2.27	.74	4.60	.54	6.46
.92	2.51	.72	4.77	.52	6.61
.90	2.76	.70	4.99	.50	6.78
.88	3.00	.68	5.20	.48	6.90
.86	3.26	.66	5.42	.46	7.08
.84	3.51	.64	5.60		
.82	3.76	.62	5.88		

Table 15

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	1.80	.80	5.12	.60	7.40
.98	2.48	.78	5.40	.58	7.60
.96	2.90	.76	5.67	.56	7.83
.94	3.22	.74	5.89	.54	8.03
.92	3.49	.72	6.12	.52	8.19
.90	3.78	.70	6.36	.50	8.36
.88	4.02	.68	6.57	.48	8.47
.86	4.30	.66	6.79	.46	8.59
.84	4.58	.64	7.00		
.82	4.75	.62	7.23		

Table 16

Echo Voltage Height vs. Reduced Temperature for
q [100] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	1.85	.80	5.20	.60	7.44
.98	2.60	.78	5.42	.58	7.70
.96	3.02	.76	5.67	.56	7.91
.94	3.34	.74	5.92	.54	8.10
.92	3.62	.72	6.19	.52	8.28
.90	3.97	.70	6.40	.50	8.42
.88	4.23	.68	6.65	.48	8.59
.86	4.49	.66	6.88	.46	8.89
.84	4.77	.64	7.10		
.82	4.99	.62	7.28		

Table 17

Echo Voltage Height vs. Reduced Temperature for
q [110] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	3.56	.80	5.61	.60	6.50
.98	4.21	.78	5.76	.58	6.55
.96	4.48	.76	5.87	.56	6.61
.94	4.67	.74	5.98	.54	6.67
.92	4.81	.72	6.02	.52	6.71
.90	4.98	.70	6.13	.50	6.77
.88	5.12	.68	6.22	.48	6.81
.86	5.27	.66	6.31	.46	6.88
.84	5.39	.64	6.39		
.82	5.51	.62	6.43		

Table 18

Echo Voltage Height vs. Reduced Temperature for
q [110] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	3.57	.80	5.51	.60	6.48
.98	4.12	.78	5.62	.58	6.53
.96	4.42	.76	5.69	.56	6.59
.94	4.62	.74	5.80	.54	6.66
.92	4.80	.72	5.91	.52	6.72
.90	4.96	.70	6.03	.50	6.81
.88	5.09	.68	6.12	.48	6.88
.86	5.22	.66	6.20	.46	6.89
.84	5.32	.64	6.28		
.82	5.43	.62	6.38		

Table 19

Echo Voltage Height vs. Reduced Temperature for
q [110] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	5.49	.80	8.17	.60	9.22
.98	6.31	.78	8.30	.58	9.29
.96	6.70	.76	8.43	.56	9.37
.94	6.91	.74	8.57	.54	9.43
.92	7.12	.72	8.69	.52	9.48
.90	7.33	.70	8.79	.50	9.51
.88	7.53	.68	8.88	.48	9.57
.86	7.71	.66	8.99	.46	9.60
.84	7.88	.64	9.09		
.82	8.01	.62	9.16		

Table 20

Echo Voltage Height vs. Reduced Temperature for
q [110] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	4.02	.80	6.27	.60	7.30
.98	4.70	.78	6.40	.58	7.39
.96	4.92	.76	6.53	.56	7.47
.94	5.12	.74	6.68	.54	7.54
.92	5.33	.72	6.72	.52	7.61
.90	5.52	.70	6.85	.50	7.71
.88	5.68	.68	6.96	.48	7.77
.86	5.73	.66	7.04	.46	7.82
.84	5.98	.64	7.13		
.82	6.11	.62	7.22		

Table 21

Echo Voltage Height vs. Reduced Temperature for
q [110] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	4.21	.80	6.41	.60	7.38
.98	4.81	.78	6.52	.58	7.42
.96	5.08	.76	6.62	.56	7.49
.94	5.29	.74	6.72	.54	7.58
.92	5.49	.72	6.82	.52	7.63
.90	5.69	.70	6.97	.50	7.71
.88	5.87	.68	7.05	.48	7.73
.86	6.02	.66	7.17	.46	7.79
.84	6.18	.64	7.25		
.82	6.29	.62	7.31		

Table 22

Echo Voltage Height vs. Reduced Temperature for
q [110] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	4.50	.80	7.20	.60	8.62
.98	5.22	.78	7.39	.58	8.09
.96	5.53	.76	7.58	.56	8.78
.94	5.79	.74	7.72	.54	8.88
.92	6.01	.72	7.80	.52	8.98
.90	6.24	.70	7.92	.50	9.09
.88	6.45	.68	8.10	.48	9.19
.86	6.62	.66	8.29	.46	9.23
.84	6.81	.64	8.43		
.82	7.01	.62	8.54		

Table 23

Echo Voltage Height vs. Reduced Temperature for
q [110] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	4.57	.80	7.23	.60	8.68
.98	5.32	.78	7.39	.58	8.72
.96	5.63	.76	7.51	.56	8.80
.94	5.90	.74	7.69	.54	8.89
.92	6.18	.72	7.80	.52	8.99
.90	6.40	.70	7.93	.50	9.10
.88	6.60	.68	8.10	.48	9.14
.86	6.78	.66	8.24	.46	9.21
.84	6.94	.64	8.38		
.82	7.10	.62	8.48		

Table 24

Echo Voltage Heights vs. Reduced Temperature for
q [110] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	3.68	.80	6.51	.60	8.00
.98	4.43	.78	6.68	.58	8.09
.96	4.83	.76	6.82	.56	8.19
.94	5.11	.74	6.94	.54	8.30
.92	5.39	.72	7.02	.52	8.39
.90	5.61	.70	7.19	.50	8.48
.88	5.81	.68	7.39	.48	8.58
.86	6.00	.66	7.52	.46	8.63
.84	6.18	.64	7.70		
.82	6.33	.62	7.87		

Table 25

Echo Voltage Heights of Reduced Temperature for
q [110] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	3.45	.80	6.32	.60	7.79
.98	4.10	.78	6.49	.58	7.89
.96	4.48	.76	6.62	.56	8.00
.94	4.71	.74	6.71	.54	8.11
.92	5.00	.72	6.92	.52	8.21
.90	5.27	.70	7.12	.50	8.32
.88	5.50	.68	7.29	.48	8.43
.86	5.71	.66	7.42	.46	8.48
.84	5.92	.64	7.55		
.82	6.13	.62	7.68		

Table 26

Echo Voltage Heights vs. Reduced Temperature for
q [110] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	3.65	.80	6.49	.60	7.87
.98	4.48	.78	6.66	.58	8.01
.96	4.82	.76	6.78	.56	8.12
.94	5.06	.74	6.88	.54	8.22
.92	5.27	.72	6.95	.52	8.34
.90	5.49	.70	7.11	.50	8.47
.88	5.70	.68	7.27	.48	8.53
.86	5.90	.66	7.42	.46	8.62
.84	6.10	.64	7.58		
.82	6.30	.62	7.72		

Table 27

Echo Voltage Heights vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	4.00	.80	6.07	.60	7.31
.98	4.49	.78	6.19	.58	7.42
.96	4.77	.76	6.32	.56	7.53
.94	4.92	.74	6.48	.54	7.66
.92	5.11	.72	6.62	.52	7.77
.90	5.30	.70	6.72	.50	7.87
.88	5.48	.68	6.84	.48	7.99
.86	5.63	.66	6.97	.46	8.09
.84	5.79	.64	7.09		
.82	5.92	.62	7.20		

Table 28

Echo Voltage Heights vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	3.81	.80	5.81	.60	7.02
.98	4.30	.78	5.96	.58	7.13
.96	4.61	.76	6.09	.56	7.24
.94	4.79	.74	6.22	.54	7.37
.92	4.94	.72	6.36	.52	7.48
.90	5.09	.70	6.48	.50	7.58
.88	5.23	.68	6.59	.48	7.69
.86	5.39	.66	6.69	.46	7.79
.84	5.52	.64	6.80		
.82	5.68	.62	6.92		

Table 29

Echo Voltage Heights vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	4.58	.80	6.01	.60	6.79
.98	4.90	.78	6.09	.58	6.86
.96	5.12	.76	6.17	.56	6.92
.94	5.25	.74	6.23	.54	7.00
.92	5.39	.72	6.31	.52	7.08
.90	5.50	.70	6.39	.50	7.13
.88	5.62	.68	6.49	.48	7.21
.86	5.72	.66	6.57	.46	7.28
.84	5.82	.64	6.03		
.82	5.92	.62	6.71		

Table 30

Echo Voltage Height vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	4.59	.80	6.00	.60	6.82
.98	5.01	.78	6.09	.58	6.90
.96	5.13	.76	6.18	.56	6.98
.94	5.27	.78	6.23	.54	7.06
.92	5.39	.72	6.32	.52	7.13
.90	5.50	.70	6.41	.50	7.21
.88	5.62	.68	6.50	.48	7.29
.86	5.72	.66	6.58	.46	7.37
.84	6.81	.64	6.67		
.82	5.91	.62	6.73		

Table 31

Echo Voltage Height vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	4.45	.80	5.75	.60	6.48
.98	4.72	.78	5.82	.58	6.54
.96	4.92	.76	5.89	.56	6.61
.94	5.07	.74	5.97	.54	6.69
.92	5.19	.72	6.03	.52	6.77
.90	5.29	.70	6.12	.50	6.82
.88	5.38	.68	6.20	.48	6.89
.86	5.48	.66	6.28	.46	6.96
.84	5.58	.64	6.34		
.82	5.67	.62	6.40		

Table 32

Echo Voltage Height vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	5.52	.80	7.00	.60	7.78
.98	5.98	.78	7.09	.58	7.82
.96	6.13	.76	7.18	.56	7.90
.94	6.28	.74	7.27	.54	7.96
.92	6.38	.72	7.34	.52	8.01
.90	6.49	.70	7.42	.50	8.08
.88	6.60	.68	7.50	.48	8.13
.86	6.71	.66	7.58	.46	8.20
.84	6.81	.64	7.63		
.82	6.91	.62	7.71		

Table 33

Echo Voltage Height vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	5.47	.80	6.86	.60	7.60
.98	5.86	.78	6.95	.58	7.67
.96	6.01	.76	7.02	.56	7.73
.94	6.13	.74	7.11	.54	7.80
.92	6.25	.72	7.13	.52	7.87
.90	6.37	.70	7.25	.50	7.92
.88	6.47	.68	7.31	.48	7.99
.86	6.58	.66	7.39	.46	8.05
.84	6.68	.64	7.47		
.82	6.78	.62	7.52		

Table 34

Echo Voltage Height vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	3.17	.80	6.08	.60	7.61
.98	3.87	.78	6.28	.58	7.73
.96	4.27	.76	6.47	.56	7.87
.94	4.58	.74	6.61	.54	7.99
.92	4.81	.72	6.77	.52	8.11
.90	5.02	.70	6.89	.50	8.21
.88	5.22	.68	7.04	.48	8.33
.86	5.43	.66	7.19	.46	8.47
.84	5.66	.64	7.32		
.82	5.87	.62	7.48		

Table 35

Echo Voltage Height vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	3.10	.80	6.69	.60	8.68
.98	3.90	.78	6.91	.58	8.83
.96	4.38	.76	7.13	.56	9.01
.94	4.73	.74	7.33	.54	9.18
.92	5.08	.72	7.51	.52	9.33
.90	5.40	.70	7.77	.50	9.49
.88	5.68	.68	7.96	.48	9.63
.86	5.93	.66	8.14	.46	9.81
.84	6.19	.64	8.32		
.82	6.42	.62	8.51		

Table 36

Echo Voltage Height vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	2.93	.80	4.92	.60	6.01
.98	3.31	.78	5.06	.58	6.11
.96	3.60	.76	5.18	.56	6.20
.94	3.87	.74	5.30	.54	6.30
.92	4.07	.72	5.43	.52	6.40
.90	4.26	.70	5.53	.50	6.50
.88	4.41	.68	5.64	.48	6.54
.86	4.53	.66	5.77	.46	6.62
.84	4.68	.64	5.87		
.82	4.80	.62	5.91		

Table 37

Echo Voltage Height vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data unsmoothed

t	V	t	V	t	V
1.00	2.99	.80	5.09	.60	6.21
.98	3.41	.78	5.22	.58	6.31
.96	3.75	.76	5.37	.56	6.41
.94	4.01	.74	5.49	.54	6.49
.92	4.22	.72	5.55	.52	6.58
.90	4.40	.70	5.08	.50	6.64
.88	4.56	.68	5.79	.48	6.73
.86	4.68	.66	5.91	.46	6.86
.84	4.81	.64	6.01		
.82	4.97	.62	6.11		

Table 38

Echo Voltage Height vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	5.28	.80	6.69	.60	7.37
.98	5.53	.78	6.78	.58	7.42
.96	5.78	.76	6.86	.56	7.47
.94	5.97	.74	6.93	.54	7.52
.92	6.11	.72	6.99	.52	7.57
.90	6.23	.70	7.07	.50	7.62
.88	6.32	.68	7.12	.48	7.67
.86	6.42	.66	7.19	.46	7.72
.84	6.52	.64	7.26		
.82	6.61	.62	7.31		

Table 39

Echo Voltage Height vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	6.70	.80	8.39	.60	9.19
.98	7.27	.78	8.50	.58	9.27
.96	7.43	.76	8.58	.56	9.31
.94	7.58	.74	8.68	.54	9.38
.92	7.72	.72	8.77	.52	9.42
.90	7.86	.70	8.84	.50	9.47
.88	7.98	.68	8.92	.58	9.50
.86	8.08	.66	9.00	.46	9.53
.84	8.19	.64	9.07		
.82	8.29	.62	9.12		

Table 40

Echo Voltage Height vs. Reduced Temperature for
q [111] at a Frequency of 11.0 MHz

Data smoothed

t	V	t	V	t	V
1.00	5.39	.80	7.90	.60	9.08
.98	6.11	.78	8.03	.58	9.17
.96	6.47	.76	8.18	.56	9.26
.94	6.67	.74	8.30	.54	9.35
.92	6.86	.72	8.42	.52	9.42
.90	7.02	.70	8.53	.50	9.50
.88	7.22	.68	8.67	.48	9.59
.86	7.41	.66	8.77	.46	9.68
.84	7.59	.64	8.88	.44	9.77
.82	7.76	.62	8.98		