

## Ultrasonic Attenuation in Superconducting Molybdenum\*

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Measurements have been made on the attenuation of 10-, 30-, and 50-MHz longitudinal sound waves in normal and superconducting molybdenum single crystals. These measurements were made for the ultrasound propagated in the [100], [110], and [111] directions. The measured attenuation changes have been analyzed in terms of the BCS theory of superconductivity. An effective minimum energy gap has been determined and has been found to be anisotropic. We have also observed a frequency-dependent behavior in the measured values of the ratio of the ultrasonic attenuation in the superconducting state over that in the normal state  $\alpha_s/\alpha_n$  and hence in the values of the energy gap  $\Delta(T)$ , calculated by fitting the data to the BCS model.

### INTRODUCTION

Superconductivity was discovered in molybdenum by Geballe *et al.*<sup>1</sup> in 1962. The consensus of work since that time indicates that this superconductor has a transition temperature of about 0.92 K.<sup>2-6</sup> The critical field at 0 K has been found to be between 95 and 114 G.<sup>6</sup>

One of the more important measurable quantities characterizing a superconductor is the value of the energy gap at 0 K,  $2\Delta(0)$ . This important quantity is predicted by the BCS theory<sup>7</sup> to be

$$2\Delta(0) = 3.52k_B T_c, \quad (1)$$

where  $k_B$  is the Boltzmann constant and  $T_c$  the superconducting transition temperature. The BCS theory was developed for an ideal superconductor with an isotropic Fermi surface and an isotropic crystal structure. Such oversimplification is no doubt not the case in a real metal with a complicated electronic structure such as molybdenum. It should be expected that the energy gap in molybdenum would be anisotropic<sup>5,8</sup> and although we have no prior evidence to support such a supposition, we must allow for the possibility that molybdenum has two or more energy gaps associated with its superconductivity.

Only a few attempts have been made to measure the 0 K energy gap in superconducting molybdenum.<sup>3-6</sup> Agreement between various investigators has been only fair. All investigators do obtain values which are below the value predicted by Eq. (1). Using ultrasonic frequencies in the approximate range of 200–1000 MHz, Jones and Rayne have found anisotropy in the energy gap.<sup>3</sup> This has been the only study of anisotropy of the energy gap in molybdenum. Horwitz and Bohm<sup>2</sup> agree, in the extremes of error, with Jones and Rayne for the energy gap in the [100] direction, while Garfunkel *et al.*,<sup>4</sup> also using the ultrasonic method, are not in close agreement with them. The energy gap has also been obtained from specif-

ic-heat and thermal-conductivity studies.<sup>5,6</sup>

In this investigation we have studied the low-frequency ultrasonic attenuation in normal and superconducting molybdenum at temperatures of 1.1–0.38 K. The ultrasound was propagated in each of three crystallographic directions [100], [110], and [111]. From these measurements a characteristic effective energy gap has been found for each orientation. A study was also made on both the frequency and amplitude dependence of the ultrasonic attenuation.

### EXPERIMENTAL PROCEDURE

The pulse-echo technique has been utilized to measure the ultrasonic attenuation in molybdenum. Figure 1 shows a block diagram of the electronic equipment. Due to the very small change in the ultrasonic attenuation between the normal and superconducting states, random noise in the data

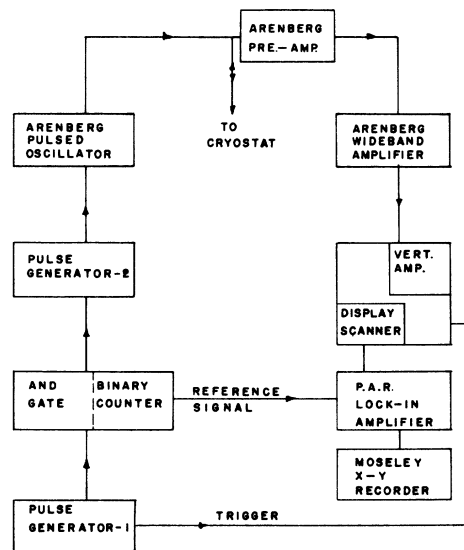


FIG. 1. Block diagram of electronic equipment.

could be quite significant. To circumvent the noise problem, the ultrasonic sending and receiving circuits were electronically chopped at a fixed reference frequency.<sup>9</sup> Echoes were then detected at the chopping frequency, and all other frequencies were discriminated against. This allowed for selective amplification of the changes in the echo heights without corresponding amplification of noise.

In the course of operation, the first Hewlett-Packard model-214 pulse generator operated in an internally triggered mode at a frequency of 800 Hz. This generator simultaneously sent a trigger signal to the Hewlett-Packard (HP) model-175A oscilloscope and produced a pulse of approximately 10- $\mu$ sec duration. The output of this pulse generator goes to the binary counter and the AND gate. The four-stage binary counter divided the 800-Hz signal to produce a 50-Hz square wave which was sent to the PAR model-121 lock-in amplifier to serve as a reference-chopping frequency. The square wave was also sent from the binary counter to the AND gate. The AND gate allowed pulses to be sent from the first pulse generator to the second pulse generator during only one-half of the period of the 50-Hz square wave. This input signal triggered the second pulse generator which in turn was used to trigger the Arenberg pulsed oscillator, producing rf pulses of about 2- $\mu$ sec duration. The voltage amplitude of these rf pulses was adjustable from about 1 V to several hundred V peak to peak. These pulses were sent through an electrical tee into the cryostat where they were converted into acoustical pulses at the quartz transducer. The usual ultrasonic echo train was received from the cryostat and sent to the Arenberg model-P. A. -620SN preamplifier. The output from the preamplifier was sent directly to the Arenberg model-W. A. -600 C wide-band amplifier which contained a video-amplifier section. The output of the video amplifier was sent to the HP oscilloscope. This oscilloscope was equipped with a HP model-1782A display-scanner plug-in unit which made it possible to sample the amplitude of the oscilloscope trace at any point along the trace. During an experiment, this point on the trace was selected to coincide with the peak of one given echo. The output of the display scanner then approximated a 50-Hz square wave whose amplitude was proportional to the amplitude of the echo. This output signal was sent to the lock-in amplifier where all noise having frequency components different from 50 Hz was filtered from it. From this signal, the lock-in amplifier put out a dc signal which was proportional to the amplitude of the echo being sampled. This output was displayed on the vertical axis of a model-2X2A Moseley X-Y recorder. The horizontal axis of

the X-Y recorder was driven by the output of a four-terminal resistance thermometer. The ultrasonic frequency was measured with a HP model-5245L frequency counter.

Due to the very low transition temperature of molybdenum ( $T_c = 0.92$  K), we had to utilize our liquid-He<sup>3</sup> refrigerator<sup>10</sup> which had been modified to make ultrasonic-attenuation studies. Figure 2 shows a diagram of the liquid-He<sup>3</sup> refrigerator. With this refrigerator, we could remain steadily on any temperature between 1.5 and 0.38 K for times ranging up to 10 h.

The temperature of the molybdenum sample was monitored with the aid of an Allen-Bradley carbon-resistance thermometer. The thermometer was mounted in a hole in a pure-copper table which supported the molybdenum samples. Both the samples and the thermometers were attached to the copper table with Dow Corning D. C. -11 stop-cock grease in order to provide good thermal contact. The carbon resistance thermometer had a nominal resistance of 5.1  $\Omega$  at room temperature. The carbon resistor was calibrated against the vapor pressure of the He<sup>3</sup> at the beginning of each experiment. This pressure was monitored on a Wallace and Tiernan absolute pressure gauge, model FA160. The  $T_{62}$  He<sup>3</sup>-vapor-pressure tables

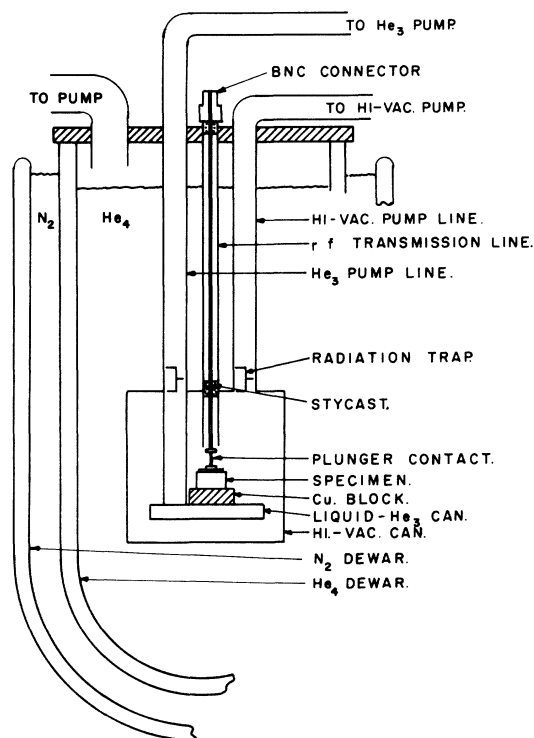


FIG. 2. Liquid-He<sup>3</sup> cryostat used in ultrasonic-attenuation studies.

prepared by Sherman, Sydoriak, and Roberts<sup>11</sup> were used in this calibration.

#### SAMPLE PREPARATION

The single crystal of molybdenum was grown by Metals Research Ltd. and it was stated to have been grown from 99.995%-pure materials. From this crystal we cut oriented samples with axis directions of [100], [110], and [111]. The samples were oriented by the Laué back-reflection method. The samples were cut and polished on an Elox model-T. Q. H. -31 electric-discharge machine. The end faces of the prepared samples were polished to within 0.0005 cm of parallel. The samples' end faces were oriented to within 1.0° of perpendicular to the desired crystallographic direction in each case and the length between the parallel faces was approximately 0.60 cm.

The strain introduced into the crystal during spark polishing was assumed to be a minimum since the Laué x-ray spots taken afterwards were very sharp.

The binder between the quartz transducer and the molybdenum sample was Dow Corning D. C. -11 stopcock grease.

#### MEAN-FREE-PATH DETERMINATION

In order to obtain a measure of the purity of the molybdenum samples studied, an estimate was made of the electron mean-free path ( $l$ ) utilizing a magnetoacoustic technique proposed by Deaton and Gavenda.<sup>12,13</sup> With this technique a study was made of the magnetic field dependence of the longitudinal ultrasonic attenuation in normal-state molybdenum for sound wave vectors ( $\vec{q}$ ) in the [100] direction. Pippard<sup>14</sup> has shown that this attenuation will vary with magnetic field strength  $H$  and approach a limiting value as  $1/H^2$  when  $H \rightarrow \infty$ . It can be shown that the attenuation in zero field equals this extrapolated attenuation when  $ql = 6.8$ .

For the magnetoacoustic experiment, a cryostat was constructed which allowed the sample to be placed between the poles of a Varian 12-in. electromagnet. Changes in the ultrasonic attenuation were measured while sweeping the  $H$  field continuously between 0 and 10 kG. The electronic equipment was the same as described earlier. The experimental apparatus was conveniently designed so that the magnetic field could be rotated in a plane perpendicular to the sound wave vector. This allowed for some information to be obtained on the anisotropy of the mean free path as a function of the magnetic field orientation with respect to the molybdenum crystallographic axes.

The data were reduced by plotting the ultrasonic attenuation for each frequency used (10, 30, or 50

MHz) as a function of  $1/H^2$  and extrapolating to  $H = \infty$ . The difference between this extrapolated attenuation and the zero-field attenuation was plotted as a function of frequency in order to obtain the frequency for which  $ql = 6.8$ .

Our results indicate that there is no anisotropy observed within experimental error.

#### ULTRASONIC ATTENUATION DATA

The data taken in this experiment consisted of continuous X-Y recorder plots of the voltage height of a given ultrasonic echo as a function of the temperature between 1.1 and 0.38 K. We have made the usual assumption that all mechanisms contributing to ultrasonic attenuation in metals at low temperatures are temperature independent except for those involving electron-phonon interactions.

The data taken to determine the ultrasonic attenuation in the normal state of molybdenum indicated that the normal-state attenuation  $\alpha_n(T)$  was a constant below about 1.2 K. These data were taken with a magnetic field of about 200 G impressed on the molybdenum sample. This field somewhat exceeded the estimated 0-K critical field<sup>6</sup> for molybdenum and ensured that the specimen would remain in the normal state while attenuation measurements were being conducted.

From the data plots we were able to obtain the ultrasonic attenuation ratio

$$\frac{\alpha_s(T)}{\alpha_n(T)} = \log_{10} \frac{V_s(0)}{V_s(T)} / \log_{10} \frac{V_s(0)}{V_n(T)}, \quad (2)$$

where  $V_s(0)$  and  $V_s(T)$  are the voltages at 0 and  $T$  K in the superconducting state, respectively, and  $V_n(T)$  is the voltage in the normal state at  $T$  K, which is constant below 1.2 K.

We were also concerned with the temperature-dependent effect associated with the interactions between ultrasound and dislocations observed in other superconductors.<sup>15</sup> This can be studied in terms of the amplitude dependence of the ultrasonic attenuation. This interaction gives rise to an increase in the ultrasonic attenuation in the superconducting state as the temperature decreases. Since this increase directly opposes the natural tendency of the superconducting-state attenuation to decrease at lower temperatures, the amplitude effect is readily discernible in ultrasonic-attenuation data. We were unable to detect any amplitude dependence in our studies; thus, the values of the superconducting energy gaps obtained from this data are independent of the ultrasonic amplitude in all cases.

#### ANALYSIS OF RESULTS

In order to calculate the limiting effective energy gap  $\Delta(0)$  from the temperature dependence

of  $\alpha_s(T)/\alpha_n(T)$ , we have utilized the result of the BCS theory<sup>7</sup> which states that

$$\frac{\alpha_s(T)}{\alpha_n(T)} = \frac{2}{e^{\Delta(T)/k_B T} + 1} \quad (3)$$

This equation can be rewritten in the form

$$\frac{\Delta(T)}{k_B T} = \ln\left(\frac{2\alpha_n(T)}{\alpha_s(T)} - 1\right) \quad (4)$$

It is customary to express the temperature dependence of  $\Delta(T)$  as

$$\Delta(t) = G(t) \Delta(0), \quad (5)$$

where we are now using the reduced temperature  $t = T/T_c$  and the function  $G(t)$  has been tabulated from the BCS theory by Mühlshlegel.<sup>16</sup> For purposes of calculation we have found it to be more convenient to use the analytical form given by Clem,<sup>17</sup>

$$G(t) = 1.7367(1-t)^{1/2} [1 - 0.4095(1-t) - 0.0626(1-t)^2]. \quad (6)$$

Numerical calculations show that Clem's formula agrees with Mühlshlegel's results within an error of 0.1% for  $t > 0.4$ .

Substituting Eq. (5) into Eq. (4) we get

$$\Delta(0) \frac{G(t)}{t} = \ln\left(\frac{2\alpha_n(t)}{\alpha_s(t)} - 1\right) \quad (7)$$

in units of  $k_B T_c$ . This expression implies that if the BCS theory is exactly correct, then a plot of  $\ln(2\alpha_n/\alpha_s - 1)$  as a function of calculated values of

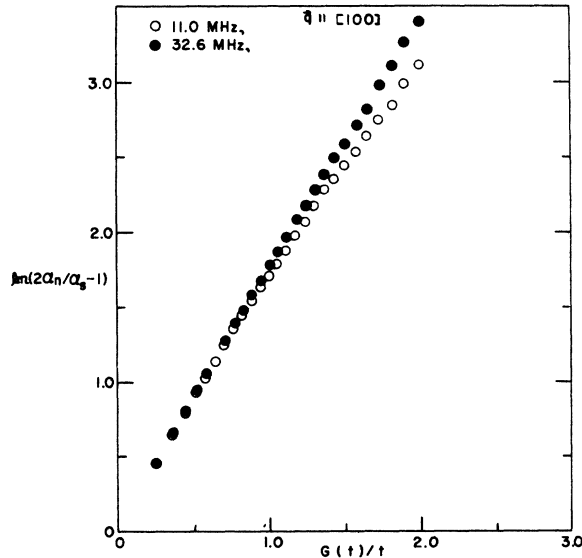


FIG. 3. Plot of  $\ln(2\alpha_n/\alpha_s - 1)$  vs  $G(t)/t$  for 11.0- and 32.6-MHz longitudinal waves propagated in the [100] direction.

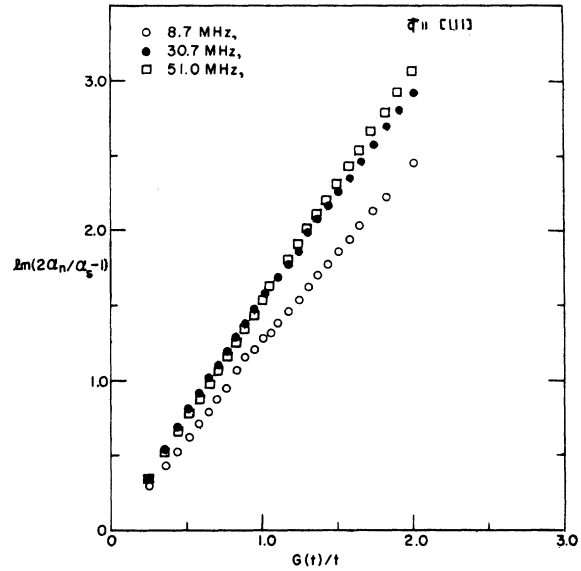


FIG. 4. Plot of  $\ln(2\alpha_n/\alpha_s - 1)$  vs  $G(t)/t$  for 8.7-, 30.7-, and 51.0-MHz longitudinal waves propagated in the [111] direction.

$G(t)/t$  should be a straight line whose slope is the energy gap at 0 K. Since our data on  $\alpha_s(t)$  was not taken below  $t = 0.45$ , it was necessary to rely on Eq. (7) as a means of estimating the echo voltage height in the superconducting state at 0 K,  $V_s(0)$ . This was accomplished by fitting each set of data separately to Eq. (7) by the method of least squares while treating  $V_s(0)$  as a variable parameter to obtain the best fit. The data fit a BCS type of equation rather well.

Although it was possible to fit each set of data over the entire temperature range  $1.0 > t > 0.45$ , it soon became evident that a slightly better fit could be obtained on the range  $0.87 > t > 0.45$ . This was particularly true at the lower ultrasonic frequencies. This finding is consistent with similar experiences by other investigators attempting similar types of fits in other superconductors.<sup>18,19</sup> Figures 3-5 show plots of  $\ln(2\alpha_n/\alpha_s - 1)$  vs  $G(t)/t$ . These plots could suggest the existence of two distinct energy gaps  $2\Delta(0)$  due to two different slopes in the high- and low-temperature ranges. On the other hand, the problem is more likely associated with an error in the determination of  $\alpha_n(T)$ . The ultrasonic echoes take on their smallest value and hence have the smallest signal-to-noise ratio when the molybdenum is in the normal state. This makes an error in the determination of  $\alpha_n(t)$  much more likely than a corresponding error in determining  $\alpha_s(t)$ . It can be shown that Eq. (7) is much less sensitive to errors in  $\alpha_n(t)$  at low reduced temperatures than for values of

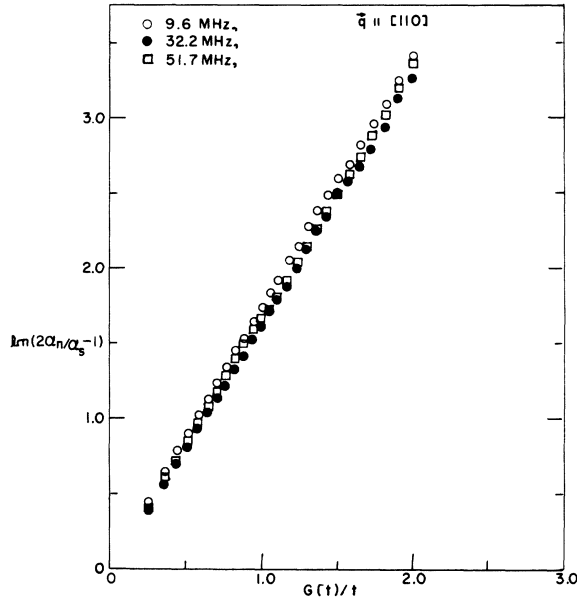


FIG. 5. Plot of  $\ln(2\alpha_n/\alpha_s - 1)$  vs  $G(t)/t$  for 9.6-, 32.2-, and 51.7-MHz longitudinal waves propagated in the [110] direction.

$t$  near the transition temperature.<sup>18</sup> Thus, it was decided to omit the data for the highest reduced temperatures from the fit.

Values obtained for the 0-K energy gap in this manner are given as  $\Delta(0)$  in Table I. The value given for each frequency represents the average over several sets of data taken at different transducer voltage levels at that frequency. The error given with the values of  $\Delta(0)$  has been estimated from the reproducibility of the determined value of the energy gap from one set of data to the next.

In order to examine variations of the data from a perfect fit to Eq. (7), we utilize the functional relationship<sup>20</sup>

$$\frac{\Delta(t)}{\Delta_{\text{BCS}}(t)} = \frac{t}{1.76G(t)} \ln\left(\frac{2\alpha_n(t)}{\alpha_s(t)} - 1\right). \quad (8)$$

For an ideal superconductor in the sense of the BCS theory,  $\Delta(t)/\Delta_{\text{BCS}}(t)$  should be independent of  $t$  and have a value of unity. Included in Table I are values of  $\Delta(t)/\Delta_{\text{BCS}}(t)$  at  $t = 0.46$  and at  $T = 0.9T_c$ , calculated in each case from the same sets of data used to determine  $\Delta(0)$ .

The values of  $\Delta(t)/\Delta_{\text{BCS}}(t)$  suggest that an equation of the BCS type [Eq. (3)] provides a good description of the ultrasonic attenuation in the [110] and [111] directions. Although the ultrasonic attenuation data seems to fit an equation of the BCS type rather well, the energy gaps differ systematically from the value predicted by the BCS isotropic model.

By way of contrast to the straightforward behavior of data for the [110] and [111] orientations, the data for  $\Delta(t)/\Delta_{\text{BCS}}(t)$  for the [100] direction give considerably different values for  $t = 0.46$  and  $t = 0.90$ . Figure 6 gives plots of  $1.76\Delta(t)/\Delta_{\text{BCS}}(t)$  as a function of  $t$ . A linear extrapolation to  $t = 0$  gives a value of  $1.76\Delta(t)/\Delta_{\text{BCS}}(t)$ , which is very close to the corresponding previously calculated value of  $\Delta(0)$ . This suggests that  $\Delta(0)$  obtained by fitting the data to Eq. (7) represents a limiting low-temperature energy gap.

Table II gives a comparison of the results of the measurements of the superconducting-ground-state energy gap  $2\Delta(0)$ , and the transition temperature  $T_c$  for molybdenum by various investigators.

The results of the present work are in reasonably good agreement with previous investigations giving an average energy gap. Comparison between the gaps obtained by different ultrasonic investigations seems to offer a consistent picture regarding the sense of anisotropy in the energy gap. There are, however, discrepancies between the results of different investigations. For the [100] direction, the results of Horwitz and Bohm<sup>2</sup> were somewhat higher than that of either Jones and Rayne<sup>3</sup> or this investigation. However, Horwitz and Bohm only attained a reduced temperature of  $t = 0.6$ , making the data fit favor the higher reduced temperatures. Utilizing our data near the transition temperature, we can obtain an energy gap close to that of Horwitz and Bohm. The  $2\Delta(0)$  as calculated from our data near  $T_c$  gives  $2\Delta(0) = 3.5k_B T_c$ , while the data favoring the lower temperature points to a limiting low-temperature gap of  $2\Delta(0) = 3.3k_B T_c$ . Furthermore, our results for the [100] direction suggest that the low-temperature energy gap is increasing with increasing frequency.

## CONCLUSION

A proper understanding of ultrasonic attenuation in a superconductor such as molybdenum will eventually require a theory that makes allowances

TABLE I. Effective energy gap  $\Delta(0)$  in units of  $k_B T_c$  and the unitless function  $\Delta(t)/\Delta_{\text{BCS}}(t)$  as a function of frequency in MHz and the crystallographic directions in molybdenum.

Direction	Frequency (MHz)	$\Delta(0)$ $k_B T_c$	$\frac{\Delta(0.46)}{\Delta_{\text{BCS}}(0.46)}$	$\frac{\Delta(0.90)}{\Delta_{\text{BCS}}(0.90)}$
[100]	11.0	$1.38 \pm 0.10$	$0.88 \pm 0.06$	$1.00 \pm 0.06$
	32.6	$1.61 \pm 0.10$	$0.95 \pm 0.06$	$1.03 \pm 0.06$
	50.0	...	...	...
[110]	9.6	$1.65 \pm 0.15$	$0.96 \pm 0.06$	$0.99 \pm 0.06$
	32.3	$1.64 \pm 0.10$	$0.91 \pm 0.06$	$0.91 \pm 0.06$
	51.7	$1.71 \pm 0.15$	$0.94 \pm 0.06$	$0.93 \pm 0.06$
[111]	8.7	$1.19 \pm 0.10$	$0.69 \pm 0.06$	$0.69 \pm 0.06$
	30.7	$1.37 \pm 0.10$	$0.84 \pm 0.06$	$0.89 \pm 0.06$
	51.0	$1.52 \pm 0.15$	$0.86 \pm 0.06$	$0.85 \pm 0.06$

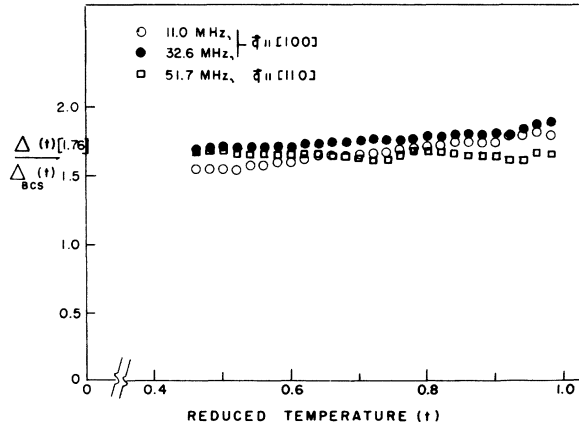


FIG. 6. Plot of  $1.76\Delta(t)/\Delta_{\text{BCS}}(t) = [t/G(t)] \ln[2\alpha_n(t)/\alpha_s(t) - 1]$  vs  $t$  for 11.0- and 32.6-MHz longitudinal waves propagated in the [100] direction and 51.7-MHz longitudinal wave propagated in the [110] direction.

for very complicated multiband Fermi surfaces in metals. One multiband model which has been utilized in other superconductors is a variation of Eq. (3).<sup>20</sup> It assumes that the ratio  $\alpha_s/\alpha_n$  depends on several energy gaps  $\Delta_i(T)$  such that

$$\frac{\alpha_n}{\alpha_s} = \sum_i \frac{A_i}{e^{\Delta_i(T)/k_B T} + 1}. \quad (9)$$

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

$$\sum_i A_i = 2 \quad (10)$$

and it is assumed that the  $\Delta_i(t)$  each have the temperature dependence given by Eq. (3). This model has been employed with some success for a two-gap superconductor by Perz and Dobbs.<sup>18,21</sup> Since

the specific-heat data on molybdenum<sup>5</sup> suggest the presence of multiple gaps, Eq. (9) could possibly be applied to molybdenum. There is, however, no reason to suppose that there are just two gaps contributing to the total effective gap in any direction in molybdenum. An estimate of the size of these several energy gaps from tunnelling experiments is generally required before one can proceed with confidence with Eq. (9). No tunnelling results have been reported for molybdenum, making quantitative calculations meaningless. Still, some general observations can be extracted from these results.

If it is assumed that one of the energy gaps is smaller than the others and that the values of the  $A_i$  in Eq. (9) are of the same order, then the term in Eq. (9) containing this smallest gap will dominate  $\alpha_s/\alpha_n$  as the reduced temperature approaches zero. This could account for the temperature dependence of  $\Delta(t)/\Delta_{\text{BCS}}(t)$  for the [100] direction. This also suggests from Table I that the smallest gap has the value given by  $\Delta(0) = 1.62k_B T_c$  at the ultrasonic frequency of 30 MHz. At higher temperatures, particularly near  $T_c$ , the value of  $\Delta(t)/\Delta_{\text{BCS}}(t)$  will be an average with all terms in Eq. (9) contributing evenly.

An extension of this type of argument to the [110] and [111] directions in molybdenum is difficult, since the  $\Delta(t)/\Delta_{\text{BCS}}(t)$  in these directions is virtually temperature independent. It is certainly possible that there are several gaps, all of which are about the same size. But until supplemental information is provided on the presence of multiple gaps, there would seem to be no reason to prefer the more complicated Eq. (9) to the simplicity of a single-gap model such as Eq. (3).

Our data indicate a frequency dependence of the energy gaps in the [100] and [111] directions. For the [111] direction, this frequency dependence applies to the effective energy gap regardless of

TABLE II. Comparison of effective energy gaps in molybdenum as determined by various investigators.  $T_c$  is given in units of K and the energy gap in units of  $k_B T_c$ .

Authors	Method	$T_c$ (K)	$2\Delta(0)/k_B T_c$ [orientation]
Horwitz and Bohm (Ref. 2)	Ultrasonic (239 MHz)	$0.92 \pm 0.01$	$3.5 \pm 0.2$ [100]
Jones and Rayne (Ref. 3)	Ultrasonic (200 to 1000 MHz)	$0.92 \pm 0.01$	$3.3 \pm 0.2$ [100]
			$3.5 \pm 0.2$ [110]
			$3.1 \pm 0.2$ [111]
Garfunkel <i>et al.</i> (Ref. 4)	Hypersonic (10 GHz)	0.914	$2.10 \pm 0.3$ to $2.88 \pm 0.4$ [111]
Rorer <i>et al.</i> (Ref. 5)	Specific heat	$0.913 \pm 0.002$	$3.5 \pm 0.2$ [av]
Waleh and Zebouni (Ref. 6)	Thermal conductivity	0.903	$3.2 \pm 0.1$ [av]
	Critical field	0.903	$3.4 \pm 0.1$ [av]
Present work	Ultrasonic (10 to 50 MHz)	$0.912 \pm 0.010$	$3.2 \pm 0.2$ [100]
			$3.4 \pm 0.2$ [110]
			$3.0 \pm 0.2$ [111]

the temperature. For the [110] direction, the frequency dependence appears to apply to only what has been interpreted to be the smallest of several possible energy gaps; the effective gap at 0 K.

Measurements of the ultrasonic attenuation were made in a range of ultrasonic frequencies such that  $ql \geq 1$ . When the principles of the conservation of energy and momentum are applied to the problem of electron-phonon interactions in normal metals, it is found that only a small fraction of the total number of electrons contribute to ultrasonic attenuation. This fraction is determined by the requirement that the velocity component  $V_f \cos \theta$  of the electrons contributing to attenuation must be equal to the sound wave velocity  $V$  and be parallel to the phonon wave vector  $\vec{q}$ . The angle  $\theta$  is the angle between the Fermi velocity vector ( $\vec{V}_F$ ) and the phonon wave vector.<sup>18</sup> Leibowitz<sup>22</sup> has discussed the electronic ultrasonic attenuation for the case of  $ql \geq 1$ . He finds that the fraction of the Fermi surface on which electrons contribute to the ultrasonic attenuation can be expressed in terms of  $\theta$  by

$$\cos \theta = V/V_F + 1/ql. \quad (11)$$

Thus, the equation favors electrons toward the equator of the Fermi surface perpendicular to the phonon wave vector. Equation (11) suggests that for an anisotropic superconductor, the energy gap should be dependent on  $ql$  for low values of  $ql$  and this dependency should vanish as  $ql \rightarrow \infty$ .

In the molybdenum samples studied the value of  $l$  was impurity limited in the entire temperature range in which attenuation measurements were made. In light of Eq. (11), this would appear to

explain the observed frequency dependence of the energy gaps in molybdenum. As expected by the above argument, the energy gap at 10 MHz ( $ql = 1$ ) goes to a constant value at the higher values of 30 MHz ( $ql = 7$ ) and 50 MHz ( $ql = 12$ ). Furthermore, the values of the gaps obtained at 30 and 50 MHz appear to be equal to or approaching the limiting value of the gaps given by Jones and Rayne at high frequencies ( $ql \rightarrow \infty$ ). The fact that the energy gap in the [100] direction appears to have reached its limiting value already at 10 MHz suggests that the effective value of  $l$  governing electron-phonon interactions for this orientation is somewhat longer than  $l$  for the other orientations.

In conclusion, our results lead us to conclude that the ultrasonic attenuation in the [110] and [111] directions can be described quite effectively by a single-gap BCS model. The value of the energy gap obtained at 50 MHz for each orientation is felt to represent the limiting frequency-independent energy gap predicted by BCS.

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

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