ULTRASONIC-ATTENUATION DETERMINATION OF
THE ANISOTROPIC ENERGY GAP IN
SUPERCONDUCTING ZINC

by

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CHAPTER I

INTRODUCTION

Three years after H. Kamerlingh Onnes¹ succeeded in liquifying Helium in 1908, he made an extremely startling discovery. Investigating the conductivity properties of pure mercury wire with the newly available low-temperature range, Onnes found that instead of the resistance decreasing smoothly as the temperature was reduced toward zero Kelvin (K), it fell sharply at about 4.2K. Below this temperature, termed the critical or transition temperature, the mercury exhibited essentially no measurable resistance. Onnes recognized that mercury had passed into a new state, which on account of its electrical properties quite unlike those previously known, he called the "Superconductive State". In later experiments, Onnes also succeeded in showing that lead, tin, and indium became superconductors at 7.2, 3.7, and 3.4K, respectively.

Since the measurements of Onnes, not only have numerous other metals and alloys been shown to become superconducting at low temperatures, but they have also been shown to possess another just as extraordinary property in the superconducting state, perfect diamagnetism. This property was discovered by Meissner and Ochsenfeld² in 1933 during their measurements on the flux distribution outside tin and lead specimens which had been cooled below their transition temperatures while in a magnetic field. Their experiments demonstrated that a metal in the superconducting state prevents any magnetic flux from

existing in its interior. This property of magnetic flux expulsion from the interior of a superconductor is called the "Meissner effect".

Shortly after the discovery of the "Meissner effect", two theories which described the macroscopic properties of superconductors were proposed. In 1934, Gorter and Casimir³ summarized and extended a thermodynamic treatment of superconductors which had been proposed by Ehrenfest and Rutgers.⁴ Their theory, sometimes called the "two-fluid model", described the conduction electrons in a superconductor as being composed of two independent electron seas. One sea consisted of normal state electrons and the other sea of superconducting state electrons which were responsible for the superconducting properties in the metal. The theory assumed that as the temperature was lowered in the superconducting state the thermodynamic properties of the superconductor could be described by an increase of the "superconducting electrons" with a resulting simultaneous decrease in the "normal electrons".

In 1935, F. and H. London⁵ proposed a phenomenological theory of the electromagnetic properties of superconductors with the resulting equations having been termed the "London equations". As a result of this theory, it was predicted that the magnetic field did penetrate into the surface of a superconductor. However, it also showed that the flux density falls off exponentially with distance into the metal and reaches $1/e$ of its value at the surface with a characteristic length called the "London penetration depth", λ_L . The field penetration predicted by the London theory was first confirmed experimentally in 1940 by Shoenberg.⁶

Although the above phenomenological theories gave an adequate description of the macroscopic properties of superconductors, it was not until after 1950 that a successful microscopic theory began to emerge. The first experimental evidence as to the type of interaction which gave rise to superconductivity were the experimental measurements published in 1950 on various isotopic mixtures of mercury by Serin, Reynolds, and Nebsitt.⁷ These measurements indicated that the critical temperature, T_c , varied approximately as $m^{-1/2}$. The importance in this discovery lies in the fact that the lattice vibrations (phonons) play a fundamental role in the occurrence of superconductivity. It should also be noted that in the same year, Fröhlich⁸ had shown independently by a theoretical calculation that the electron-phonon interaction could possibly be the determining factor for the development of a microscopic theory of superconductivity.

The development of a successful microscopic theory was not only a result of the isotopic mass dependence; perhaps the most significant experimental evidence for the development came from the accumulation of data indicating there was a gap in the energy spectrum describing the "normal" and "superconducting" states of the electrons. The first fairly direct experimental evidence indicating the existence of an energy gap came from the thermal conductivity measurements on superconducting tin by Goodman⁹ in 1953. Further support was given by the specific heat measurements on vanadium¹⁰ in 1956. The first direct spectroscopic indication of an energy gap was published by Glover and Tinkham¹¹ simultaneously with what is now the presently accepted microscopic theory of superconductivity, the Bardeen, Cooper, and

Schrieffer¹² "Theory of Superconductivity" (hereafter designated as BCS). A discussion of this theory is given in Appendix A.

I.1 Anisotropy Effects

BCS neglect effects due to anisotropy and assume that the interaction matrix element $V_{\vec{k}\vec{k}'}$, seen in Eq.(A.9) in Appendix A, can be replaced by a constant average matrix element

$$V = \langle V_{\vec{k}\vec{k}'} \rangle_{\text{ave.}} \quad (1)$$

for pairs making transitions in the region $-\hbar\omega_D < \epsilon < \hbar\omega_D$. Here ω_D is the Debye¹³ frequency.

However, as numerous experiments including the present experiment indicate, for real superconductors a complete description should allow for anisotropy. Mackowitz and Kadanoff¹⁴ proposed a model to include the effects of anisotropy by assuming that $V_{\vec{k}\vec{k}'}$ has the form

$$V_{\vec{k}\vec{k}'} = \begin{cases} -(1+a_{\vec{k}})V(1+a_{\vec{k}'}) & \text{For } |\epsilon_{\vec{k}}|, |\epsilon_{\vec{k}'}| < \hbar\omega_D \\ 0 & \text{Otherwise .} \end{cases} \quad (2)$$

Here ω_D is again the Debye frequency, V is a positive constant and $a_{\vec{k}}$ is a small number which depends only on direction. If $a_{\vec{k}} = 0$, Eq.(2) gives the original BCS expression.

Substitution of Eq.(2) into Eq.(A.9) immediately yields a gap parameter of the form

$$\Delta_{\vec{k}}(T) = \overline{\Delta(T)}(1+a_{\vec{k}}) \quad (3)$$

where $\overline{\Delta(T)}$ is the average gap parameter if Eq.(1) had been the form of $V_{\vec{k}\vec{k}'}$. Therefore $a_{\vec{k}}$ is seen to be a small number describing the gap anisotropy in a real superconductor.

BCS show in the "weak-coupled" limit ($K_B T_c \ll \hbar \omega_D$) that the average energy gap at zero Kelvin for an ideal isotropic superconductor is related to the transition temperature, T_c , by

$$\overline{\Delta(0)} = 1.76 K_B T_c . \quad (4)$$

In the experiment to be described, that is a real anisotropic superconductor, the coefficient of $K_B T_c$ in Eq.(4) is left as an adjustable parameter for each crystallographic direction studied:

$$\overline{\Delta_{\vec{k}}(0)} = B K_B T_c . \quad (5)$$

Then using Eq.(5) in conjunction with Eq.(3) at $T = 0K$ and with data from various crystallographic directions the anisotropy factor, $a_{\vec{k}}$, can be estimated for each of these directions.

II.2 Ultrasonic Attenuation in Normal Metals

The first adequate theory of ultrasonic attenuation in normal metals was proposed by Pippard¹⁵ on the idea of a distorted local Fermi surface. Using a free electron model for an isotropic metal with a well defined relaxation time τ , he has shown the overall dependence of the longitudinal lattice wave (phonon) attenuation on $q\ell_e$ is given by:

$$\alpha_N = \frac{Nm_e}{\rho_o v_s \tau} \left[\frac{(ql_e)^2 \tan^{-1}(ql_e)}{3(ql_e - \tan^{-1} ql_e)} - 1 \right] \quad (6)$$

Here α_N is the impurity limited longitudinal attenuation in the normal metal, N is the number of electrons per unit volume, m_e is the mass of a free electron, ρ_o is the density of the metal, v_s is the longitudinal wave velocity, τ is the isotropic electron relaxation time, q is the wave number of the ultrasonic wave, and l_e is the electron mean-free-path.

In ultrasonic measurements, it is convenient to speak of two regimes. They are for $ql_e < 1$ and $ql_e > 1$. Normally, $ql_e \geq 1$ for the electronic attenuation to be sufficiently large to be readily measurable. For the two regimes, Pippard's calculations yield the following results:

$$\alpha_N = \frac{\pi N m_e v_F}{6 \rho_o v_s^2} \cdot \omega \quad (ql_e > 1) \quad (7)$$

and

$$\alpha_N = \frac{2 N m_e v_F \omega}{15 \rho_o v_s^2} \cdot ql_e \quad (ql_e < 1) \quad (8)$$

where v_F is the Fermi electron velocity, ω is the angular frequency of the ultrasonic wave, and the other terms were previously defined. Therefore for $ql_e > 1$ the normal state electronic attenuation, α_N , varies linearly with frequency and is independent of l_e ; while for $ql_e < 1$, α_N has a square-law frequency dependence with a temperature

dependence of ℓ_e .

For more complicated Fermi surfaces than free electron spheres, Pippard¹⁶ has shown that in general the longitudinal attenuation can be written

$$\alpha_N = \frac{h\omega}{4\pi^2 \rho_0 v_s^2} \oint R_1 R_2 K_z^2 d\psi. \quad (q\ell_e > 1) \quad (9)$$

Here R_1 and R_2 are the principle radii of curvature of the Fermi surface; K_z is the deformation parameter which gives the displacement of the Fermi surface normal to itself when the lattice is strained by a unit dilation. The "Deformation Integral" is over all parts of the Fermi surface where $\vec{v}_F \cdot \vec{q} = 0$ which defines the so-called "effective zone".

The "effective zone" essentially indicates which electrons on the Fermi surface enter into the electron-lattice interaction causing the attenuation of the ultrasonic waves. For the case $q\ell_e \gg 1$, Morse¹⁷ has shown that the electron-lattice interaction can be treated as a quantum-mechanical electron-phonon scattering process. For this type of process, conservation of energy and momentum requires only that fraction of electrons having a velocity component $v_F \cos \theta$ approximately equal to the sound velocity, v_s , in the direction of $\vec{q}$ to enter into the electron-phonon interaction. The angle θ is the angle between the Fermi velocity vector, $\vec{v}_F$, and the sound wave vector $\vec{q}$. Therefore these electrons lie in a narrow band near the equator of the Fermi surface.

For the case $q\ell_e \ll 1$, the electron-lattice interaction is no

longer a simple scattering process, but must be described by a relaxation process of all the electrons to a Fermi surface deformed by a local deformation of the lattice.

For the intermediate case $ql_e \geq 1$, which is the main concern of this paper, Leibowitz¹⁸ has given the selectivity of the electron-lattice interaction in terms of θ as

$$\cos \theta = \frac{v_s}{v_F} + \frac{1}{ql_e} . \quad (10)$$

Thus for $ql_e \geq 1$, the interaction is weighted toward the electrons near the equator perpendicular to the sound wave vector $\vec{q}$. Also, not only should the selectivity of the electronic attenuation of an anisotropic superconductor be a function of ql_e for low values of ql_e , but likewise it is expected the energy gap, $\overline{\Delta_k(0)}$, should be a function of ql_e .

I.3 Ultrasonic Attenuation in Superconductors

For low frequency sound waves ($\nu \leq 10^8$ Hertz) propagating in a superconductor, the energy associated with each phonon is less than 10^{-6} electron volts (eV). Unless the temperature is very close to the transition temperature T_c , this phonon energy will be much less than $2\Delta(3K_B T_c \sim 10^{-4} \text{ eV})$ which is the minimum energy required to create a pair of quasiparticles. Therefore, the phonons can only be absorbed by scattering already existing quasiparticles from one k-state to another. Thus the superconducting state attenuation, α_s , should only depend on the probability distribution of quasiparticles as given by Eq.(A.8). BCS, using this distribution function, showed

that the ratio of the superconducting to normal state ultrasonic attenuation for longitudinal waves in the regime $q\ell_e > 1$ is given by:

$$\frac{\alpha_s}{\alpha_N} = \frac{2}{e^{\Delta(T)/K_B T} + 1} \quad (11)$$

Here $\Delta(T)$ is the isotropic temperature-dependent energy gap. Tsuneto¹⁹ has shown that this result holds equally well for all values of $q\ell_e$ in the region of impurity-limited scattering.

As mentioned previously, for a real anisotropic superconductor the value of the $T = 0K$ energy gap can assume a value different from the BCS value of $1.76 K_B T_c$ for each crystallographic direction studied. In general, the energy gap depends on the direction of q and as Eq.(10) indicates if the electron mean-free-path, ℓ_e , is small enough it can depend on the magnitude of $\vec{q}$.

I.4 Ultrasonic Attenuation in Zinc

A large anisotropy in the superconducting energy gap in zinc has been suggested by measurements of thermal conductivity,²⁰ electronic specific heat,^{21,22} microwave absorption,²³ and depression of the transition temperature by nonmagnetic impurities.²⁴ The mean anisotropy has been suggested by these measurements to be as much as 22%.

The only published ultrasonic attenuation measurements on superconducting zinc to date are summarized in Table 1.^{25,26,27} The zero Kelvin energy gap data, $\overline{2\Delta_k^+}(0)$, of Lea and Dobbs²⁵ are the

Table 1

Ultrasonic Energy Gap Data from Previous Investigations

Authors	Direction of Propagation	$\text{Lim}(\alpha/\nu)$ $q\ell_e \rightarrow \infty$ (dB/cm-MHz) $\pm 5\%$	ℓ_e (μm) $\pm 5\%$	$2\Delta(0)/K_B T_c$
Lea and Dobbs	$[11\bar{2}0]$	0.067	79.0	3.64 ± 0.1
$(T_c \approx 0.84 \text{ K})$	$[10\bar{1}0]$	0.128	29.6	3.79 ± 0.1
	$[0001]$	1.29	17.1	3.41 ± 0.1
Bohm and Horwitz	$[11\bar{2}0]$	---	---	3.8 ± 0.2
$(T_c = 0.85 \pm 0.01 \text{ K})$ (233 MHz only)	$[10\bar{1}0]$	---	---	3.4 ± 0.2
Goncuz and Neighbours	$[0001]$	---	---	3.2 ± 0.4

only data from which the anisotropy of the energy gap can be confidently deduced and their measurements indicate an anisotropy no larger than $\pm 5\%$. Also it is noted that the data of Lea and Dobbs²⁵ and Bohm and Horwitz²⁶ for the $[11\bar{2}0]$ and $[10\bar{1}0]$ crystallographic directions are not in agreement within their stated experimental error.

In the measurements of Farrell, Park, and Coles²⁴ on the variation of T_c in zinc based alloys and also in the measurements of Duclaux-Soares and Cheeke²² on the electronic specific heat of zinc, both groups have used a simple two gap model (to be discussed in Chapter IV) to obtain a good fit to their data. Therefore, the present ultrasonic measurements will allow not only for anisotropy in the energy gap, but the data will also be analyzed in such a manner so as to allow for the possibility of multiple energy gaps.

As was indicated by Eq.(10), the superconducting energy gaps in the various crystallographic crystal directions could possibly be functions of the sound wave frequency in these directions. Therefore the present measurements are made over the widest possible frequency range consistent with the sensitivity of the experimental attenuation measurement apparatus. A complete description of this apparatus is given in Chapter II.

As previously discussed, an important quantity in the interpretation of data is the regime in which the attenuation measurements are made, where the regime is determined by the quantity $q\ell_e$. In order to have an estimate of the mean-free-path, ℓ_e , a magnetoacoustic technique previously employed by Deaton²⁸ to determine ℓ_e in zinc and

cadmium was used. This technique and the results of these measurements will be found in Chapter III.

Briefly then, this investigation is primarily concerned with the measurement of the anisotropic superconducting energy gap of pure crystalline zinc in the three crystallographic directions: $[0001]$, $[11\bar{2}0]$, and $[10\bar{1}0]$. The data are obtained with an improved continuously measuring ultrasonic system, and a conventional He^3 refrigerator-cryostat was employed to achieve sufficiently low temperatures ($<1\text{K}$) necessary to these measurements. The data were fit to the theoretical equation of BCS, Eq.(11), while allowing for anisotropy in the energy gap and the possibility of multiple energy gaps. Also it will be determined if the energy gap has a dependence on the sound wave frequency as previously indicated by Eq.(10).

CHAPTER II

EXPERIMENTAL

One method to study the propagation behavior of ultrasonic stress waves in solids is by the measurement of the attenuation of the stress waves as a function of some variable of interest. This type of measurement permits one to observe the influence on the propagation behavior of properties of a solid which are sufficiently well coupled to the lattice. As discussed in the previous chapter, one such property in a metal is the coupling of the electrons to the lattice. Therefore, the ultrasonic stress wave is found to interact with the electrons via the lattice.

In the ultrasonic attenuation measurements in a superconducting material, one of the variables of interest is the temperature. In earlier measurements by various investigators,^{29,25,23} zinc was found to exist in the superconducting state at temperatures less than approximately 0.84 K. Therefore in order to make ultrasonic attenuation measurements in superconducting zinc, a cryogenic system capable of sustained operation at temperatures below 0.84 K was essential. This was accomplished by employing a He³ evaporative refrigerator; since the measurements were made as a function of temperature, an accurate thermometry system which would continuously monitor these temperatures was also essential. Therefore this chapter is concerned mainly with the following four principle areas: (1) the ultrasonic attenuation method, (2) the electronic equipment

used to measure the ultrasonic attenuation, (3) the He^3 refrigerator-cryostat system, and (4) the thermometry system. Two other topics will also be discussed in this chapter which pertain to the ultrasonic measurements. They are the transducers used to generate the ultrasonic stress waves and the "binder" used to bond the transducer to the crystal specimen.

II.1 Measurement of Attenuation by the Pulse Method

The ultrasonic pulse-echo technique employed in these measurements is actually a form of spectroscopy not unlike that found in other branches of physics. Normally, spectroscopists are concerned with the propagation of electromagnetic radiation. In contrast, the vehicle of information in ultrasonic spectroscopy of solids is the mechanical stress wave or ultrasonic sound wave. In particular, the ultrasonic study here is concerned with the measurement of the absorption or attenuation of a single short-duration pulse of ultrasonic waves.

About 1954, Bommel³⁰ and MacKennon³¹ first demonstrated that at sufficiently low temperatures and high frequencies there is an energy transfer from ultrasonic waves to conduction electrons, the electron-phonon interaction, which is detectable in ultrasonic attenuation measurements. As a consequence of these measurements, ultrasonic techniques have been used extensively to investigate many of the electrical properties of solids, one being superconductivity.

In order to introduce the pulse of ultrasonic waves into the sample, a piezoelectric transducer is normally bonded or evaporated

onto a flat sample surface. Then a radio frequency (R.F.) signal from a pulsed oscillator operating at the fundamental frequency or at one of its odd harmonics is impressed across the faces of the transducer. Due to the piezoelectric effect³² an ultrasonic wave is generated which propagates into and through the sample. If the transducer is bonded on one face of parallel sample faces, the pulse will be reflected at the opposite air-sample interface and returned back to the sample-transducer interface, where all but a small fraction of the energy is again reflected into the sample. Before the pulse has returned to the transducer, the pulsed oscillator has been turned off. The transducer converts a small portion of the returned pulse, again by the piezoelectric effect, back into electrical energy. This electrical signal is then amplified by an appropriate receiver system and displayed on an oscilloscope's cathode ray tube (CRT). The pulse energy that was not converted back into electrical energy has in the meantime been reflected at the sample-transducer interface and begun another round trip through the sample. Therefore as this process is repeated as a function of time, a series of echoes appear on the oscilloscope's CRT. Each successive echo is found to be smaller than the proceeding one, because as each echo passes through the sample, part of its energy is absorbed or scattered from the beam.

Shown in Figure 1 is a typical example of an echo pattern taken directly from an oscilloscope trace using a display scanner to be described in a later section. The echo pattern is for 50 megahertz (MHz) longitudinal waves propagating in a zinc sample in the super-

FIGURE 1
ECHO PATTERN FOR 50 MHz LONGITUDINAL WAVES

conducting state. Each echo represents the envelope of a rectified R.F. wave group that has traversed the sample length twice.

Attenuation Factor α

It is evident from the foregoing discussion that the amplitude decrease of each succeeding echo must represent, in some manner, the energy dissipation mechanisms and scattering losses from the beam. The manner in which these losses are represented will not be discussed. It will be shown how the attenuation of the sound pulse can be expressed in terms of a parameter which is called the attenuation factor α . Also the discussion will focus on how this attenuation factor relates to the superconducting attenuation equation (Eq.11).

Consider a plane stress wave that is attenuated as it propagates through a sample:

$$u(x,t) = u_0 e^{i(\omega t - kx)} \quad (12)$$

Where ω is the angular frequency, k is the propagation vector, and u is the amplitude of the stress wave.

The attenuation factor α is introduced into Eq.(1) by assuming that the propagation vector and velocity are complex.³³

Taking

$$v = v' + v'' \quad , \quad (13)$$

and

$$k = k' - i\alpha \quad , \quad (14)$$

Eq.(12) becomes for an attenuated plane wave:

$$u(x,t) = u_0 e^{-\alpha x} e^{i(\omega t - k'x)} . \quad (15)$$

It is assumed that α is not dependent on x , which is a legitimate assumption if the sample is homogeneous.

Since the attenuation is determined from the envelope of the high-frequency wave, it is sufficient to write Eq.(15) as

$$u(x) = u_0 e^{-\alpha x} \quad (16)$$

to specify the attenuation α .

Taking the natural logarithm of both sides of Eq.(15) gives

$$\text{Log}_e u(x) = \text{Log}_e u_0 - \alpha x . \quad (17)$$

Writing Eq.(17) for two different points x_1 and x_2 along the sound path where $x_1 < x_2$, and then taking the difference of these two equations gives the result:

$$\alpha = \frac{1}{x_2 - x_1} \text{Log}_e \left(\frac{u(x_1)}{u(x_2)} \right) \quad (18)$$

Here α is expressed in nepers per unit length. Eq.(18) is normally seen expressed in decibels (dB), i.e., Eq.(18) is expressed by definition as

$$\alpha = \frac{20}{x_2 - x_1} \text{Log}_{10} \left(\frac{u(x_1)}{u(x_2)} \right) \quad (19)$$

where α is now in units of dB per unit length.

Assume now that point x_1 corresponds to an echo at the transducer and point x_2 corresponds to any succeeding echo at the transducer. Since the voltage on the transducer must be proportional to the amplitude of the plane stress wave at the transducer, Eq.(19) may be expressed as

$$\alpha = \frac{20}{x_2 - x_1} \text{Log}_{10} \left(\frac{V(x_1)}{V(x_2)} \right) \quad (20)$$

where $V(x_1)$ and $V(x_2)$ are the corresponding voltages on the transducer.

Now let n be an index indicating the number of echoes that have arrived at the transducer between the times corresponding to x_1 and x_2 . Also let L be the sample length, then Eq.(20) may be expressed as

$$\alpha = \frac{20}{2(n-m)L} \text{Log}_{10} \left(\frac{V_m}{V_n} \right) \quad (21)$$

where V_m and V_n are the voltages on the transducer corresponding to the m^{th} and n^{th} echoes, respectively.

It should be emphasized, pertaining to Eq.(21), that V_m and V_n are voltages at the transducer. Therefore if the attenuation is determined by measuring voltage heights of echoes displayed on the CRT, the amplification of these electrical signals must be linear. In the attenuation measurement equipment to be discussed in the next section, extreme care was taken to insure that all amplifier systems operated in their linear regions.

In this experiment, the interest does not lie in the absolute magnitude of α , but in the functional dependence of α on temperature as expressed in Eq.(11). Therefore introducing the temperature dependence of α into Eq.(21) gives

$$\alpha(T) = \frac{20}{2(n-m)L} \text{Log}_{10} \left(\frac{V_m(T)}{V_n(T)} \right) . \quad (22)$$

Then for convenience let $V_m(T)$ represent the voltage at the initial generation of the echo train. Thus

$$\alpha(T) = \frac{20}{2nL} \text{Log}_{10} \left(\frac{V_o(T)}{V_n(T)} \right) . \quad (23)$$

The attenuation factors α_s and α_N seen in the BCS Eq.(11) represent only the attenuation due to the electron-phonon interaction, whereas the experimentally measured attenuation includes not only contributions from electronic loss mechanisms but also contributions from many non-electronic loss mechanisms. Fortunately at low temperatures where these measurements were made, the non-electronic loss mechanisms are found, for the most part, to be temperature independent. For the discussion here it will be assumed that all non-electronic loss mechanisms are temperature independent. The limitations of this assumption are deferred to Chapter IV.

With this assumption, Eq.(23) can be written as

$$\alpha(T) = \frac{20}{2nL} \text{Log}_{10} \left(\frac{V_o(T)}{V_n(T)} \right) - \alpha_B , \quad (24)$$

where the non-electronic attenuation has been grouped into a temperature independent term, α_B . This term represents the "background" or "residual" attenuation when the electronic attenuation is absent.

Eq.(24) is now in the form where the superconducting attenuation ratio, α_s/α_N , in Eq.(11) can be reduced from the experimental data.

In the experiment, $V_o(T)$ in Eq.(24) is taken as an arbitrary reference voltage and is held constant during a given temperature cycling. In other words, the initial generating voltage of the echo train is held constant during this temperature cycling. Therefore $\alpha_s(T)$ and $\alpha_N(T)$ in Eq.(11) can be written as

$$\alpha_s(T) = \frac{20}{2nL} \text{Log}_{10} \left(\frac{V_o}{V_{ns}(T)} \right) - \alpha_B \quad (25)$$

and

$$\alpha_N(T) = \frac{20}{2nL} \text{Log}_{10} \left(\frac{V_o}{V_{nN}(T)} \right) - \alpha_B \quad (26)$$

respectively. $V_{ns}(T)$ and $V_{nN}(T)$ represent the voltages of the n^{th} echo at a given temperature in the superconducting and normal states, respectively.

As seen from Eq.(11), BCS assume that at zero Kelvin all of the electrons which would be capable of interacting with the ultrasonic wave are in the superconducting state. Therefore at zero Kelvin

$$\alpha_s(0) = 0 \quad (27)$$

or this implies that

$$\alpha_B = \frac{20}{2nL} \text{Log}_{10} \left(\frac{V_o}{V_{ns}(0)} \right) \quad (28)$$

Therefore the ratio of attenuations in the superconducting and normal states in terms of the experimental quantities is expressed as

$$\frac{\alpha_s}{\alpha_N} = \frac{\text{Log}_{10} \left(\frac{V_{ns}(0)}{V_{ns}(T)} \right)}{\text{Log}_{10} \left(\frac{V_{ns}(0)}{V_{nN}(T)} \right)} \quad (29)$$

Thus Eq.(29) can then be compared to that of BCS, Eq.(11).

II.2 Electronic Attenuation Measurement Equipment

From previous ultrasonic measurements in zinc,^{25,26} it was anticipated that there would be a large variation in attenuation as a function of frequency and crystallographic direction. For example, at 10 MHz, the minimum frequency used in this study, a total electronic attenuation of less than 1 dB per centimeter was anticipated in the $[11\bar{2}0]$ direction, while in the c-axis direction at 100 MHz, a total electronic attenuation of 100 dB per centimeter was anticipated.

In most conventional ultrasonic attenuation measuring systems,³⁴ measurements of less than 1 dB are normally inhibitive due to small

signal-to-noise ratios. To overcome this difficulty, the system to be described here utilizes sampling integration and phase sensitive detection for enhancement of the signal-to-noise ratio in the amplification of the echoes. This part of the electronic system was designed using the technique described by Hemphill³⁵ and briefly by Claiborne and Einspruch.³⁶

A block diagram of the complete ultrasonic attenuation measuring system is shown in Figure 2. To clarify the discussion, the ultrasonic system is divided into three essentially independent subsystems. These are (1) the transmitting and receiver system, (2) the display and recorder system, and (3) the phase detection system.

Transmitting and Receiver System

The transmitter which produced the R.F. pulses was an Arenberg model PG-650C pulsed oscillator. The voltage amplitude of these R.F. pulses could be varied from about 1 volt to over 300 volts peak to peak into 93 ohms (Ω). The oscillator was operated in an externally triggered mode with the triggering pulse supplied by a Hewlett-Packard model 214A pulse generator. It was recommended by the manufacturer that the most stable amplitude of the R.F. pulse was achieved when a negative pulse of approximately 0.5 volts was used to trigger the oscillator. The pulse width of the R.F. pulse was adjustable from about 0.5 microseconds (μ SEC) to 20 μ SEC. A pulse width of 1-2 μ SEC was used throughout these measurements. The frequency of the pulsed oscillator was tuneable, by interchanging the appropriate coil in the oscillator circuit, from about 0.5 MHz to approximately 225 MHz. The various frequencies were measured on a Hewlett-Packard 524L electronic counter.

The R.F. pulses generated by the transmitter travelled to an electrical "Tee" where one-half of the R.F. energy was directed to the cryostat. The other half was dissipated by a clipping circuit in the first stage of the pre-amplifier. The R.F. pulse that travelled to the transducer in the cryostat produced an echo train as previously described.

In a similar manner, the R.F. signal corresponding to the echo train would travel to the "Tee" and then a proportionate part would travel to one of two receiving systems. For R.F. frequencies in the range of 10 MHz to 65 MHz, the signal would first enter an Arenberg model PA-620SN pre-amplifier. This pre-amplifier had an input tuning circuit which could be adjusted to match the impedance of the cryostat. The tuning circuit was essentially two LC resonant circuits with selectable inductances for tuning. As previously mentioned the first stage of this amplifier would clip any R.F. signal greater than 1 volt peak to peak to prevent saturation of the pre-amplifier. The last stage of the pre-amplifier was a cathode-follower with an output impedance of 92Ω . The signal then travelled to the Arenberg model WA-600-D wide-band amplifier with an input impedance matching the output impedance of the pre-amplifier. The amplifier consisted of a strip-line R.F. amplifier, a video detection circuit, and video amplification of the detected signal. The overall gain of this amplifier system was approximately 85 dB.

For the R.F. frequency range of 55 MHz to 210 MHz, the signal from the transducer was sent to an Arenberg VHF receiver. This

receiver consisted of a clipping circuit, a tuned amplifier, a wide-band amplifier, video detection, and a video amplifier all contained in one unit. Except for the clipping circuit (Nuvistor) the entire VHF receiver was transistorized. Essentially, the only operational difference between this and the previous receiver system was the tuning circuit. Here the tuning circuit was a ganged cascaded tuned amplifier.

After the video amplification in either receiver system, the signal then travelled to the Hewlett-Packard 175A oscilloscope where it was displayed on the CRT. Linearity in both amplifier systems could be assured by observing the voltage height of the video signal on the oscilloscope. It was determined, that as long as the video signal strength remained less than 10 volts in amplitude, both receivers would remain in their linear amplification regions. Therefore during any given temperature cycling, the gain of the appropriate amplifier was adjusted so that the video signal strength would not exceed 10 volts.

Display and Recorder System

The Hewlett-Packard 175A oscilloscope was equipped with a Hewlett-Packard model 1782A display scanner plug-in. Using the display scanner in its manual scan mode, the amplitude of the video signal at any point on the trace may be sampled and stored between traces. Then if the point sampled corresponds to the video display of an acoustic echo peak, the output of the display scanner will be a D.C. voltage proportional to the echo height. As will be shown,

when phase detection is employed, the output of the display scanner will appear as an A.C. signal with an amplitude proportional to the amplitude of the echo. Without phase detection, the D.C. output voltage of the display scanner is either displayed directly on the Y-axis of the Moseley model 2D-2A X-Y recorder or first sent to the Moseley logarithmic converter before being displayed on the X-Y recorder.

The logarithmic converter automatically converted the variations of the echo height voltage into decibels (first term of Eq.(25)). The data had to still be corrected for "background attenuation", α_B . The logarithmic converter aided in the data taking only where large variations in attenuation were observed. If the total electronic attenuation was less than approximately 15 dB, the logarithmic converter was not employed since smaller variations had limited accuracy compared to direct voltage readings. In these measurements, only part of the C-axis data was taken using this instrument.

When small voltage variations (small dB variations) of the echo height were measured, a large amount of amplification of the echoes was needed to observe these variations. In other words, the D.C. level which corresponded with the echo peak was at a high voltage level compared to the small voltage variations of that level. Therefore it was necessary to zero suppress, by a known amount, the major portion of the echo height voltage so that the small voltage variations were observable on the X-Y recorder. This problem was conveniently solved by the Princeton Applied Research (PAR) model 121 lock-in

amplifier. Incorporated into the output of the PAR amplifier was a calibrated (ten turn potentiometer) suppression voltage ranging from 0 to ± 100 volts with the smallest unit change of 0.1 volt. The output voltage of the PAR amplifier, which was directly proportional to the variation in echo height, varied between 0 and 10 volts. Therefore with the Y-axis of X-Y recorder set at 2 volt per inch (vertical dimension of the Y-axis was 10 inches subdivided by 0.1 inch) the minimum detectable decibel change was less than 0.01 dB. Of course, this value was directly effected by the signal-to-noise ratio and instrument stability. But it does represent the overall sensitivity of the electronic measuring equipment.

Phase Sensitive Detection System

Basically the operation of the phase sensitive detection system was to electronically chop the transmitter triggering frequency at a fixed reference frequency. Then as the echo trains were received at the reference frequency, one echo was selected to be sampled from the repetitive echo train by means of sampling integration. The resulting A.C. signal, which was proportional in amplitude to the amplitude of the echo and varying at the reference frequency, was sent to a lock-in amplifier. Then this signal was detected at the chopping frequency while discriminating against all other frequencies. Therefore any noise components appearing at any frequency other than the reference frequency were eliminated.

Since the system will not discriminate against frequencies at the reference frequency, one of the most important design considerations was the selection of the reference or chopping frequency.

This frequency was selected to be 50 Hz. Mainly, because this frequency was well away from the extremely noisy fundamental line frequency of 60 Hz or one of its harmonics. Also this frequency represented a good compromise between total acoustic power to the He^3 cryostat, sampling rate at the display scanner for accurate integration, and ease of obtaining the reference frequency with an N-stage binary counter.

To understand the details of operation, the signal processing as observed at various points in the circuit is illustrated in Figure 3.

A 4-6 volt trigger pulse of about 10 μSEC in duration at a repetition rate of 800 Hz was generated by pulse generator one. This signal was simultaneously fed to an AND gate, to a 4-stage binary counter, and after travelling through a delaying circuit to the horizontal sweep of the oscilloscope as a trigger pulse. The binary counter was composed of four bistable multi-vibrators which divided the 800 Hz trigger signal by sixteen, i.e., for sequences for eight pulses the binary output would alternate periodically between a high and low states. Therefore the output of the binary counter was 50 Hz square wave. This output was clamped between -0.02 and +3.5 volts and fed simultaneously to the lock-in amplifier as a 50 Hz reference signal and to the AND gate as a control signal. The AND gate was composed of a single transistor amplifier stage. The 50 Hz square wave output of the binary counter either biased this transistor in an "ON" or "OFF" state. In the "ON" state the

FIGURE 3
SIGNAL PROCESSING WITHIN PHASE DETECTION SYSTEM

transistor would amplify the 800 Hz trigger signal from the pulse generator one, while in the "OFF" state the transistor terminates the 800 Hz trigger signal. Thus the output of the AND gate was an 800 Hz trigger signal gated at 50 Hz. The output of the AND gate was fed into pulse generator two. This generator was used primarily to invert the gated 800 Hz trigger signal from the AND gate into negative pulses. It also aided in the synchronization of the echoes and the horizontal sweep trigger signal at the oscilloscope. The trigger signal from pulse generator two then triggered the R.F. pulsed oscillator which in turn produced a series of R.F. pulses at a pulse rate of 800 Hz and gated at 50 Hz. As described earlier, each of these R.F. pulses produced an echo train which travelled to an appropriate receiver system. The display scanner was manually set to coincide with one echo of the echo train as observed on the oscilloscope trace. Since the display scanner sampled and stored a voltage proportional to the echo height between each trace, the output of the display scanner was essentially a 50 Hz square wave whose amplitude was proportional to the echo height. Since the storage circuit of the display scanner was only about 70% efficient, the leading and trailing edges of this signal were steplike. This signal was the input for the lock-in amplifier and was phase coherent with the reference signal. The lock-in amplifier, operating at a frequency of 50 Hz, provided a D.C. output proportional to the amplitude of the echo being sampled.

The system was calibrated by simultaneously measuring the echo height voltage change with a Tektronic type W comparator plug-in

unit and reading the voltage change directly from the X-Y recorder.

II.3 The He³ Refrigerator-Cryostat System

At temperatures below 1 K, liquid He³ has two principle advantages over liquid He⁴ as a coolant; namely, (1) at the same vapor pressure the temperature of liquid He³ is much lower than that of liquid He⁴ and (2) the evaporation rate of liquid He³ can be kept much smaller than for liquid He⁴ since the former does not become superfluid.³⁷ Thus in order to achieve and sustain sufficiently low temperatures in the study of superconducting zinc, a conventional He³ evaporative refrigerator was utilized. The cryostat to be described here was specifically designed to incorporate an R.F. transmission line for the generation of ultrasonic wave pulses. The discussion of the He³ refrigerator-cryostat system will be separated into two subtopics. First, the discussion will center on the lower section of the He³ cryostat, and second on the various vacuum systems used to pump on the coolants and to provide vacuum isolation for the condensed He³.

Cryostat

Seen in Figure 4 is a drawing of the lower section of the He³ cryostat. It is of the single cycle or "one shot" variety using approximately four to five liters of He³ gas. In operation this portion of the cryostat was completely immersed in liquid He⁴. The liquid He⁴ was contained in a glass Dewar system. The Dewar system was composed of an outer Dewar filled with liquid nitrogen at 77.4 K and an inner Dewar filled with the liquid He⁴. The He⁴ Dewar was

FIGURE 4
 He^3 CRYOSTAT

so that the vapor pressure above the liquid He^4 could be lowered. Pumping on the liquid He^4 in this manner lowered its boiling point from about 4.2 K to 1.4 K as measured by the He^4 vapor pressure.³⁸

After the temperature of the liquid He^4 was lowered to approximately 1.4 K, He^3 gas was allowed to flow from the He^3 reservoir tank into the He^3 pumping line. Since a portion of the wall of the He^3 pumping line was at approximately 1.4 K, the He^3 gas condensed somewhere on this portion and dripped into the He^3 condensing can. Initially the condensed He^3 evaporated as it came in contact with the warmer He^3 condensing can. But eventually as more gaseous He^3 condensed and dripped into the He^3 can, a sufficient amount of thermal energy was removed by the evaporation of liquid He^3 so that the condensed He^3 collected and filled the He^3 can. This cyclic process of condensation and evaporation is referred to as the reflux stage. After the collection of the He^3 liquid was completed (approximately one hour after transferring He^4 liquid), the He^3 refrigerator-cryostat was ready for operation.

The temperature of the He^3 condensing can and likewise the specimen could be lowered further by pumping on the liquid He^3 . Temperature control was attained by regulating the vapor pressure above the liquid He^3 . Regulation of the vapor pressure was accomplished by feeding back a controlled amount of He^3 gas into the He^3 pumping line. This had the effect of controlling the pumping rate of the He^3 pump, and therefore, the temperature of the He^3 liquid. As the pressure of the He^3 vapor above the liquid was reduced, the temperature which the liquid He^3 attained was such that the rate of

heat removal by evaporation equaled the rate of heat influx. Thus the ultimate temperature obtained depended on (1) the heat leak to the liquid He^3 and (2) the rate that the He^3 vapor was pumped from the liquid He^3 .

The second of these two quantities was essentially determined by two factors: (1) the vacuum pump used to pump on the He^3 vapor and (2) the tubing which carried the He^3 vapor from the liquid He^3 to room temperature. Since the maximum pumping rate of the He^3 vacuum pump was fixed by the choice of pump, the only design parameter for the maximization of the pumping rate was the determination of the He^3 pump line as seen in Figure 4.

Kennard³⁹ has shown that for a circular long tube the mass of gas flowing through it per unit time is directly proportional to the cube of the radius and inversely proportional to the length. The length of the tube was determined by the requirement that the high-vacuum can be immersed as deeply as possible into the liquid He^4 . This was to insure the longest possible running time per liquid He^4 transfer. For an increase in tube diameter, the heat leak between the 1.4 K He^4 bath and the 0.3 K He^3 bath increases due to greater thermal conduction through the tube wall and the He^3 vapor. However, the heat leak increases as the radius squared at most, whereas the pumping rate increases as the radius cubed. Therefore the most efficient pumping rate was obtained by using the largest possible diameter tube without unduly increasing the heat leak to the liquid He^3 .

The tubing material used to construct the He^3 pump line was

0.010 inch wall thickness type 304 stainless steel tubing. Thus using the thermal conductivity data of Berman⁴⁰ for stainless steel and Fokkens, et.al.⁴¹ for He^3 gas, and also the condition that the total heat leak to the 0.3 K He^3 bath be less than 100 erg/sec; the diameter of the He^3 pump line was chosen to be 1.27 cm.

The first of the two aforementioned quantities, the heat leak to the liquid He^3 , was due not only to conduction down the He^3 pump line, but also to several other sources. These sources will now be discussed in detail.

Using a design developed by Wheatly,⁴² black radiation traps were placed in both the He^3 pump line and the high vacuum line as illustrated in Figure 4. These radiation traps thermally grounded radiation heat leaks emanating from the room temperature end of the pumping lines to the 1.4 K He^4 bath in contact with the pumping lines. Therefore any radiation coming down from the pumping lines and striking the He^3 condensing can or liquid He^3 radiated from a source at 1.4 K.

Originally the radiation traps were held in place by slightly crimping the pumping lines above and below the traps. Subsequently it was found that the radiation trap in the high vacuum line became dislodged and moved to the room temperature end of the pumping line. Therefore this trap was epoxied into place using Stycast 2850 Ft⁴³ low temperature epoxy. Also as a precaution a second trap was installed external to the pumping line. This trap was epoxied directly beneath the location where the pumping line entered the high vacuum can lid. No difficulties were encountered with the radiation trap

in the He^3 pump line.

Radiation down the R.F. transmission line, to be discussed later, was terminated in a manner similar to the pumping lines by the Stycast thermal short at 1.4 K illustrated in Figure 4. Since the high vacuum can was in direct contact with the 1.4 K He^4 bath, it is evident then the total heat leak due to radiation emanated from a source at 1.4 K. Applying the Stefan-Boltzman law to this configuration indicated the heat leak due to radiation was negligible compared to other sources of heat transfer.

Convection of the He^3 gas was not expected to cause any appreciable heat transfer. Simply because as the temperature continuously decreases down the length of the He^3 pumping line, the density of the He^3 gas continuously increases to its greatest density at the He^3 condensing can.

The high vacuum line mentioned previously was used to provide vacuum isolation for the inner He^3 condensing can and sample from the He^4 bath. This line was constructed of 304 stainless steel tubing 1.27 cm in diameter and was connected externally to an oil diffusion pump. This pump reduced the pressure within the high vacuum can to approximately 5×10^{-5} Torr before liquid He^4 was transferred into the helium Dewar. On the basis of the work of Garfunkel and Wexler,⁴⁴ it was expected that cryo-pumping by the liquid He^4 lowered the pressure in the high vacuum can to approximately 10^{-10} Torr when the high vacuum valve was closed. This valve provided isolation of the high vacuum can from the diffusion pump. With the pressure at about

10^{-10} Torr, heat transfer by any residual gas remaining was estimated to be on the order of 1 erg/sec or less.

The production of heat by mechanical vibrations was not easily estimated. However, it was reduced by damping vibrations of the cryostat with a rigid stainless steel support as illustrated in Figure 4. Also the He^3 mechanical pump was mounted separately from the He^3 cryostat and vibrations in the pumping line were damped by a connecting set of stainless steel bellows.

Conduction and Joule heating by the electrical leads between the high vacuum can and the He^3 condensing can were kept to a minimum by using American Wire Gauge (AWG) #38 niobium-titanium (52-48) and AWG #38 manganin (82Cu-15Mn-3Ni) alloy wire. These wire materials were chosen because of the very low thermal conductivity of the manganin alloy at low temperatures and because below approximately 10 K the niobium-titanium alloy is superconducting, implying no Joule heating. Also in the superconducting state a superconductor has somewhat lower thermal conductivity.⁴⁵ These leads were used to provide current to the CRT's, the sample heater, and the superconducting solenoid. They were also used as voltage probes for the CRT's and the superconducting solenoid. Voltage probes were supplied to the solenoid so that its resistance could be monitored in the normal state (the four-terminal resistance measuring technique will be discussed in the thermometry section).

From the room temperature end of the cryostat to the high vacuum can the electrical leads were AWG #36 insulated copper wire (except for the current leads to the solenoid which were AWG #24

insulated copper wire). Outside the vacuum can these leads were soldered to the niobium-titanium leads which passed through the vacuum can by means of the electrical feed-throughs indicated by Figure 4. The feed-throughs were made by drilling small holes in a copper disk through which stripped niobium-titanium wire could pass. The wires were then electrically insulated from the vacuum can and vacuum sealed by epoxying them in place with Stycast.

To further lower the thermal conduction through the leads to the He^3 condensing can, short sections of about 3 cm lengths of manganin wire were soldered on the niobium-titanium leads after they passed through the feed-throughs. Then niobium-titanium wire was again used to extend the leads to the He^3 can, where they were thermally grounded to a common point. From this point the leads were separated and sent to either the CRT's, the sample heater, or the superconducting solenoid.

Since manganin has a low electrical conductivity even at low temperatures, the manganin sections of wire were not inserted in the current leads to the superconducting solenoid. If inserted, the current to the solenoid would normally always cause excessive Joule heating of these sections.

The last source of conduction to the inner assembly was the R.F. transmission line. This line was constructed in accordance with the design characteristics given by Moreno⁴⁶ and the restriction of minimal heat leak. The outer conductor was 0.25 inch O.D. type 304 stainless steel tubing of 0.010 inch wall thickness. The inner

conductor was 0.040 inch O.D. cupro-nickel (70-30) tubing of 0.002 inch wall thickness. The inner conductor was kept coaxial to the outer conductor by using teflon washers placed approximately 3.0 inches apart down the length of the transmission line. On the room temperature end of the transmission line was soldered a female B.N.C. connector. Also this end was vacuum sealed by filling approximately 0.5 inch of the annular region between the inner and outer conductors with Stycast. At the section of the transmission line that passed through the high vacuum can lid, approximately 1.0 inch of the annular region was filled with Stycast. This was done for two reasons. First this served as a thermal short for the inner conductor to the 1.4 K He^4 bath. Secondly, as previously mentioned, any radiation coming from the room temperature end of the transmission line down the annular region was thermally grounded to the He^4 bath. To thermally ground any radiation down the inner conductor, it was also filled with Stycast at the can lid. At the lower end of the transmission line, contact was made with the transducer by means of a spring loaded plunger. This plunger was screwed onto a 0.25 inch long 00-90 screw which had been soldered into the end of the inner conductor.

During some earlier measurements, it was found the section of transmission line at the high vacuum can lid broke down electrically after two or three temperature cycles. There appeared to be two possible explanations for the electrical breakdown: (1) the dielectric properties of the Stycast changed after temperature cycling or (2) the residual gas trapped (this includes vapors due to the curing

of the Stycast epoxy) between the B.N.C. connector and the section at the can lid condensed out as the temperature was lowered. Then as the residual gas condensed, it produced a conductive film on the surface of the Stycast in the annular region at the can lid.

In order to eliminate either of these possibilities from reoccurring, the inner conductor was first coated with G.E. 7031 varnish before the annular region at the lid was filled with Stycast. Also two small holes were made in the inner conductor above and below this annular region. This allowed the upper section of the transmission line to be evacuated as the high vacuum can was evacuated. Stycast radiation traps were also placed above the upper hole and below the lower hole in the inner conductor. After these modifications were made no further problems were experienced with the R.F. transmission line.

In the final configuration, the transmission line had a nominal impedance of 105Ω . This was an acceptable match to the nominal 93Ω impedances of the Arenberg ultrasonic equipment.

In order to determine if the transmission line had any effect on the ultimate low temperature or on the thermometry, some data were taken with the plunger raised so that it was no longer in direct contact with the transducer. Data taken in this manner showed no difference than data obtained with the plunger in direct contact with the transducer. Therefore any heat transfer down the transmission line was considered negligible. It was found, however, that if the R.F. power level (transducer voltage) was set moderately

high, R.F. heating occurred in the transducer which produced small temperature shifts. Thus care had to be exercised in setting the R.F. power level so that R.F. heating would not occur even at the lowest temperatures.

Vacuum System

Illustrated in Figure 5 is a representation of the vacuum system for the He^3 refrigerator-cryostat system. This system was composed of three essentially independent vacuum subsystems: (1) the He^3 vacuum system, (2) the high vacuum system, and (3) the He^4 vacuum system.

When the He^3 refrigerator was not in operation, the He^3 gas was confined to the He^3 gas reservoir and pump when the He^3 pump cut-off valve, the coarse needle valve, and the micrometer needle valve were all closed. In this state, the pressure in the reservoir was slightly less than one atmosphere as measured by the Ashcroft vacuum gauge.

In order to put the He^3 refrigerator into operation, both the high vacuum isolation valve and the connecting valve were opened to the high vacuum system. Then the Welch Duo-Seal rotary forepump was turned on. When the pressure reached approximately 1.0 Torr the liquid nitrogen cold trap was filled. The pressure was measured on a Hastings model GV-38 thermocouple vacuum gauge. When the pressure reached approximately 10 microns the connecting valve was closed isolating the He^3 system from the high vacuum system. Any residual gas left in the He^3 system condensed by cryo-pumping onto the walls of the He^3 pump line and condensing can when the He^4 liquid was

FIGURE 5
VACUUM SYSTEMS

transferred. Thereby, the He^3 gas was purified.

After the connecting valve was closed, the Distillation Products 6.0 inch diameter oil diffusion pump was turned on. This pump lowered the pressure in the high vacuum can to approximately 10^{-5} Torr as measured by the Consolidated Vacuum Corporation (CVC) type GPH-100A cold cathode ionization vacuum gauge. Liquid nitrogen was then poured into the outer Dewar and the temperature of the cryostat lowered to 78 K in about 24 hours. The pressure in the high vacuum can also dropped below 5×10^{-6} Torr.

At this point, the refrigerator was ready to have He^4 liquid transferred into the inner Dewar. After the liquid He^4 was transferred, the inner Dewar was sealed and the He^4 pump cut-off valve was simultaneously opened. The Stokes 105 cubic feet per minute (CFM) vacuum pump lowered the vapor pressure above the He^4 liquid to approximately 2.4 Torr (1.4 K). At this time the high vacuum isolation valve was closed. Then, as previously discussed, the pressure in the high vacuum can lowered to approximately 10^{-10} Torr.

Also at this time, the Hoke coarse needle valve and Whitey type 316 micrometer needle valve were opened to bleed He^3 gas into the He^3 condensing can and pump line. After the He^3 gas cooled and condensed into the He^3 condensing can in approximately one hour, the refrigerator-cryostat was ready for operation.

To reduce the temperature of the He^3 can further, the specially sealed Welch 5.6 CFM Duo-Seal model 1402 vacuum pump was turned on. The He^3 pump cut-off valve was then opened and the pumping rate of the He^3 pump stabilized at some pumping rate corresponding to the

amount of feedback through the coarse and micrometer needle valves. A further reduction and stabilization of the vapor pressure above the He^3 liquid was then controlled by closing the coarse and micrometer needle valves. The lowest attainable He^3 vapor pressure (temperature) was thus determined when both control valves were completely closed. The He^3 vapor pressure in the pressure range of 20.00 Torr to 1.00 Torr was measured by the Wallace and Tiernan model FA-160 absolute pressure gauge. In the pressure range of 1.0 Torr to 1.0 micron, the pressure was measured by the Hastings Thermocouple Gauge.

The ultimate low temperature as indicated by the thermometry, to be discussed, was 0.37 K. It was expected that the refrigerator-cryostat should have reached approximately 0.30 K. It is believed that the main cause of this higher minimum temperature was the pumping rate and not the heat leak. An improvement of the pumping rate would have been achieved by incorporating a diffusion pump in the He^3 vacuum system. However, in the study of zinc, it was felt that the possible small improvement of the ultimate low temperature with the incorporation of a diffusion pump did not merit the modification of the He^3 vacuum system.

II.4 Thermometry System

The primary temperature reference in these measurements was the He^3 vapor pressure as measured by the precision Wallace and Tiernan absolute pressure gauge. This gauge indicated the absolute pressure in the range of 20.00 Torr to 0.10 Torr with an absolute accuracy

of 0.33% of full scale anywhere within this range. Since this inaccuracy becomes quite large below 1.00 Torr, measurements of absolute pressure were limited to pressures of approximately 1.00 Torr and above. As shown in Figure 5 of the preceeding section, the Wallace and Tiernan gauge measured the pressure at the room temperature end of the He^3 pumping line. Roberts and Sydoriak⁴⁷ employed a procedure, the thermomolecular correction, to correct the He^3 pressure measured at room temperature to the vapor pressure measured above the He^3 liquid. However, their work indicated that for pressure measurements above 1.00 Torr this correction was negligible. Therefore the temperatures of the He^3 condensing can were determined simply by finding the corresponding temperatures and pressures from the $T_{62} \text{He}^3$ Thermometry Tables prepared by Sherman, Sydoriak, and Roberts.⁴⁸

In order to record the temperature variations on the X-Y recorder, secondary thermometers which gave D.C. voltages proportional to the temperature variations were employed. The thermometers used for this purpose were carbon resistance thermometers (CRT). For this study, two CRT's of different ohmage were mounted on a pure copper crystal stand as indicated in Figure 4. One thermometer, labeled CRT A, was a one-half watt Allen-Bradley carbon resistor which had a nominal room temperature resistance of 5.1Ω . The other thermometer, labeled CRT B, was also a one-half watt Allen-Bradley carbon resistor. However, it had a nominal room temperature resistance of 2.7Ω . To insure good thermal contact between both

CRT's, and the copper mounting block, the resistors were coated with DC-11 silicon grease before mounting them in the copper block.

The basic resistance measuring circuit is seen in the block diagram of the electronic equipment of Figure 2. The method indicated in this figure is the well-known four-terminal resistance measurement technique. A constant current power supply provided a current to either a 1 K or a 10 K precision 0.05% standard resistor (SR) in series with a CRT. The current was continuously adjustable from 0.3 microamperes (μa) to approximately 1.0 milliamperes (ma). The voltage drop across the SR was constantly measured and displayed on a Hewlett-Packard model 3440A digital voltmeter. Thus knowing the current passing through the SR and likewise the CRT, the measurement of the voltage drop across the CRT allowed the direct calculation of resistance of the CRT. During the temperature measurements the constant current was set at 1.000 μa . Therefore the voltage output of the CRT times 10^6 equaled the resistance of the CRT. During the calibration procedure, to be discussed, the CRT output voltage was monitored on a second Hewlett-Packard digital voltmeter. During data taking, the CRT output voltage was amplified by a Leeds and Northrup model 9835-B D.C. microvolt amplifier. The output of this amplifier then drove the X-axis of the X-Y recorder.

It was determined experimentally that if the CRT output voltage exceeded 10 millivolts the CRT would "self-heat". This effect was attributed to excessive Joule-heating within the CRT causing the CRT to no longer be in thermal equilibrium with the copper block.

With the CRT warmer than its surroundings, the CRT would measure a higher temperature than the actual temperature of the copper block or likewise the crystal sample. Therefore with a 1.000 μ a current, the largest measurable resistance without "self-heating" was 10 K Ω .

It was determined that CRT A would "self-heat" at approximately 0.5 K, while CRT B would not "self-heat" to the lowest temperature obtainable with the He³ refrigerator. However, CRT A was an order of magnitude more sensitive than that of CRT B in the transition temperature region of zinc (0.84 K). It was also recommended by the Leeds and Northrup Company that in order to remain within measurement specifications, the largest source impedance as seen by the D.C. amplifier should not exceed 10 K Ω . Therefore wishing to have the greatest sensitivity while remaining within the limitations of the equipment, data were taken with the aid of both thermometers. CRT A was employed in the approximate temperature region of 1.2 K to 0.6 K and CRT B was employed in the approximate temperature region of 0.6 K to 0.37 K.

Between He³ vapor pressures of 20.00 Torr and 1.00 Torr both CRT A and CRT B were calibrated directly against the Wallace and Tiernan gauge. This represented a temperature range of 1.3 K to 0.65 K. In order to interpolate between the calibration points in this temperature range and also to extend the resistance versus temperature data from 0.65 K to 0.37 K, the calibration data were fit to the Clement-Quinnell⁴⁹ equation:

$$\text{Log } R + K/\text{Log } R = B\left(\frac{1}{T}\right) + A. \quad (31)$$

Here R is the resistance of the CRT, T is the absolute temperature corresponding to this resistance, and A , B , and K are experimental constants.

To fit the calibration data to Eq.(31), a computer program was written for the IBM 360/50 computer. This computer program estimated the constant K from the room temperature resistance value of the CRT by an empirical equation given by Clement and Quinnet. Then the program used the method of least squares⁵⁰ to fit the calibration data to Eq.(31), while varying the estimated K value to give the least percentage scatter for the least squares fit. After the values of A , B , and K were determined, a complete table of resistance versus temperature values could be generated using Eq.(31) over the entire temperature range of the CRT.

The calibration procedure was performed on both CRT A and CRT B at the beginning of each experiment and any time the He^3 refrigerator was recycled. In all cases, the percentage scatter of the calibration data from the curves generated by Eq.(31) was found to be much less than $\pm 0.5\%$ with a measurement sensitivity of approximately 1 millikelvin.

II.5 Ultrasonic Transducer Bonding

The pulse-echo technique required that a rigid uniform bond exist between the quartz wafer transducer and the single crystal specimen. There were two major requirements that any bonding material had to meet to be used in these measurements: (1) It had to be prepared at room temperature and be compatible with the high vacuum

requirements (low vapor pressure). (2) It had to be compatible with the differential thermal contraction of the crystal and transducer. It was also desirable to make the bond as thin as possible to reduce real attenuation losses in the bond and to eliminate the apparent losses due to "wedging effects".⁵¹

Bateman⁵² has given a summary of a number of bonding materials for cryogenic temperatures, however, none of these were found completely suitable in the measurements on zinc. The bonding material which was found to satisfactorily meet the above requirements was Dow Corning⁵³ DC-11 stopcock silicon grease. It has a vapor pressure of less than 10^{-9} Torr at room temperature and could be applied in very thin films. Bonds formed with this material were found never to break even when cycled repeatedly between cryogenic and room temperatures.

This bonding material becomes rigid at approximately 210 K. Therefore in order to evaluate the quality of any bond, the prepared specimen was immersed in liquid nitrogen (78 K) and an echo pattern was observed for its exponential decay. Once a satisfactory echo pattern was obtained, the prepared specimen could be reliably sealed in the high vacuum can and a good exponential echo pattern could be expected at He³ temperatures.

II.6 Ultrasonic Transducers

The quartz wafer transducers used to convert the R.F. signals to mechanical stress waves were obtained from the Valpey Crystal Corporation.⁵⁴ The transducers were cut and polished with highly

parallel faces in a cylindrical shape with a diameter of 1/8 inch. The thickness of the transducers corresponded to the quarter wavelength of a 10 MHz sound wave propagated in a crystallographic direction parallel to the cylindrical axis of the quartz wafer. Since the transducers were bonded rigidly on one face, 10 MHz represented the fundamental resonance vibration frequency of the transducers. Also due to the rigid bonding of one face, only odd harmonics of the fundamental 10 MHz resonance frequency were generated in the transducers. The transducers were crystallographically oriented in such a manner that they would vibrate only in a longitudinal mode, "X-cut".

In order to impress the R.F. electrical field across the transducers, the transducers were placed between parallel plate capacitors. The capacitors were formed by having the transducers plated at the factory with a thin layer of gold over a thin layer of chrome on each face of the transducers. Gold was used as the outer layer because of its high electrical conductivity and its ability to resist tarnish and wear. The chrome was necessary since gold will not adhere directly to quartz.

CHAPTER III

SAMPLE PREPARATION

The high purity zinc single crystal used in these measurements was obtained from Materials Research Corporation in Orangeburg, New York. This company certified that the crystal had a purity of 99.9999% (6N). This crystal was received in the form of a rectangular parallelepiped with dimensions 0.5 in x 0.5 in x 2.5 in. In this chapter will be described the techniques used in machining and aligning this crystal into the crystallographic orientations and sample sizes needed for these measurements. Also in this chapter, determination of the electron mean-free-path will be discussed.

III.1 Spark Machining

The largest rectangular sample that could be accommodated in the He³ cryostat had to be of approximate dimensions 0.9 cm x 0.9 cm x 0.9 cm. Therefore samples had to be machined to these dimensions or smaller before they could be studied.

The main criterion in machining single metal crystals is that the machining of the crystals be as nearly stress free as possible. This criterion is most nearly accomplished by using a machining technique called "electric-discharge machining (EDM)".⁵⁵ Basically, this machining process is an eroding away of surface material by an electrical spark between the metal crystal and metal tool while

both are immersed in a dielectric fluid. In this type of machining process, there is no contact made between the tool and work piece. Thus, the only strains being induced arise from thermal expansions and contractions due to the heating and cooling of the crystal surface by the electric discharge and dielectric fluid respectively.

The spark machining of the zinc crystal used in this study was performed on an Elox TQH-31 electric-discharge machine. The energy produced by the Elox TQH-31 per discharge was adjusted to the lowest obtainable level (approximately 10 erg/discharge) so that there would be minimal heating of the crystal surface. Also the frequency of the discharges was set at the highest possible rate of 250 KHz. This frequency and energy per discharge setting produced the finest finish and caused the least amount of damage to the zinc surface. It was estimated from measurements during the etching procedure (to be described in Section III.4) that the damaged surface layer had a depth of approximately 0.1 mm.

III.2 X-Ray Alignment

Before the zinc crystal could be spark machined into the appropriate samples, two considerations had to be taken into account. The first consideration was concerned with the crystallographic directions in which this study would be made. Since zinc has a close-packed hexagonal (hcp) structure,⁵⁶ the three independent crystallographic directions chosen for this study, as seen in Figure 6, were the $[0001]$ or c-axis, the $[10\bar{1}0]$, and the $[11\bar{2}0]$ directions. It will be noted from Figure 6 that these three axes are 90° with

FIGURE 6
HEXAGONAL CLOSE-PACKED STRUCTURE

respect to one another. Therefore it was possible to make all the ultrasonic measurements on one zinc sample in the form of a rectangular parallelepiped with appropriate dimensions to be discussed in this and the following section.

In order to determine these crystallographic directions during the machining process, the well known Laue Back-Reflection Technique⁵⁷ was used. The Laue technique requires knowledge of the angles which are formed by the intersection of different crystallographic planes. Especially those angles formed by various planes and the three planes designated by the principle axes used in this study.

A literature search showed that the best tabulated values of these angles were calculated by Lawley.⁵⁸ But these proved to be incomplete for the crystal orientations used in this study. Therefore a Fortran computer program for the IBM 360/50 computer was written which calculated the angles between any two crystallographic planes of Miller indices (h,k,i,l) and (H,K,I,L) . This program was written specifically for any hexagonally structured crystal using the following equation given by Cullity⁵⁷ which is the defining relation between any two crystallographic planes:

$$\cos \theta = \frac{hH+kK+1/2(hK+Hk)+\frac{3a^2}{4c^2}lL}{[(h^2+k^2+hk+\frac{3a^2}{4c^2}l^2)(H^2+K^2+HK+\frac{3a^2}{4c^2}L^2)]^{1/2}} \quad (32)$$

The c/a ratio used in this calculation is taken from the x-ray powder diffraction data of Swanson and Tatge.⁵⁹ The final crystal alignments along the three crystallographic axes $[0001]$, $[10\bar{1}0]$, and

$[11\bar{2}0]$ were determined to have deviations of less than 1° from these axes.

The x-ray alignment procedure was performed on a Rigaku Geiger-flex x-ray system with a Polaroid XR-7 Land diffraction Cassette attachment.

III.3 Sample Path-Lengths

The second consideration was concerned with the determination of the path-lengths over which the ultrasound would propagate. The path-lengths used in this study for the three different directions studied were a compromise between two restrictions placed on the propagation of ultrasound in zinc.

The first restriction arises due to the attenuation (anomously high attenuation^{26,60} in the c-axis direction) of ultrasound in zinc. At low temperatures (below ~ 10 K) the attenuation of ultrasound in a metal is predominately due to the electron-phonon interaction. In the superconducting state this is assumed to be the only temperature dependent interaction if the electron mean-free-path is impurity limited and there is no amplitude dependence due to dislocations. Thus, if an estimate of the magnitude of the electron-phonon interaction is known, an upper and lower limit to the sound-path-length can be estimated which is compatible with the sensitivity of the ultrasonic attenuation measuring equipment.

In order to have an estimate of the magnitude of this interaction, the limiting attenuation data of Lea and Dobbs²⁵ were employed. These data, α/v , are seen in Table 1 in units of decibels per centi-

meter per megahertz. These data were used only as an order of magnitude estimate since α/v is frequency dependent.¹⁶

The second restriction is a result of the time required for an echo to traverse the sound-path-length. As discussed in Chapter II a train or series of echoes evolve following the initial pulse. In order that these echoes do not overlap, the time for any given echo to travel the sound-path-length must be greater than the pulse-width (PW). With the sound-path-length being twice the sample length, L , and knowing the velocity of sound, v_s , the following restriction is placed on the sample length:

$$\frac{2L}{v_s} > PW \quad (33)$$

or

$$L > \frac{PW \cdot v_s}{2} \quad (34)$$

In this study, a pulse-width of approximately 1 μ s was used. The velocities of compressional sound waves propagated in the different crystallographic directions studied were calculated from the measured adiabatic elastic constants of zinc at 4.2 K.⁶¹ These velocities are in units of 10^5 cm/sec:

$$\begin{aligned} v_{[0001]} &= 3.097 \\ v_{[10\bar{1}0]} &= v_{[11\bar{2}0]} = 4.979 \end{aligned} \quad (35)$$

After these considerations were taken into account, the zinc crystal was spark machined into an appropriate sample suitable for ultrasonic measurements. Each pair of opposite end faces were carefully polished on the Elox discharge-machine until they were within 0.0005 cm of parallel. If care is not exercised in making each pair of end faces parallel, non-parallelism will cause adverse effects⁶² in the data interpretation.

III.4 Etching Techniques

During the spark machining of the zinc sample, small surface fissures were observed to form oriented parallel to the basal plane (perpendicular to the c-axis). In Figure 7 a is shown a Laue x-ray photograph of one of these surfaces ($[11\bar{2}0]$ surface). This photograph indicates that as the fissures were formed, small surface crystallites were also formed with the same basic crystal structure. But differing in that the $[11\bar{2}0]$ axis of each crystallite shows a distribution of angles from the perpendicular to the c-axis. The fissures are believed to form due to the sudden thermal expansion and contraction of the surface in the weak binding c-axis direction in the crystal. As mentioned earlier, the thermal expansions and contractions are due to the sudden heating by the electric-discharge and then be the sudden cooling by the dielectric fluid in which the crystal is immersed.

In order to remove these surface irregularities, an etching solution⁶³ was found in which the crystal could be etched. The etching solution was 3-4% concentrated nitric acid in methyl alcohol. After the crystal was completely aligned and polished on the Elox

FIGURE 7·a
LAUE X-RAY BEFORE ETCHING

FIGURE 7·b
LAUE X-RAY AFTER ETCHING

discharge-machine, it was totally immersed in the slow etching solution to remove the surface irregularities. It was experimentally determined that totally immersing the crystal produced the most even etch and the least rounding of the crystal surfaces.

The crystal was again x-rayed immediately after the fissures had disappeared. This Laue photograph is seen in Figure 7:b. It is noted from this photograph that the Laue spots have become very sharp, indicating that the surface irregularities were etched away. Also, the alignment of the crystal in the $[11\bar{2}0]$ direction was measured to have a deviation of less than 1° from the $[11\bar{2}0]$ axis. The same results were found for the fissures lying in the $[10\bar{1}0]$ plane.

After completion of the crystal preparations, the three sound path-lengths were accurately measured. These path-lengths (actually $1/2$ sound path-length) are in millimeters at room temperature:

$$[0001] - 4.198$$

$$[10\bar{1}0] - 5.786$$

$$[11\bar{2}0] - 7.870$$

III.5 Determination of Electron Mean-Free-Path

One of the more important quantities characterizing the regime in which ultrasonic attenuation data are measured is the electron mean-free-path, ℓ_e . In ultrasonic investigations, the quantity $q\ell_e$ is normally specified instead of ℓ_e , where $\vec{q}$ is the phonon wave

number, $\vec{q}$ is given by

$$q = \frac{2\pi\nu}{v_s} \quad (36)$$

where ν is the sound wave frequency and v_s is the velocity of sound. As previously mentioned, the two regimes for ultrasonic data as a function of frequency and ℓ_e are $q\ell_e > 1$ and $q\ell_e < 1$.

If the temperature at which the ultrasonic measurements are made is low enough, ℓ_e becomes impurity limited, i.e., ℓ_e is no longer a function of temperature. In this temperature region the functional dependence of $q\ell_e$ will be determined solely by q . For the zinc crystal used in this investigation, the impurity limited region was determined to be below approximately 4 K. Therefore if an estimate of ℓ_e is known below 4 K, then the regime in which the superconducting measurements were made will be known.

Normally the average electron mean-free-path, ℓ_e , is estimated from residual resistivity measurements.⁶⁴ This method utilizes the fact that in the free electron theory the mean-free-path is related to the resistivity, ρ , by the equation⁶⁵

$$\rho = \frac{m_e v_F}{Ne^2 \ell_e} \quad (37)$$

where 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. Again at low temperatures, ℓ_e becomes impurity limited making ρ temperature independent. ρ has then reached its

residual resistivity region. It is apparent then that either the mean-free-path or the purity of a metal may be adequately described by the ratio of the room temperature resistivity to the resistivity when the metal becomes impurity limited (ρ_{RT}/ρ_{ILT}). This ratio is called the residual resistivity ratio (RRR).

Another method also utilizing the free electron model for measuring mean-free-paths was proposed by Deaton and Gavenda.⁶⁶ This method has been used with success by Deaton²⁸ for mean-free-path determinations in zinc and cadmium. The method is essentially a magnetoacoustic analysis of the high-magnetic-field attenuation of compressional ultrasonic waves. This method is better suited to our study than the RRR measurements since the magnetoacoustic method selects essentially the same electrons and the same phonon-electron interactions that occur in the ultrasonic superconducting measurements.

Pippard¹⁶ has shown, using the free electron model, that the relationship between the high-field-attenuation saturation value and the mean-free-path for compressional waves attenuation, α_L , in the limit as the magnetic field $H \rightarrow \infty$ is

$$\lim_{H \rightarrow \infty} \alpha_L(H) = \frac{N_m v_F q^2 \ell_e}{15 \rho_o v_s} \quad . \quad (38)$$

Here ρ_o is the metal density and all the other symbols have been previously defined. It is observed that the limit of the attenuation in high magnetic fields is proportional to $q^2 \ell_e$, and it has been shown⁶⁶ that this limit is approached as $1/H^2$.

In the analysis of the experimental data, the difference between $\alpha_L(H)$ and the zero-field attenuation $\alpha(0)$ is usually determined. It has been shown in a numerical calculation⁶⁶ that the high-field-saturation-attenuation is equal to the attenuation in zero-field for $q\ell_e = 6.8$. Thus, this affords a rather simple and direct experimental determination of the mean-free-path using the free-electron model.

Since the determination of the mean-free-path involves an average over that part of the Fermi surface being traversed, different orbits can be selected by changing the configurations of sound and field direction. If the Fermi surface is spherical, then the mean-free-path will be isotropic, but for metals with Fermi surfaces of several sheets, the mean-free-path may show anisotropy effects for different sound and H-field configurations.

Since the Fermi surface of zinc is believed to consist of six sheets,^{60,67,68} the occurrence of anisotropy in the mean-free-path is expected. Deaton's²⁸ magnetoacoustic measurements in zinc show a variation in ℓ_e for $\vec{q}$ in a given crystallographic direction of approximately six in good agreement with the estimation given by Gibbons and Falicov.⁶⁰ The magnetoacoustic data of Galkin and Korolyuk⁶⁹ in zinc indicate that the average mean-free-path for $\vec{q}$ propagating in the c-axis direction is approximately twice that in the basal plane directions, $[10\bar{1}0]$ and $[11\bar{2}0]$. Their estimate is made from the number of magnetoacoustic oscillations⁷⁰ observed and thus may not give an accurate determination of the mean-free-path for these directions.⁶⁶

Experimental Apparatus

The electronic equipment used in making the magnetoacoustic

measurements for the determination of the mean-free-path is exactly the same as that described in Chapter II.

A drawing of the magnetoacoustic cryostat is seen in Figure 8. The inner and outer conductors of the transmission line were constructed of non-magnetic thin walled type 304 stainless steel tubing. The nominal impedance was calculated to be 50 ohms. The crystal stand and spring loaded contact were constructed of brass. On the lower portion of the crystal stand was wound a manganin coil to serve as a heater. A hole was also drilled in the crystal stand to accommodate a Cryocal germanium resistance thermometer which was factory calibrated.

In order to thermally isolate the sample from the He^4 bath, a 0.75 inch O.D. thin walled type 304 stainless steel tube was permanently sealed at the lower end and fitted with an O-ring seal at the upper end. The tube then served as a vacuum can which could be either evacuated or back-filled with an exchange gas to aid in temperature regulation. The pressure in the vacuum can was monitored with a Hasting model T thermocouple gauge.

The magnetoacoustic cryostat was constructed to fit down into a Janis low-temperature research Dewar system. The Dewar system had a tail section which fit between the pole faces of a Varian 12 inch electromagnet with 10 inch diameter pole faces. The separation of the pole faces was 2.5 inch. In the final configuration, the sample was placed as close as possible to the center-point of the cylindrical axis between the poles faces.

FIGURE 8
MAGNETOACOUSTIC CRYOSTAT

The field strength was monitored with a Hall probe mounted on one of the pole faces. A voltage output, which was directly proportional to the magnetic field strength, was supplied through a linear amplifier system from the Hall probe and fed into the X-axis of the X-Y recorder.

The method of data collection was exactly the same as that discussed previously for the collection of the superconducting data. The only exception is that here the magnetoacoustic attenuation data are a function of magnetic field, whereas the superconducting attenuation data are a function of temperature. The temperature in these measurements was held constant by pumping on the He⁴ bath and letting the temperature stabilize at the lowest obtainable temperature. The germanium thermometer indicated this temperature to be 1.50 K.

Experimental Results

All of the magnetoacoustic data were taken with the aid of the Moseley logarithmic converter. Therefore, the attenuation as a function of magnetic field can be written as

$$\alpha(H) = \alpha_{\text{REF}}(H_{\text{REF}}) + \frac{1}{2Ln} \alpha'(H) \quad . \quad (39)$$

Here $\alpha'(H)$ is the actual data from the X-Y recorder, L is the crystal length, and n is the echo number. $\alpha'(H) = 0$ when $H = H_{\text{REF}}$. For convenience in the analysis of the data, H_{REF} was chosen to be zero field strength and $\alpha_{\text{REF}}(0)$ was arbitrarily set equal to zero.

Measurements for the determination of the mean-free-path were

limited to two crystallographic directions: (1) longitudinal waves propagated in the c-axis direction and (2) longitudinal waves propagated in the $[11\bar{2}0]$ direction. An average mean-free-path for the $[10\bar{1}0]$ direction could then be estimated from the work of Deaton⁷¹ where he measured the mean-free-path in the $[11\bar{2}0]$ and $[10\bar{1}0]$ crystallographic directions. The anisotropy of the mean-free-path on the Fermi surface in a given crystallographic direction was measured by rotating the magnetic field vector in a plane perpendicular to the sound wave propagation directions $[11\bar{2}0]$ and $[0001]$. Therefore, the results shown in this work are for the sound wave propagation and magnetic field directions: $\vec{q} \parallel [0001]$ and $H \perp [0001]$; $\vec{q} \parallel [11\bar{2}0]$ and $H \perp [11\bar{2}0]$.

Recorder tracings made at 9.29 MHz and 33.9 MHz with $\vec{H} \parallel [11\bar{2}0]$ are shown in Figures 9 and 10. The zero of attenuation, $\alpha(0)$, is defined for $H = 0$. The high field limit of attenuation, $\lim_{H \rightarrow \infty} \alpha(H)$, is found by plotting the experimental attenuation values from approximately 2 kilogauss to 10 kilogauss as a function of $1/H^2$. The data is then extrapolated by means of a straight line to $H = \infty$. This extrapolated value then represents the difference between the zero field and infinite field attenuation. This difference is then plotted as a function of frequency. A plot of this type using the data in Figures 9 and 10 is seen in Figure 11. As previously stated, when the difference equals zero $q\ell_e = 6.8$.

It is evident from this graph that $q\ell_e$ is greater than 6.8 at the lowest measured frequency, 9.29 MHz. Therefore the curve was

FIGURE 9
RECORDER TRACING FOR 9.29MHz LONGITUDINAL WAVE $\bar{q}_{II}(OOOI)$

FIGURE 10
RECORDER TRACING FOR 33.9MHZ LONGITUDINAL WAVE $\bar{q}_{II}(OOOI)$

FIGURE 11
DIFFERENCE OF ZERO FIELD AND INFINITE FIELD ATTENUATION VERSUS
FREQUENCY

extrapolated linearly to intercept the zero difference line. The effect, if any, of the extrapolation procedure will be to shorten the calculated mean-free-path. This is seen from the frequency dependence of the infinite and zero field attenuation. As seen in Eq.(36) and (38), the infinite field attenuation is proportional to q^2 (i.e., ν^2). For $q\ell_e > 1$ Pippard has shown that the zero field attenuation is proportional to ν , Eq.(7). Therefore the frequency dependence of the attenuation difference near $q\ell_e = 6.8$ will be quadratic with curvature toward lower frequencies or longer mean-free-paths.

For the curve in Figure 11, this extrapolated value gives $q\ell_e = 6.8$ at 5.0 MHz with $\vec{H} \parallel [11\bar{2}0]$. Then using Eq.(36) the mean-free-path is calculated from

$$\ell_e = \frac{6.8v_s}{2\pi\nu} \quad . \quad (40)$$

All of the data shown in Table 2 for $\vec{q} \parallel [0001]$ were calculated in the above manner. The angle ϕ represents the angle between the magnetic field vector and the $[10\bar{1}0]$ axis. The data were collected over a 60° arc. Since the c-axis has six-fold rotational symmetry, these data represent all possible orientations of the magnetic field vector in the basal plane.

Measurements made in the configuration $\vec{q} \parallel [11\bar{2}0]$ and $\vec{H} \perp [11\bar{2}0]$ did not meet with the difficulties encountered in the c-axis. The data in this sound direction were analyzed in the same manner as the

c-axis data but with the exception the extrapolation technique was not necessary in the analysis. These results are summarized in Table 2 under the heading $q||[11\bar{2}0]$. Here the angle ϕ represents the angle between the magnetic field vector and the c-axis. For q in this crystallographic direction the data were collected over a 90° arc. Since the $[11\bar{2}0]$ axis has two-fold rotational symmetry and inversion symmetry in the $[11\bar{2}0]$ plane, these data represent all possible orientations of the magnetic field vector in the $[11\bar{2}0]$ plane. From this data, an average mean-free-path for this sound direction was estimated to be approximately 0.005 cm. For the c-axis the average mean-free-path was estimated to be approximately 0.1 cm. Then using the previous work of Deaton, the average mean-free-path in the $[10\bar{1}0]$ sound direction was estimated to be approximately 0.006 cm.

Table 2
Electron Mean-Free-Paths for $\vec{q}||[0001]$ and $\vec{q}||[11\bar{2}0]$

ϕ	Freq. (MHz) where $q\ell_e = 6.8$	ℓ_e (cm)
$\vec{q} [0001]$		
-33	4.9	0.068
-23	4.0	0.084
-13	1.8	0.186
-3	*	*
0	*	*
+7	*	*
+17	2.8	0.120
+27	3.8	0.088
+37	4.3	0.078
$\vec{q} [11\bar{2}0]$		
0	26	0.0207
10	47	0.0114
20	69	0.0078
30	88	0.0061
40	130	0.0041
50	136	0.0040
60	119	0.0045
70	100	0.0054
80	71	0.0076
90	62	0.0087

*Mean-free-paths in these magnetic field directions were too large to measure by this method.

CHAPTER IV

FINDINGS AND INTERPRETATIONS

Illustrated in Figure 12 is a recorder tracing of the attenuation data as displayed by the Moseley X-Y recorder. This plot represents the temperature (resistance) variation of a given ultrasonic echo in the superconducting and normal state as discussed in Chapter II. The analysis of the data consisted of interpreting these recorder plots in terms of the theories discussed in Chapter I. The voltages indicated in this figure correspond to the voltages expressed in Eq.(38) for the ratio of superconducting to normal states attenuation.

The normal state data below the transition temperature were taken by applying a magnetic field larger than the critical field, H_c , of zinc. This field was determined from previous measurements⁷² to be approximately 53 Gauss. The field was produced by the superconducting solenoid seen in Figure 5 and it could be varied from zero field to approximately 1500 Gauss by adjusting the magnetic power supply.

It was found that if the magnetic field was increased too much above the critical field, the normal state attenuation decreased with increasing field. This effect has been previously reported by McKinnon and Daniel⁷³ for zinc and cadmium and has been termed the "parallel-magnetoacoustic effect". Therefore, measurements in the normal state were limited to field strengths below which this effect was not discernible, approximately 100 Gauss and below.

FIGURE 12
RECORDER TRACING OF ATTENUATION DATA

It will be noted in Figure 12 that the normal state attenuation was constant below about 1.2 K to the lowest attainable temperatures (actually it was found to be constant below approximately 4.0 K). This indicates that the electron mean-free-path was impurity limited in this temperature region. Also it indicated that the background attenuation, α_B , discussed in Chapter II was constant in the normal state below 1.2 K.

In the superconducting state, allowance must be made for the possibility of other types of temperature-dependent attenuation other than that due to electron-phonon interactions. Of the various possibilities, only one other temperature-dependent loss mechanism has been found to exist in superconductors at these low temperatures. This loss mechanism is due to the interaction of the ultrasonic wave and dislocations in the crystal, the "Amplitude Effect". This effect was first shown to exist in the superconducting state by Love, Shaw and Fate.⁷⁴ They showed that if the amplitude of the sound wave was large enough, the interaction of the sound wave and the dislocations in the crystal gave rise to an increase in the ultrasonic attenuation in the superconducting state as the temperature decreases. This effect is illustrated by the dotted line in Figure 12. Since this effect is seen to directly oppose the change in attenuation due to the electron-phonon interaction as the temperature is lowered, there was no difficulty in determining whether the data had a dependence on the sound wave amplitude. In the calculation of the superconducting energy gap, to be discussed, it was found for various sound wave amplitudes (transducer voltages) that the energy gap was

independent of the sound wave amplitudes used in this study.

The procedure for collecting the attenuation data was to cycle the He³ refrigerator between about 1.0 K and 0.37 K while recording two sets of attenuation data, either normal or superconducting, on the X-Y recorder; one while the temperature was falling and the other while it was rising. In order to insure that the zinc specimen remained in thermal equilibrium with the thermometers during the temperature cycling, the time for one complete cycle was always kept greater than thirty minutes. This length of time was determined by comparing the rising and falling attenuation data and observing that there was no thermal hysteresis.

IV.1 Analysis of Data

In order to fit the BCS theory (Eq.11) and determine the limiting effective energy gap, $\overline{\Delta_k^+}(0)$, from the attenuation data, Eq.(11) was rewritten in a linearized form:

$$\text{Log}_e [2(\alpha_N/\alpha_s) - 1] = \left[\frac{\overline{\Delta_k^+}(0)}{K_B T_c} \right] G(t)/t \quad (41)$$

where $G(t) = \overline{\Delta(T)}/\overline{\Delta(0)}$ and $t = T/T_c$, the reduced temperature. The introduction of the function $G(t)$ enables the temperature dependence of the data to be expressed in terms of the limiting effective energy gap $\overline{\Delta_k^+}(0)$. The function $G(t)$ has been tabulated for an ideal superconductor from the BCS theory by Muhlschlegel.⁷⁵ However, for purposes of calculation of the attenuation data, it was found more

convenient to use an analytical form of $G(t)$ developed by Clem:⁷⁶

$$G(t) = 1.7367 (1-t)^{1/2} \cdot [1 - 0.4095 (1-t) - 0.0626 (1-t)^2] \quad (42)$$

This analytical form has been shown to reproduce Muhlschlegel's values for $G(t)$ with an error of less than 0.1% for $t > 0.4$ and less than 0.5% for $t = 0.3$. The lowest reduced temperature reached in these measurements was $t = 0.44$. Therefore in the analysis of data, the error in the calculated value of $G(t)$ was always less than 0.1%.

$\overline{\Delta_{\vec{k}}(0)}$ in Eq.(41) has been written with a subscript $\vec{k}$ in accordance with Eq.(5) indicating that in each crystallographic direction studied the effective energy gap at zero Kelvin may differ from the BCS isotropic value of $1.76 K_B T_c$. Therefore allowance for anisotropy in the attenuation data was included in the analysis by leaving $\overline{\Delta_{\vec{k}}(0)}/K_B T_c$ as an adjustable parameter.

Eq.(41) suggests that a plot of $\text{Log}_e [2(\alpha_N/\alpha_S) - 1]$ as a function of $G(t)/t$ should be a straight line whose slope is the effective energy gap at zero Kelvin if the BCS theory is the correct description of superconductivity. It will also be observed that the form of Eq.(41) gives allowance for the possibility of multiple energy gaps. If more than one zero Kelvin energy is present, then the plot of Eq.(41) will exhibit more than one slope.

Recall from Eq.(30) that in order to obtain the superconducting to normal state attenuation ratio, α_S/α_N , from the experimental data,

it was necessary to know the echo voltage height in the superconducting state at zero Kelvin, $V_s(0)$. This estimate was arrived at by treating $V_s(0)$ as an adjustable parameter where $V_s(0)$ was varied until the attenuation data obtained the best fit by the method of least squares to Eq.(41). As will be shown, the justification of this extrapolation technique lies in the fact that extremely good fits of the attenuation data to the BCS theory (Eq.41) are obtained.

It should be noted here that the difference between the attenuation value corresponding to the extrapolated value $V_s(0)$ and the attenuation value corresponding to the normal state echo voltage height, $V_N(0)$ where $V_N(0) = V_N(t)$, represents the total electronic attenuation, α_e , of the sound wave. This is simply due to the fact that at zero Kelvin the attenuation of the sound wave due to the electron-phonon interaction in the superconducting state is zero. Therefore if the superconducting data is taken as a function of frequency, the electronic attenuation values, α_e , can be fit to the Pippard theory (Eq.6, 7, 8, and 9). This will allow any frequency dependence in the effective energy gap, $\overline{\Delta_k^+}(0)$, to possibly be correlated with the frequency dependence of the electronic attenuation, α_e .

Since the above mentioned extrapolation technique and fitting procedure is extremely tedious and time consuming, a Fortran computer program was written incorporating the least squares method to fit the attenuation data to Eq.(41). Since the fitting procedure allowed for multiple energy gaps (more than one slope), the program was written in such a manner so that if more than one slope occurred

in the fit, $V_s(0)$ was varied until the best fit was obtained for the slope which occurred at the lower reduced temperatures. Then this value of $V_s(0)$ was used to fit the slope or slopes occurring at the higher reduced temperatures. It will be seen that the "best fit" to determine $V_s(0)$ could always be estimated from the fit to the attenuation data for $0.44 \leq t \leq 0.80$. Also it will be shown that most of the data fit a single gap model while, at most, only a few sets at the lower ultrasound frequencies indicated a possibility of a secondary gap.

IV.2 Results of Analysis

In order to analyze the attenuation data, an accurate determination of the transition temperature was required. The transition temperature was determined in each crystallographic direction studied by observing (see Figure 12) at what temperature the echo voltage height abruptly changed from the normal state to the superconducting state and vice versa. Using this criterion the transition temperatures, T_c , was determined to be 0.840 ± 0.005 K in all three crystallographic directions.

Results for $\vec{q} || [0001]$

Shown in Figures 13, 14, and 15 are plots of $\text{Log}_e [2(\alpha_N/\alpha_s) - 1]$ as a function of $G(t)/t$ at frequencies of 9.0, 32.0, and 50.3 MHz for the c-axis sound wave propagation direction. These plots are representative of the data taken at each of these frequencies. The actual data from which these plots were calculated will be found in Appendix B along with representative data from the other two

FIGURE 13
 PLOT OF LOG_e(2 α_N/α_S -1) VERSUS G(t)/t AT 9.0MHz FOR $\bar{q}_{11}(0001)$

FIGURE 14
PLOT OF $\text{LOG}_e(2a_N/a_S - 1)$ VERSUS $G(t)/t$ AT 32.0MHz FOR $\bar{q}||(\text{OOO})$

FIGURE 15
 PLOT OF LOG_e(2α_N/α_S-1) VERSUS G(t)/t AT 50.3MHz FOR $\bar{q}_{||}(0001)$

crystallographic directions studied.

It is observed in these plots that for each of the three frequencies investigated the entire temperature range, $1.0 > t > 0.44$, was fit very well with one slope, i.e., one zero Kelvin limiting energy gap, $\overline{\Delta_{\vec{k}}(0)}$. The values of $\overline{2\Delta_{\vec{k}}(0)}$ in units of $K_B T_c$ are tabulated for each frequency in Table 3 under the heading $\vec{q}||[0001]$. The stated error given with each value of $\overline{2\Delta_{\vec{k}}(0)}$ have been estimated from the reproducibility of the energy gap from one data set to another. It is observed from these values of $\overline{2\Delta_{\vec{k}}(0)}$ that the measured zero Kelvin energy gap for ultrasound propagating in the c-axis direction is frequently independent over the frequency range investigated.

Also tabulated in Table 3 are the extrapolated total electronic attenuation values, α_e , in units of dB/cm for each of these three frequencies. These values of α_e are plotted as a function of frequency in Figure 16 where the scatter in the extrapolated value is indicated by the error bars. This curve is seen to be linear in frequency over the frequency range investigated. Therefore as indicated by the Pippard theory, Eq.(7), $q\ell_e > 1$. This agrees well with the magnetoacoustically determined mean-free-paths where it was determined that $q\ell_e > 6.8$ for $\vec{q}||[0001]$ and all magnetic field orientations.

Results for $\vec{q}||[10\bar{1}0]$

Shown in Figures 17, 18, 19, and 20 are the representative plots of Eq.(4) at frequencies of 9.0, 31.5, 51.1, and 70.6 MHz for ultrasound propagating in the $[10\bar{1}0]$ crystallographic direction.

Table 3
Effective Energy Gaps and Total Electronic
Attenuation Determined by Ultrasonic Attenuation

Average $q\ell_e$	Frequency (MHz)	α_e (dB/cm)	$\overline{2\Delta_{\vec{k}}^{\uparrow}(0)^*}$	$\overline{2\Delta_{\vec{k}}^{\uparrow}(0)}$
$\vec{q} [0001]$				
180	9.0	4.5	---	3.00 ± 0.10
650	32.0	19.8	---	3.00 ± 0.10
1010	50.3	33.0	---	3.02 ± 0.10
$\vec{q} [10\bar{1}0]$				
0.39	9.0	0.3	2.48 ± 0.20	2.74 ± 0.10
1.15	31.5	1.8	2.62 ± 0.20	2.78 ± 0.10
1.92	51.1	3.9	---	2.94 ± 0.20
2.69	70.6	6.4	---	2.82 ± 0.10
$\vec{q} [11\bar{2}0]$				
0.13	9.4	0.6	3.58 ± 0.20	2.96 ± 0.10
0.38	31.5	0.2	---	3.20 ± 0.10
0.64	53.0	4.4	4.66 ± 0.20	3.52 ± 0.10
0.90	70.6	6.5	4.80 ± 0.20	3.78 ± 0.20
1.15	90.5	7.3	5.00 ± 0.20	4.02 ± 0.20
1.41	110	6.9	4.42 ± 0.20	3.96 ± 0.20
1.67	130	6.2	---	3.76 ± 0.10
1.92	150	7.5	---	3.74 ± 0.10
2.18	170	9.2	---	3.80 ± 0.10

FIGURE 16
 PLOT OF ELECTRONIC ATTENUATION VERSUS FREQUENCY FOR $q_{11}(0001)$

FIGURE 17
 PLOT OF $\text{LOG}_e(2\alpha_N/\alpha_S - 1)$ VERSUS $G(t)/t$ AT 9.0 MHz FOR $q_{||}(10\bar{1}0)$

FIGURE 18
 PLOT OF LOG_e(2α_N/α_S - 1) VERSUS G(t)/t AT 31.5MHz FOR q̄₁₁(1010)

FIGURE 19
 PLOT OF $\text{LOG}_e(2\alpha_N/\alpha_S - 1)$ VERSUS $G(t)/t$ AT 51.1 MHz FOR $\bar{q}||10\bar{1}0$

FIGURE 20
 PLOT OF $\text{LOG}_e(2\alpha_N/\alpha_S - 1)$ VERSUS $G(t)/t$ AT 70.6 MHz FOR $\bar{q}_{11}(10\bar{1}0)$

At the lower ultrasonic frequencies, 9.0 and 31.5 MHz, it is observed that a better fit to the data is obtained by fitting the temperature region $0.80 \geq t \geq 0.44$ with one slope, $\overline{\Delta_k^+(0)}/K_B T_C$, and the temperature region $0.98 \geq t \geq 0.8$ with another slope, $\overline{\Delta_k^+(0)^*}/K_B T_C$. However, it is observed that as the ultrasonic frequency was increased from 10 MHz to 70.6 MHz the slope at higher reduced temperatures progressively tends toward the slope at lower reduced temperatures until at 51.1 and 70.6 MHz the curve is fit with only one slope, $\overline{\Delta_k^+(0)}/K_B T_C$. The values of the effective energy gaps in units of $K_B T_C$ calculated from the slopes of these plots are tabulated in Table 3 under the heading $\vec{q}||[10\bar{1}0]$. Looking at these results, it is noted that the energy gap $\overline{\Delta_k^+(0)}$ is essentially independent of frequency while the possible energy gap $\overline{\Delta_k^+(0)^*}$ is frequency dependent and equals $\overline{\Delta_k^+(0)}$ at higher ultrasonic frequencies. Therefore $\overline{\Delta_k^+(0)}$ at 70.6 MHz is believed to represent the limiting frequency independent zero Kelvin energy gap as predicted by BCS theory.

In Figure 21 are the total electronic attenuation values α_e plotted as a function of frequency for $\vec{q}||[10\bar{1}0]$. The dashed line in this figure represents the fit of the electronic attenuation data to the Pippard theory. Since this curve is not linear, ($q\ell_e \sim 1$ at 9.0 MHz), over the entire frequency range, the fit was made to Eq.(6). Using Eq.(7), Eq.(6) may be rewritten as

$$\alpha_N/\nu = (\alpha_N'/\nu) \frac{6}{\pi} \left\{ \frac{q\ell_e \tan^{-1}(q\ell_e)}{3[q\ell_e - \tan^{-1}(q\ell_e)]} - \frac{1}{q\ell_e} \right\} \quad (43)$$

FIGURE 21
PLOT OF ELECTRONIC ATTENUATION VERSUS FREQUENCY FOR $q_{11}(10\bar{1}0)$

where α'_N/ν is the limiting attenuation in dB/cm-MHz and ℓ_e is the average mean-free-path.

In order to fit the electronic attenuation data, α'_N/ν and ℓ_e are left as adjustable parameters. For the data in Figure 21, the best fit was obtained with $\ell_e = 0.003$ cm. This value is seen to be consistent with the value of 0.006 cm estimated from the magneto-acoustic data in Chapter III.

Results for $\vec{q}||[11\bar{2}0]$

Shown in Figures 22 through 30 are the representative plots of Eq.(41) at the odd harmonic frequencies of 9.4 through 170 MHz for ultrasound propagating in the $[11\bar{2}0]$ crystallographic direction. It is observed that for all ultrasonic frequencies below 130 MHz except 31.5 MHz that the best fit is obtained with two slopes - one slope, $\overline{\Delta_k^+}(0)/K_B T_c$, in the lower temperature region for $0.88 \geq t \geq 0.44$ and another slope, $\overline{\Delta_k^+}(0)^*/K_B T_c$, in the higher temperature region for $0.98 \geq t \geq 0.88$. It is also observed in these data, as tabulated in Table 3 under the heading $\vec{q}||[11\bar{2}0]$, that below 130 MHz both slopes are frequency dependent. While at 130 MHz and above the curve is fit extremely well with one slope, $\overline{\Delta_k^+}(0)/K_B T_c$, which is frequency independent. In Figure 31 is shown the frequency dependence of $\overline{\Delta_k^+}(0)$.

The electronic attenuation, α_e , as a function of frequency for $\vec{q}||[11\bar{2}0]$ is seen in Figure 32. Again the dashed line represents the fit of the data to the Pippard theory where the data were fit in the same manner as discussed for $\vec{q}||[10\bar{1}0]$. The only exception

FIGURE 22
 PLOT OF LOG_e(2Q_N/Q_S-1) VERSUS G(t)/t AT 9.4MHz FOR $\bar{q}||(\bar{1}\bar{1}\bar{2}0)$

FIGURE 23

PLOT OF $\text{LOG}_e(2Q_N/Q_S - 1)$ VERSUS $G(t)/t$ AT 31.5MHz FOR $\bar{q} \parallel (11\bar{2}0)$

FIGURE 24

PLOT OF LOG_e(2α_N/α_S-1) VERSUS G(t)/t AT 53.0MHz FOR q̄₁₁(1120)

FIGURE 25
 PLOT OF $\text{LOG}_e(2a_N/a_S - 1)$ VERSUS $G(t)/t$ AT 70-6MHz FOR $\bar{q}1(11\bar{2}0)$

FIGURE 26
 PLOT OF LOG_e(2α_N/α_S-1) VERSUS G(t)/t AT 90.5MHz FOR $\bar{q}_{11}(11\bar{2}0)$

FIGURE 27
 PLOT OF $\text{LOG}_e(2\alpha_N/\alpha_S - 1)$ VERSUS $G(t)/t$ AT 110MHz FOR $\bar{q}11(11\bar{2}0)$

FIGURE 28
 PLOT OF $\text{LOG}_e(2\alpha_N/\alpha_S - 1)$ VERSUS $G(t)/t$ AT 130MHz FOR $\bar{q}_{11}(11\bar{2}0)$

FIGURE 29
 PLOT OF $\text{LOG}_e(2\alpha_N/\alpha_S - 1)$ VERSUS $G(t)/t$ AT 150MHz FOR $\bar{q} \parallel (11\bar{2}0)$

FIGURE 30
 PLOT OF $\text{LOG}_e(2\alpha_N/\alpha_S - 1)$ VERSUS $G(t)/t$ AT 170MHz FOR $\bar{q}11(11\bar{2}0)$

FIGURE 31
LIMITING EFFECTIVE ENERGY GAP VERSUS FREQUENCY FOR $\bar{q}(1120)$

FIGURE 32
PLOT OF ELECTRONIC ATTENUATION VERSUS FREQUENCY FOR $\bar{q}|| (11\bar{2}0)$

here being that the curve was fit for the electronic attenuation data above 110 MHz and then it was extended below 110 MHz using Eq.(43). The average mean-free-path which gave the best fit to the data was $\ell_e = 0.001$ cm which is again found to be consistent with the value, 0.005 cm, estimated from the magnetoacoustic results.

For the high-magnetic-field magnetoacoustic data for $\vec{q} || [11\bar{2}0]$, Table 2, it is observed that the "hump" in the α_e versus frequency plot, Figure 32, occurs in the frequency region where the average $q\ell_e$ values are mixtures of $q\ell_e \leq 1$ and $q\ell_e > 1$ values. Also this data indicates for all parts of the "effective zone" that $q\ell_e > 1$ where $\nu > 130$ MHz and $q\ell_e < 1$ where $\nu \leq 30$ MHz. Therefore the "hump" appears in the frequency region where the "effective zone" is making its transition from the $q\ell_e < 1$ regime to be $q\ell_e > 1$ regime and this region is seen to span approximately 100 MHz.

It is also noted in Figure 32 that the "hump" cannot be due to dislocation-phonon interactions. It was shown earlier, Figure 12, that interactions of the sound wave with dislocations cause the total electronic attenuation to have an apparent decrease in magnitude and not an increase in magnitude as observed in Figure 32.

IV.3 Interpretation of Results

The results presented in Table 3 indicate as $q\ell_e$ becomes greater than one, the effective zero Kelvin energy gap tends toward a single limiting frequency independent value in each of the three crystallographic directions studied. These results also indicate that a good fit to the Pippard theory is obtained as shown in Figures 16,

21, and 32 when all parts of the "effective zone" have $q\ell_e \geq 1$. Therefore the energy gaps corresponding to $q\ell_e > 1$ for each crystallographic direction studied are interpreted as representing the frequency independent energy gaps as predicted by the BCS theory (Eq. 11). From Table 3, the limiting zero Kelvin energy gaps, $\overline{2\Delta_{\vec{k}}(0)}$, are seen to be 3.00 ± 0.10 , 2.82 ± 0.10 , and 3.80 ± 0.10 in units of $K_B T_c$ for the crystallographic directions $[0001]$, $[10\bar{1}0]$, and $[11\bar{2}0]$ respectively.

These results indicate that the superconducting energy gap in zinc is highly anisotropic. Using Eq.(3) and the isotropic BCS values of $1.76 K_B T_c$ as the average zero Kelvin energy gap $\overline{\Delta(0)}$, the calculated anisotropy in the limiting gap, $\overline{\Delta_{\vec{k}}(0)}$, is approximately 20%. As will be discussed, this large anisotropy is in agreement with previous investigations except those made by ultrasonic-attenuation methods.

Since the Pippard theory, Eq.(6), was developed using a free electron model, the "hump" observed in the electronic attenuation data for $\vec{q} \parallel [11\bar{2}0]$ would possibly indicate a strong deviation in zinc from the free electron model. However, it was determined from the magnetoacoustic measurements in Chapter III that a large anisotropy of the electron mean-free-path exists in zinc. Therefore an Eq.(10) indicates for $q\ell_e \leq 1$, the "effective zone" is strongly influenced by the anisotropy in the electron mean-free-path. Thus for a very complicated Fermi surface such as zinc possesses (six sheets), deviations from the Pippard theory can also be expected to arise from the selectivity of the electron-phonon interaction as

expressed by Eq.(10) for $q\ell_e \leq 1$. Obviously then, a proper understanding of the electronic attenuation data for $\vec{q}||[11\bar{2}0]$ and $q\ell_e \leq 1$ will require a detailed theory which makes allowance for deviations from the free electron model and anisotropy in the electron mean-free-path. To date there is not a detailed theory which may be compared with the electronic attenuation data presented here for $\vec{q}||[11\bar{2}0]$.

As previously discussed, Eq.(10) also suggests that for an anisotropic superconductor the effective energy gap might show a dependence on $q\ell_e$ for lower ultrasonic frequencies. As the sound wave interacts with a larger portion of the Fermi surface (lower $q\ell_e$ values), the effective energy gap will represent a weighted average of the gap anisotropy for that "effective zone". Then as $q\ell_e \rightarrow \infty$ the dependence on $q\ell_e$ should disappear since Eq.(10) indicates that the "effective zone" becomes a very narrow band near the equator of the Fermi surface perpendicular to the phonon wave vector.

As was the case for the "hump" in the frequency dependence in the electronic attenuation for $\vec{q}||[11\bar{2}0]$, the effective energy gap exhibits essentially the same frequency dependence, Figure 31, and it is again attributed to the strong influence of the anisotropy of the mean-free-path on the "effective zone" for $q\ell_e \leq 1$. Also the assignment of multiple gaps for $\vec{q}||[10\bar{1}0]$ and $\vec{q}||[11\bar{2}0]$ is at most tentative since the apparent gap at higher reduced temperatures is a strong function of $q\ell_e$ and never approaches a limiting value

as does the gap at lower reduced temperatures. Therefore in comparing this investigation with previous investigations in superconducting zinc only the limiting zero Kelvin energy gap values for $ql_e > 1$ will be used.

Comparison with Previous Investigations

In Table 1 were given the results of previous ultrasonic-attenuation investigations in superconducting zinc. It is observed that the results of Lea and Dobbs²⁵ and Bohm and Horwitz²⁶ indicate an anisotropy no larger than 5%. The discrepancy with the results presented in this work lies mainly in the value of the energy gap obtained for $\vec{q} || [10\bar{1}0]$. Without access to their data and their experimental method (both investigators used adiabatic demagnetization refrigerators), it is difficult to speculate as to the cause of this large discrepancy in anisotropy. However, as previously mentioned the thermal conductivity data of Zarvaritskii,²⁰ the microwave-absorption data of Evans, et al.,²³ and the specific heat data of Ducla-Soares and Cheeke²² all indicate an anisotropy of about the same magnitude as reported in this investigation.

Zarvaritskii's measurements on the anisotropic electronic thermal conductivity using a prolate spheroidal model for the energy gap as a function of direction indicated a maximum gap of $3.5 K_B T_c$ along the c-axis and a minimum gap of $2.4 K_B T_c$ perpendicular to the c-axis. The anisotropic microwave-absorption measurements of Evans et al. conclude that most of Fermi surface is associated with an energy gap of $3.0 \pm 0.1 K_B T_c$ while the energy

gap near the c-axis is approximately $4.0 \pm 0.2 K_B T_c$. The value they assigned to the energy gap near the C-axis was uncertain due to the effects of the surface on their results. The surface caused in general a large-angle scattering of the electrons which mixed the energy gaps from two different directions.

Since the "effective zone" in the ultrasonic-attenuation measurements is perpendicular to the sound wave propagation direction, the gap found near the c-axis in the thermal conductivity and microwave-absorption measurements corresponds to the gap measured ultrasonically for either $\vec{q} || [10\bar{1}0]$ or $\vec{q} || [11\bar{2}0]$. Consequently, it is concluded that the maximum gap measured by Zarvaritskii and the large gap measured by Evans et.al. are the same gap measured ultrasonically in this investigation for $\vec{q} || [10\bar{1}0]$. Also the gap indicated for most of the Fermi surface by Evans et.al. of $3.0 \pm 0.1 K_B T_c$ is found consistent with the results in this investigation of $3.00 \pm 0.10 K_B T_c$ and $2.82 \pm 0.10 K_B T_c$ for $\vec{q} || [0001]$ and $\vec{q} || [10\bar{1}0]$ respectively.

The specific heat measurements by Ducla-Soares and Cheeke found that their data were fit best with two average zero Kelvin energy gaps of $3.58 K_B T_c$ and $2.00 K_B T_c$ and a mean anisotropy of approximately 15%. Although the results presented here do not completely substantiate two energy gaps, their measured anisotropy of the gap is consistent with the present measurements.

Other determinations of the superconducting energy gap in zinc were made by Zemon and Boorse⁷⁷ for the onset frequency for microwave absorption in polycrystalline samples and by Donaldson⁷⁸ for tunneling

measurements of zinc films. These measurements, however, only give average gaps and therefore do not give any indication of the anisotropy. Zemon and Boorse found an average gap of $3.01 \pm 0.09 K_B T_c$ while Donaldson found an average gap of $3.2 \pm 0.1 K_B T_c$. These measurements are also found to be consistent with the results of this investigation.

IV.4 Summary

This investigation has been primarily concerned with the measurements of the anisotropic energy gap in superconducting zinc in the $[0001]$, $[10\bar{1}0]$, and $[11\bar{2}0]$ crystallographic directions. This investigation has been made in order to clarify discrepancies found between the ultrasonically determined anisotropic energy gap and the anisotropy determined by other experimental means. The results presented here have been shown to be in disagreement with previous ultrasonic-attenuation measurements but consistent with the larger anisotropy determined by thermal conductivity, microwave-absorption, and specific heat measurements.

It has also been found that the effective energy gap is dependent on $q\ell_e$. This dependence has been related by magnetoacoustic measurements and the Pippard theory of electronic attenuation of ultrasound to the "effective zone".

It has been determined that at sufficiently high $q\ell_e$ values that the effective energy gap reaches a single limiting energy gap value in each crystallographic direction studied. Although these measurements do not rule out the possibility of multiple energy gaps, it is found that they occur only at the lower $q\ell_e$ values.

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APPENDIX A

BCS THEORY OF SUPERCONDUCTIVITY

Basic to the BCS theory is the assumption that the net attractive interaction which produces the energy difference between the normal and superconducting phases arises essentially from two interactions: (1) the virtual exchange of phonons and (2) the short-range screened Coulomb repulsion between conduction electrons. Any other interactions are thought to be essentially the same in both states and thus their effects cancel in the energy difference. Therefore BCS were able to reduce the problem to one of calculating the ground state and excited states of a dense system of fermions interacting via two-body potentials.

In order that the net interaction be attractive, the attractive "phonon interaction" must dominate the repulsive Coulomb interaction for those matrix elements which are of importance in the superconducting wave function. This criterion, i.e. the strongest phonon interaction, is obtained by considering first the Fröhlich electron-electron interaction ("phonon interaction") shown schematically in Figure A.1 where the straight lines represent electron paths and the wavy line represents a virtual phonon.

Figure A.1

Since momentum is conserved during phonon emission, the emission of the phonon by electron 1 can be written

$$\vec{k}_1 = \vec{k}'_1 + \vec{q} \quad (\text{A.1})$$

where $\vec{k}_1$ and $\vec{k}'_1$ are the wave vectors before and after scattering, and $\vec{q}(q = \frac{2\pi}{\lambda})$ is the wave vector of the phonon. Then in the same way when the phonon is absorbed by electron 2, the momentum of the phonon changes $\vec{k}_2$ to $\vec{k}'_2$ so that

$$\vec{k}_2 + \vec{q} = \vec{k}'_2 \quad (\text{A.2})$$

Then eliminating $\vec{q}$ from Eq. (A.1) and (A.2) gives

$$\vec{k}_1 + \vec{k}_2 = \vec{k}'_1 + \vec{k}'_2 . \quad (\text{A.3})$$

Thus showing momentum is conserved between the initial and final states. Although energy is necessarily conserved between the initial and final states, due to the Heisenberg uncertainty relationship it does not have to be conserved in the intermediate electron-virtual phonon interactions. All that is required is that there be an electron in the near vicinity to immediately accept the emitted phonon (BCS showed the distance between electrons to be less than about 10^{-4} cm).

Cooper⁷⁹ then used Fröhlich's discovery that the electron-

electron interaction could be transmitted by phonons and demonstrated what happened to two electrons if they were added to a metal at zero Kelvin so that they were forced by the Pauli principle to occupy states with $\vec{k} > \vec{k}_F$ ($\vec{k}_F$ is the momentum at the Fermi level). His calculation indicated that if there is a phonon attraction between them, however weak, they are able to form a bound state (Cooper pair) so that their total energy is less than $2\epsilon_F$ (ϵ_F is the Fermi energy).

BCS took this result and applied it to a dense system of fermions. They showed that by forming Cooper pairs from the free electron Bloch states that an overall lowering of the total energy was achieved. The maximum lowering is obtained by having all the pairs with the same net momentum,

$$\vec{k}_1 + \vec{k}_2 = \vec{q} \quad (\text{A.4})$$

Also it is further desirable to take pairs of opposite spin, because exchange terms reduce the interaction for parallel spins. For the case of zero electric current, $\vec{q} = 0$, electrons in Bloch states $\vec{k}\uparrow$ and $-\vec{k}\downarrow$ are most effectively attracted.

BCS were then able to work with a reduced problem in which they only included configurations in which the states were occupied in pairs, $(\vec{k}\uparrow, -\vec{k}\downarrow)$. This simply requires that if $\vec{k}\uparrow$ is occupied so is $-\vec{k}\downarrow$. A pair is then designated by wave vector $\vec{k}$, independent of spin (only spin-independent quantities are considered in this paper).

That part of the Hamiltonian relevant to the discussion of superconductivity can be written then in terms of creation and annihilation operators for pairs relative to the Fermi sea as:

$$\begin{aligned}
 H_{\text{red}} = & 2 \sum_{\vec{k} > \vec{k}_F} \epsilon_{\vec{k}} b_{\vec{k}}^{\dagger} b_{\vec{k}} + 2 \sum_{\vec{k} < \vec{k}_F} |\epsilon_{\vec{k}}| b_{\vec{k}}^{\dagger} b_{\vec{k}} \\
 & - \sum_{\vec{k}, \vec{k}'} V_{\vec{k}\vec{k}'} b_{\vec{k}}^{\dagger} b_{\vec{k}'}^{\dagger} b_{\vec{k}} b_{\vec{k}'} .
 \end{aligned} \tag{A.5}$$

Here $b_{\vec{k}}^{\dagger}$ and $b_{\vec{k}}$ are respectively the creation and annihilation operators for pairs, and $\epsilon_{\vec{k}}$ is the familiar Bloch energy measured from the Fermi level. The first two terms are the kinetic energy of the pairs, and the 2 appears since two electrons compose each pair. The third term is the interaction term and it includes not only the phonon exchange interaction, but also the screened Coulomb interaction. This term has been defined with a negative sign, so the criterion for superconductivity is that the $V_{\vec{k}\vec{k}'}$'s be predominately positive.

The ground state of a superconductor is specified by forming a superposition of pair configurations $(\vec{k}\uparrow, -\vec{k}\downarrow)$. That is, the ground state wave function is composed only of pair configurations where states $\vec{k}\uparrow$ and $-\vec{k}\downarrow$ are either both occupied or both empty. In order for the electrons to take advantage of the attractive interaction, they must slightly increase their kinetic energy. Therefore not all the pair states with lowest $|\vec{k}|$ are occupied if the electrons are to

take advantage of the attractive interaction and lower their total energy. The ground state energy of the superconductor is then found using a variational calculation on H_{red} .

The excited states of the superconductor are treated in much the same manner as the ground state. Only now the excited state is formed by specifying the sets of states which are occupied by single particles and sets of states occupied by excited pairs. A single particle state is one in which either $\vec{k}\uparrow$ or $-\vec{k}\downarrow$ is occupied, but not both. BCS show that at zero Kelvin there is a minimum energy required to form an excitation of a single particle or an excited pair. Since the minimum energy is the same for either type of excitation, there appears in the energy spectrum a gap of width $2\Delta_{\vec{k}}$ between the ground state and the lowest excited state.

It is also seen that the excitations of single particles or excited pairs can be treated in a scheme whereby an excited state is specified by quasiparticle occupation. To create each quasiparticle requires a minimum energy of $\Delta_{\vec{k}}$ (quasiparticles are created two at a time). A quasiparticle in a state, $\vec{k}$, will have an energy

$$E_{\vec{k}} = (\epsilon_{\vec{k}}^2 + \Delta_{\vec{k}}^2)^{1/2} \quad (\text{A.6})$$

measured relative to the Fermi level. For the first excited state

$$E_{\vec{k}} = \Delta_{\vec{k}} \quad , \quad (\text{A.7})$$

the minimum excitation energy. BCS has shown that the probability

distribution of quasiparticles at finite temperatures is given by Fermi function,

$$f(E_{\vec{k}}) = \frac{1}{e^{\beta E_{\vec{k}} + 1}} \quad (\text{A.8})$$

where $\beta = (K_B T)^{-1}$ and K_B is Boltzman's constant.

The energy gap parameter, $\Delta_{\vec{k}}$, has a functional dependence on temperature and it satisfies the condition:

$$\Delta_{\vec{k}}(T) = \sum_{\vec{k}'} \frac{V_{\vec{k}\vec{k}'}, \Delta_{\vec{k}'}(T) \tanh(\beta E_{\vec{k}'}/2)}{2E_{\vec{k}'}} \quad (\text{A.9})$$

where the various quantities have been previously defined.

APPENDIX B

The data contained in this appendix were taken directly from the X-Y recorder plots of the ultrasonic attenuation data in the superconducting state at intervals of 0.02 reduced temperature. Then as previously discussed, these data were read into the computer program which calculated the various energy gap and total electronic attenuation values presented in Chapter IV.

Table 4

Experimental Data for the Second Echo with $\vec{q}||[0001]$ at 9.0 MHz

t	Voltage (V)	t	Voltage (V)
1.000	7.15	.70	13.75
.98	8.70	.68	14.02
.96	9.30	.66	14.27
.94	9.82	.64	14.52
.92	10.26	.62	14.75
.90	10.69	.60	14.98
.88	11.05	.58	15.21
.86	11.40	.56	15.44
.84	11.72	.54	15.65
.82	12.03	.52	15.85
.80	12.34	.50	16.04
.78	12.64	.48	16.22
.76	12.93	.46	16.37
.74	13.21	.44	16.56
.72	13.49	.42	---

Table 5

Experimental Data for the First Echo with $\vec{q} || [0001]$ at 32.0 MHz

t	Voltage (V)	t	Voltage (V)
1.000	1.30	.70	10.84
.98	2.43	.68	11.42
.96	3.18	.66	12.01
.94	3.78	.64	12.61
.92	4.35	.62	13.21
.90	4.91	.60	13.80
.88	5.51	.58	14.40
.86	6.12	.56	14.99
.84	6.71	.54	15.59
.82	7.30	.52	16.17
.80	7.90	.50	16.70
.78	8.48	.48	17.22
.76	9.08	.46	17.64
.74	9.66	.44	---
.72	10.23	.42	---

Table 6

Experimental Data for the First Echo with $\vec{q}||[0001]$ at 50.3 MHz

t	Decibels (dB)	t	Decibels (dB)
1.00	0.0	0.70	22.85
0.98	5.0	0.68	23.65
0.96	7.65	0.66	24.15
0.94	9.75	0.64	25.0
0.92	11.55	0.62	25.65
0.90	13.05	0.60	26.3
0.88	14.45	0.58	26.95
0.86	15.70	0.56	27.5
0.84	16.9	0.54	28.05
0.82	17.95	0.52	28.6
0.80	18.9	0.50	29.05
0.78	19.7	0.48	29.5
0.76	20.05	0.46	29.9
0.74	21.3	0.44	30.3
0.72	22.15	--	---

Table 7

Experimental Data for the Fifteenth Echo with $\vec{q}||[10\bar{1}0]$ at 9.0 MHz

t	Voltage (V)	t	Voltage (V)
1.000	17.58	.70	26.00
.98	20.00	.68	26.33
.96	20.88	.66	26.67
.94	21.47	.64	26.99
.92	21.92	.62	27.30
.90	22.39	.60	27.62
.88	22.80	.58	27.94
.86	23.19	.56	28.25
.84	23.55	.54	28.53
.82	23.92	.52	28.81
.80	24.29	.50	29.09
.78	24.63	.48	29.35
.76	24.98	.46	29.59
.74	25.32	.44	29.82
.72	25.67	.42	---

Table 8

Experimental Data for the Third Echo with $\vec{q}||[10\bar{1}0]$ at 31.5 MHz

t	Voltage (v)	t	Voltage (V)
1.000	10.23	.70	16.87
.98	11.90	.68	17.12
.96	12.53	.66	17.38
.94	13.00	.64	17.67
.92	13.40	.62	17.89
.90	13.73	.60	18.11
.88	14.09	.58	18.37
.86	14.42	.56	18.60
.84	14.77	.54	18.82
.82	15.09	.52	19.03
.80	15.40	.50	19.24
.78	15.70	.48	19.45
.76	16.00	.46	19.65
.74	16.29	.44	---
.72	16.59	.42	---

Table 9

Experimental Data for the Third Echo with $\vec{q}||[10\bar{1}0]$ at 51.1 MHz

t	Voltage (V)	t	Voltage (V)
1.000	2.05	.70	5.55
.98	2.39	.68	5.75
.96	2.65	.66	6.00
.94	2.89	.64	6.22
.92	3.10	.62	6.43
.90	3.34	.60	6.66
.88	3.55	.58	6.88
.86	3.79	.56	7.10
.84	4.01	.54	7.31
.82	4.22	.52	7.52
.80	4.43	.50	7.77
.78	4.65	.48	8.00
.76	4.88	.46	8.22
.74	5.10	.44	---
.72	5.32	.42	---

Table 10

Experimental Data for the Second Echo with $\vec{q}||[10\bar{1}0]$ at 70.6 MHz

t	Voltage (V)	t	Voltage (V)
1.000	5.10	.70	16.85
.98	6.90	.68	17.50
.96	7.70	.66	18.16
.94	8.48	.64	18.81
.92	9.22	.62	19.44
.90	9.96	.60	20.10
.88	10.70	.58	20.73
.86	11.41	.56	21.36
.84	12.10	.54	21.98
.82	12.80	.52	22.60
.80	13.48	.50	23.20
.78	14.17	.48	23.80
.76	14.84	.46	24.38
.74	15.50	.44	25.00
.72	16.18	.42	---

Table 11

Experimental Data for the Second Echo with $\vec{q} || [11\bar{2}0]$ at 9.4 MHz

t	Voltage (V)	t	Voltage (V)
1.000	75.70	.70	91.54
.98	78.90	.68	91.96
.96	80.98	.66	92.35
.94	82.65	.64	92.72
.92	84.10	.62	93.09
.90	85.25	.60	93.42
.88	86.21	.58	93.78
.86	87.04	.56	94.09
.84	87.80	.54	94.39
.82	88.48	.52	94.67
.80	89.09	.50	94.98
.78	89.70	.48	85.30
.76	90.20	.46	---
.74	90.68	.44	---
.72	91.11	.42	---

Table 12

Experimental Data for the Third Echo with $\vec{q}||[11\bar{2}0]$ at 31.5 MHz

t	Voltage (V)	t	Voltage (V)
1.000	58.80	.70	62.49
.98	60.08	.68	62.59
.96	60.44	.66	62.68
.94	60.72	.64	62.77
.92	60.95	.62	62.85
.90	61.13	.60	62.92
.88	61.30	.58	63.01
.86	61.47	.56	63.08
.84	61.61	.54	63.15
.82	61.76	.52	63.22
.80	61.90	.50	63.30
.78	62.02	.48	63.35
.76	62.15	.46	---
.74	62.27	.44	---
.72	62.38	.42	---

Table 13

Experimental Data for the Second Echo with $\vec{q}||[11\bar{2}0]$ at 53.0 MHz

t	Voltage (V)	t	Voltage (V)
1.000	1.65	.70	6.62
.98	2.44	.68	6.82
.96	3.00	.66	6.99
.94	3.48	.64	7.16
.92	3.87	.62	7.32
.90	4.22	.60	7.47
.88	4.55	.58	7.63
.86	4.83	.56	7.78
.84	5.09	.54	7.92
.82	5.34	.52	8.04
.80	5.59	.50	8.16
.78	5.80	.48	8.26
.76	6.02	.46	8.35
.74	6.23	.44	---
.72	6.42	.42	---

Table 14

Experimental Data for the Second Echo with $\vec{q} || [11\bar{2}0]$ at 70.6 MHz

t	Voltage (V)	t	Voltage (V)
1.000	1.20	.70	9.18
.98	2.59	.68	9.50
.96	3.36	.66	9.80
.94	3.98	.64	10.10
.92	4.55	.62	10.37
.90	5.05	.60	10.61
.88	5.58	.58	10.88
.86	6.07	.56	11.10
.84	6.55	.54	11.32
.82	7.00	.52	11.53
.80	7.40	.50	11.72
.78	7.79	.48	11.90
.76	8.16	.46	12.04
.74	8.50	.44	12.17
.72	8.85	.42	---

Table 15

Experimental Data for the Second Echo with $\vec{q} || [1120]$ at 90.5 MHz

t	Voltage (V)	t	Voltage (V)
1.000	.90	.70	9.26
.98	2.36	.68	9.56
.96	3.18	.66	9.85
.94	3.90	.64	10.12
.92	4.52	.62	10.40
.90	5.12	.60	10.64
.88	5.70	.58	10.88
.86	6.23	.56	11.10
.84	6.72	.54	11.29
.82	7.13	.52	11.45
.80	7.50	.50	11.59
.78	7.89	.48	11.75
.76	8.26	.46	11.86
.74	8.60	.44	11.98
.72	8.92	.42	---

Table 16

Experimental Data for the First Echo with $\vec{q} || [11\bar{2}0]$ at 110 MHz

t	Voltage (V)	t	Voltage (V)
1.000	2.64	.70	8.21
.98	3.60	.68	8.40
.96	4.23	.66	8.58
.94	4.73	.64	8.72
.92	5.21	.62	8.40
.90	5.62	.60	9.04
.88	6.00	.58	9.15
.86	6.35	.56	9.26
.84	6.65	.54	9.36
.82	6.91	.52	9.45
.80	7.16	.50	9.53
.78	7.40	.48	9.61
.76	7.61	.46	9.70
.74	7.80	.44	---
.72	8.00	.42	---

Table 17

Experimental Data for the First Echo with $\vec{q} || [11\bar{2}0]$ at 130 MHz

t	Voltage (V)	t	Voltage (V)
1.000	4.90	.70	9.76
.98	5.70	.68	9.97
.96	6.19	.66	10.15
.94	6.59	.64	10.32
.92	6.95	.62	10.49
.90	7.29	.60	10.66
.88	7.60	.58	10.80
.86	7.90	.56	10.96
.84	8.17	.54	11.10
.82	8.44	.52	11.21
.80	8.70	.50	11.31
.78	8.95	.48	11.40
.76	9.18	.46	11.46
.74	9.37	.44	---
.72	9.56	.42	---

Table 18

Experimental Data for the First Echo with $\vec{q}||[11\bar{2}0]$ at 150 MHz

t	Voltage (V)	t	Voltage (V)
1.000	2.75	.70	7.36
.98	3.36	.68	7.58
.96	3.81	.66	7.79
.94	4.15	.64	7.99
.92	4.48	.62	8.18
.90	4.81	.60	8.38
.88	5.12	.58	8.57
.86	5.40	.56	8.73
.84	5.66	.54	8.89
.82	5.92	.52	9.01
.80	6.18	.50	9.12
.78	6.43	.48	9.22
.76	6.67	.46	---
.74	6.91	.44	---
.72	7.14	.42	---

Table 19

Experimental Data for the First Echo with $\vec{q} || [1120]$ at 170 MHz

t	Voltage (V)	t	Voltage (V)
1.000	1.62	.70	6.02
.98	2.18	.68	6.24
.96	2.60	.66	6.43
.94	2.92	.64	6.61
.92	3.24	.62	6.80
.90	3.55	.60	6.99
.88	3.85	.58	7.17
.86	4.12	.56	7.31
.84	4.39	.54	7.48
.82	4.64	.52	7.60
.80	4.88	.50	7.71
.78	5.12	.48	7.82
.76	5.35	.46	7.92
.74	5.58	.44	---
.72	5.80	.42	---