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Ultrasonic attenuation in superconducting cadmium*

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Ultrasonic-attenuation measurements have been conducted on high-purity cadmium single crystals in both the normal and superconducting states. These studies have been made with longitudinal sound waves propagated in the [0001], [10$\bar{1}$0], and [11$\bar{2}$0] crystallographic directions. Analysis of the data indicates the presence of a single frequency-independent superconducting energy gap associated with each crystallographic direction studied.

INTRODUCTION

Recent electronic-specific-heat data on the complex, multiband superconductors cadmium and zinc[1] seem to indicate the presence of two energy gaps in these crystals.

In addition to the specific-heat results, some recent ultrasonic-attenuation measurements on the crystallographic similar metal zinc[2] indicated a connection between the supposed presence of multiple energy gaps and the crystal purity. This connection is believed to arise through the magnitude of the ql product. Since the ultrasonic-attenuation technique samples the energy gap of a selectable group of electrons on an effective zone about the equator of the Fermi surface,[3] it was anticipated that an ultrasonic-attenuation study of cadmium might supply additional evidence to indicate the nature of multiple energy gaps. Therefore, this paper is concerned with the results of an experimental investigation of the ultrasonic attenuation in cadmium. Supporting experiments were also performed to determine the magnetic purity of the crystal and also to determine electron mean-free-path lengths.

SAMPLE PREPARATION

In order to study the superconducting properties of cadmium, with a minimum effect from dislocations and impurities, a zone-refined single crystal, grown from greater than 99.9999%-pure cadmium melt, was purchased from Metals Research Ltd.[4] The crystal came in the form of a $\frac{1}{2}$-in. diam right circular cylinder about 1 in. long. This crystal was then cut into a rectangular parallelepiped exposing the three independent crystallographic directions [0001], [10$\bar{1}$0], and [11$\bar{2}$0]. All cutting and polishing of the cadmium single crystal were performed with an Elox TQH-31 electric discharge machine. Crystallographic directions were determined by the Laue back-reflection method.[5] Once the proper directions were established, the opposite sides of the crystal were spark planed parallel to a precision of about 0.0005 cm over the crystal faces. The distances between the parallel faces were 0.4767, 0.7276, and 0.4093 cm for the [10$\bar{1}$0], [11$\bar{2}$0], and [0001] directions, respectively. The Laue photographs along with the micrographs of the polished crystal surfaces indicated small areas of surface irregularities produced by the spark erosion machine. Using a three-step etching process[6] of (a) (1–2)% nitric acid by volume in alcohol, (b) ammoniacal ammonium persulphate in water (various strengths), and (c) dilute alcoholic feric chloride (various strengths), these irregularities were etched away. After the etching the sample was again x rayed to recheck the alignment of the end faces and the faces were measured for parallelism. It was found that each pair of end faces had a deviation of less than 1° from its respective lattice planes and that each pair was parallel to within 0.0005 cm over the entire surface.

The binder utilized between the quartz transducer and the cadmium sample was Dow Corning DC-11 stopcock grease.

EXPERIMENTAL

The pulse-echo technique was utilized to measure the ultrasonic attenuation in cadmium. When passing from the normal to the superconducting state, the change in the ultrasonic attenuation is quite small (~1 dB). In order to enhance the small signal-to-noise ratio, we used a sampling integration and phase-sensitive detection system.[2]

To acquire the very low temperatures required of these studied ($T_c = 0.503$ K) we utilized a conventional liquid-^{3}He refrigerator.

Both the electronic equipment and the liquid-^{3}He refrigerator have been described in detail by both O'Hara and Marshall[7] and Cleavelin and Marshall.[2]

In order to determine the magnetic purity of the sample, we used the Faraday method to measure its magnetic susceptibility. The Faraday method consists of measuring the force exerted on a hypothetical point source of the magnetic material placed in a magnetic field gradient. The gradient field was produced by a Varian V-3700 15-cm electromagnet, a V-FR 2902 Fieldial regulated power supply and a set of constant HdH/dz pole faces. The small sample was suspended in the gradient field by a thin glass fiber which was connected to the lever arm of a Cahn R.M. automatic electrobalance. The electrobalance combined with a Hewlett-Packard 3400A digital voltmeter allowed a visual readout to the nearest 98×10^{-9} N change of force. The gradient field was calibrated, for all "fieldial" settings, with Mohr's salt [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$]. The magnetic cryostat was equipped with a liquid-helium Dewar system to allow measurements between 300 and 1.5 K. Figure 1 shows the results of this measurement compared with the work of Marcus.[8] The slightly greater diamagnetism in the present crystal is attributed to its greater purity.

In order to obtain a measure of the electron mean-free-path length l we have utilized a magnetoacoustic technique proposed by Deaton and Gavenda[9,10] which is based on the free-electron theory. Although cadmium is quite anisotropic this technique appears to be best suited to determine l for the purpose of comparison with values in the literature.[10,11] Peck and Dobbs[11] have pointed out that for their data the limiting attenuation versus frequency follows the expectations of the free electron theory for $ql \sim 1$ and above. This would indicate that the resulting ql values represent an appropriate average over the relevant effective zones of the Fermi surface. Deaton has also expressed a similar opinion.[10] With this technique, a study was made of the magnetic field dependence of the longitudinal ultrasonic attenuation in normal-state cadmium for sound wave vectors ($\vec{q}$) in the [0001], [11$\bar{2}$0], and [10$\bar{1}$0] directions. Pippard[12] has shown that the attenuation will vary with an applied magnetic field strength H and approach a limiting value as $1/H^2$ when $H \rightarrow \infty$. It can be shown[9] that the attenuation in zero field equals this extrapolated attenuation when $ql = 6.8$.

In the magnetoacoustic experiment the sample was placed between the poles of a Varian 12-in. electromagnet with the ultrasound directed perpendicular to the magnetic field. Changes in the ultrasonic attenuation were measured while continuously sweeping the H field between 0 and 10 000 G.

In order to gauge the magnitude and relative anisotropy of the electron mean-free-path lengths, zone plots were recorded by setting the magnetic

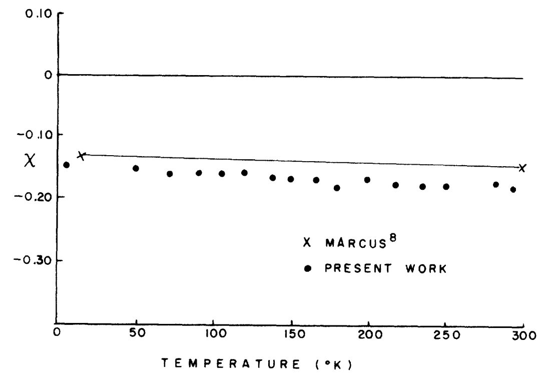

FIG. 1. Experimentally measured magnetic susceptibility of cadmium in units of 10^{-6} cgs vs temperature in (°K).

field at 10 kG and measuring the ultrasonic attenuation as the sample was slowly rotated in the field. The results are shown in Figs. 2–4.

The smallest ql product in effect at any time in this experiment was 1.6. Thus, at no time do the superconducting ultrasonic attenuation data result from interactions in the region where $ql \leq 1$. This again indicates a crystal of extremely high purity.[9,10]

The normal-state attenuation data were taken below the transition temperature by applying a magnetic field greater than[13] 30 G in order to quench the superconductivity in cadmium. This field was parallel to the sound direction in the crystal. The normal-state attenuation was found to be a function of the strength of the magnetic

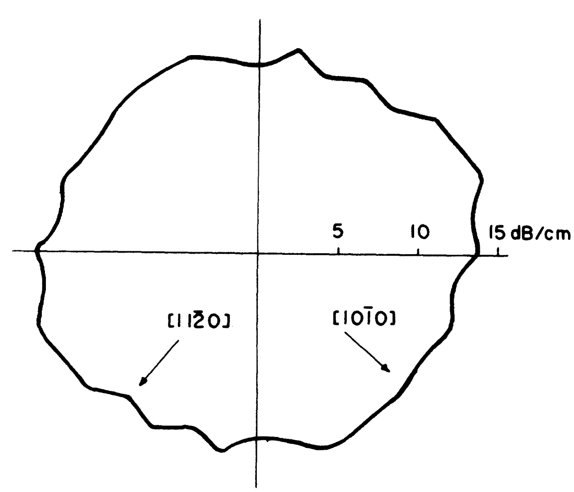

FIG. 2. Zone plot showing the relative anisotropy of the electron mean free path for $\vec{q} \parallel$ [0001] in a 10 kG magnetic field.

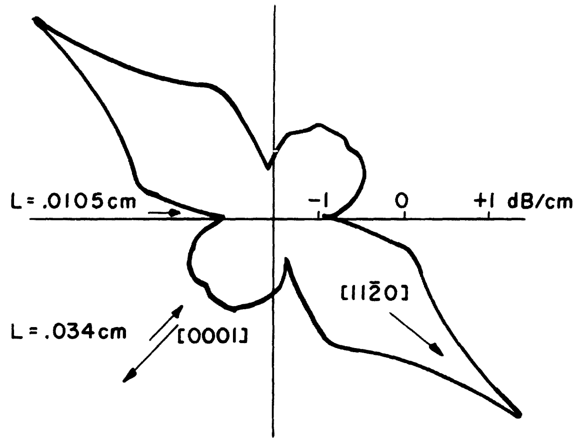

FIG. 3. Zone plot showing the relative anisotropy of the electron mean free path for $\vec{q} \parallel [10\bar{1}0]$ in a 10 kG magnetic field.

field. This is known as the parallel field magnetoacoustic effect and is easily corrected.[14] The transition temperature of the cadmium sample was determined from the ultrasonic attenuation data for each crystallographic direction by observing the temperature at which the attenuation abruptly changed from the normal to the superconducting state. The transition temperature was found to be isotropic with a value of $T_c = 0.503 \mp 0.005$ K.

The amplitude of the ultrasound was varied considerably for every crystallographic direction, but no amplitude dependence was found.

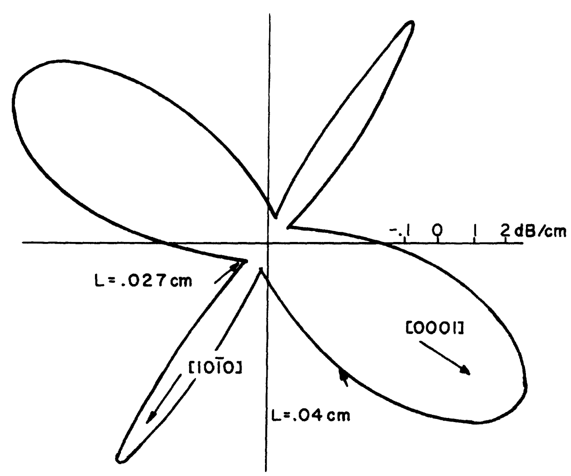

FIG. 4. Zone plot showing the relative anisotropy of the electron mean free path for $\vec{q} \parallel [11\bar{2}0]$ in a 10 kG magnetic field.

DATA ANALYSIS

Of the several methods currently used[15] for analyzing attenuation data, the following modified method appears to be most appropriate for observing the presence of more than one energy gap in cadmium.

From the BCS attenuation equation[16]

$$\alpha_s(T)/\alpha_n(T) = 2/(e^{\Delta(T)/kT} + 1), \tag{1}$$

the temperature-dependent energy gap can be found as

$$\ln[2\alpha_n(T)/\alpha_s(T) - 1] = \Delta(T)/kT, \tag{2}$$

where $\alpha_s(T)$ and $\alpha_n(T)$ are the attenuation coefficients in the superconducting and normal states, respectively, $\Delta(T)$ is the temperature-dependent energy gap, and k is Boltzmann's constant.

Since there is a nonzero energy gap only at temperatures below the transition temperature T_c, we let $\Delta(T)$ be described as a function of a reduced temperature t,

$$t = T/T_c, \tag{3}$$

such that the energy gap can be written in terms of the reduced temperature as

$$\Delta(t) = G(t)\,\Delta(0), \tag{4}$$

where $\Delta(0)$ is the energy gap at $T = 0$ K and $G(t)$ is a function that has been tabulated from the BCS theory by Mühlschlegel.[17] For convenience in the computer program, the power-series expansion given by Clem[18] was utilized as

$$G(t) = 1.7367(1-t)^{1/2} \times [1 - 0.4095(1-t) - 0.0626(1-t)^2 + \cdots]. \tag{5}$$

Substituting Eq. (4) into Eq. (2) we get

$$\ln\left(\frac{2\alpha_n(t)}{\alpha_s(t)} - 1\right) = \frac{\Delta(0)}{kT_c}\,\frac{G(t)}{t}. \tag{6}$$

Plotting the ultrasonic attenuation data in the form $\ln[2\alpha_n(t)/\alpha_s(t) - 1]$ as a function of the calculated BCS values of $G(t)/t$, the resulting curve should be linear if the data follow the BCS theory. The slope of this line should be equal to the zero Kelvin superconducting energy gap divided by kT_c.

In order to isolate the nonelectronic attenuation and consequently arrive at a value for the ultrasonic attenuation $\alpha_s(0)$ at $T = 0$ K, $\alpha_s(0)$ was treated as an adjustable parameter which best linearized the experimental data consistent with Eq. (6). The computation of the experimental data was performed on an IBM 360/50 computer facility using the method of least squares where $\alpha_s(0)$ and $\Delta(0)$ were left as adjustable parameters.

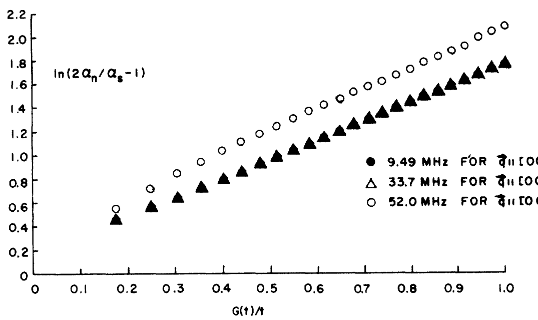

FIG. 5. Experimentally measured values of $\ln(2\alpha_n/\alpha_s-1)$ vs $G(t)/t$ for ultrasound with frequencies 9.49, 33.7, and 52.2 MHz propagated in the [0001] direction.

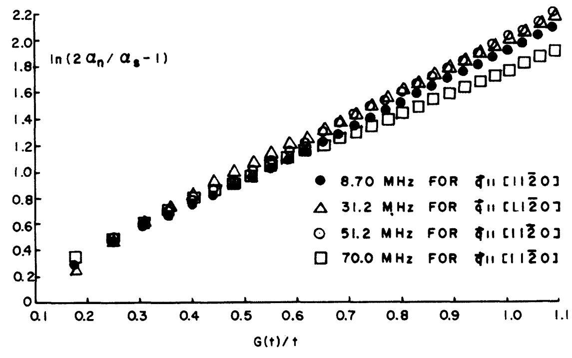

FIG. 7. Experimentally measured values of $\ln(2\alpha_n/\alpha_s-1)$ vs $G(t)/t$ for ultrasound with frequencies of 8.70, 31.2, 51.2, and 70.0 MHz propagated in the [11$\bar{2}$0] direction.

EXPERIMENTAL RESULTS

The results of the computer analysis is divided into three areas corresponding to the three principal axes [0001], [10$\bar{1}$0], and [11$\bar{2}$0]. The data for each of these directions will be presented in graph form plotting $\ln[2\alpha_n(t)/\alpha_s(t)-1]$ vs $G(t)/t$, so that the slope of the line will represent $\Delta(0)/kT_c$.

The results for $\vec{q}\parallel[0001]$, $\vec{q}\parallel[10\bar{1}0]$, and $\vec{q}\parallel[11\bar{2}0]$ are shown in Figs. 5–7, respectively. The energy gaps determined for each direction are given in Table I. Although only one energy gap was found for each direction the results indicate a small degree of anisotropy.

Figure 8 indicates that the limiting ultrasonic attenuation owing to electronic absorption is linear in frequency in accordance with the theory by Pippard.[12] This result corroborates the magnetoacoustic data in showing the ql product to be greater than one.

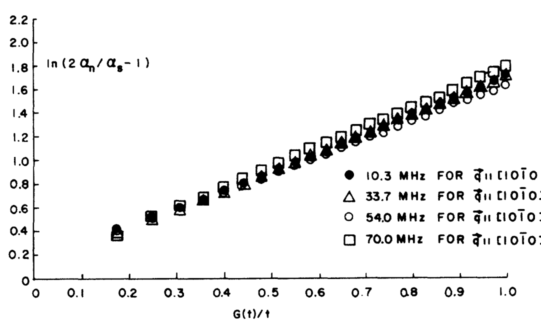

FIG. 6. Experimentally measured values of $\ln(2\alpha_n/\alpha_s-1)$ vs $G(t)/t$ for ultrasound with frequencies of 10.3, 33.7, 54.0, and 70.0 MHz propagated in the [10$\bar{1}$0] direction.

DISCUSSION

The very high purity of this cadmium single crystal has been indicated by the high-field magnetoacoustic data, open orbit resonance studies, and the magnetic susceptibility study. As a result of this high purity, the ql values are much larger than unity for all crystallographic directions and all frequencies utilized in this study.

Results of recent ultrasonic measurements on the crystallographically similar crystal zinc[2] seem to indicate that ultrasonic measurements tend to show multiple energy gaps when the ql is near or below unity. The energy-gap values appear to merge into one limiting energy-gap value when ql becomes much greater than unity. For both cadmium and zinc only one energy gap is detected in each crystallographic direction when ql becomes much greater than one. Comparing this result with the multiband theory of Tang,[19] it would appear that the ultrasonic measurements in the high ql region are actually sampling the energy gaps of electrons in only one band of these metals thereby measuring only one energy gap.

The other ultrasonic study on cadmium[11] has also indicated an anisotropy of the energy gap but only one energy gap was found for each direction studied. The specific-heat data of the Ducla-Soares and Cheeke[1] study have indicated the presence of multiple energy gaps in cadmium. It has been shown that specific-heat data contain contributions to the energy gap from electrons in all populated energy bands. On the other hand, Leibowitz[3] has shown for ultrasound studies that by utilizing the free-electron model and $ql \gtrsim 1$ the "effective zone" specifying which electrons on the Fermi surface will interact with ultrasound can be found from

$$\cos\theta = \vec{v}_s/\vec{v}_f + 1/\vec{q}l\,,$$

where θ indicates the angle between the Fermi

TABLE I. Experimentally measured superconducting transition temperatures, T_c(K), and superconducting energy gap values at 0 K, expressed as $2\Delta(0)/kT_c$, for the [0001], [10$\bar{1}$0], and [11$\bar{2}$0] directions in cadmium.

Source	Method	T_c (K)	$2\Delta(0)/kT_c$ [0001]	[10$\bar{1}$0]	[11$\bar{2}$0]
Ref. 11	ultrasonic atten.	0.520	3.2 ±3%	2.80 ±4%	3.87 ±3%
Present work	ultrasonic atten.	0.503	3.2 ±12%	3.14 ±9%	3.70 ±8%
Ref. 20	hypersonic atten.	0.500	2.48–3.66 ±7%		
Ref. 1	specific heat	...	$2\Delta_1(0)=3.76kT_c \pm 25\%$, $2\Delta_2(0)=2.16kT_c \pm 25\%$		

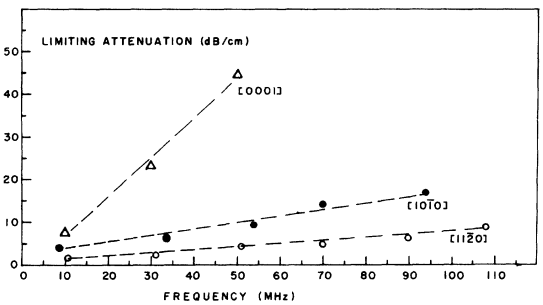

FIG. 8. Experimentally measured limiting ultrasonic attenuation in dB/cm vs frequency of the ultrasound in MHz.

velocity $\vec{v}_f$ and the sound velocity $\vec{v}_s$ parallel to $\vec{q}$. Thus, with our high-purity sample of cadmium we have very high ql values and the "effective zone" is only a very small portion of the Fermi surface. With lower ql values one could sample more of the Fermi surface and possibly detect the multiple gaps reported by Ducla-Soares and Cheeke.

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