ANOMALOUS ULTRASONIC ATTENUATION IN PURE SUPERCONDUCTING Pb

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Recent efforts to determine ultrasonically the energy-gap anisotropy in superconducting Pb have been complicated by the occurrence of amplitude-dependent effects[1] which are caused by dislocation motion.[2] The purpose of this Letter is to report the observation of an apparently unrelated anomaly in the ultrasonic attenuation of compressional waves in high-purity Pb single crystals at low temperatures. Measurements using the Pb crystals reveal a striking frequency dependence of the shape of the normalized ultrasonic attenuation curves in the superconducting state. An explanation is suggested in terms of similar deviations from theory in the thermal conductivity of superconducting Pb.

Ultrasonic attenuation data in superconductors are usually analyzed according to the equation derived in the Bardeen-Cooper-Schrieffer (BCS) theory,[3]

$$\frac{\alpha_s}{\alpha_n}=\frac{2}{\exp[\Delta(T)/kT]+1}, \tag{1}$$

where α_S and α_n are the attenuation coefficients in the superconducting and normal states, respectively, T is the absolute temperature, $2\Delta(T)$ is the temperature-dependent energy gap which has a zero-temperature value of $3.5kT_c$, and T_c is the transition temperature. This equation was derived for an isotropic superconductor with $ql \gg 1$, where q is the magnitude of the sound-wave vector and l is the electron mean free path. Later theoretical investigations[4] have shown that Eq. (1) holds as well when $ql < 1$ so that this result should be independent of ultrasonic frequency and electron mean free path. One anticipated exception to the independence of α_S/α_n on ql is that in the case $ql \gg 1$, any anisotropy of the energy gap in different crystalline directions should appear. Although derived for an isotropic superconductor, Eq. (1) is commonly used with considerable success for such anisotropy determinations by treating the limiting gap $2\Delta(0)$ as a variable parameter.[5] Therefore it might be expected that $2\Delta(0)$ would be isotropic for $ql < 1$ and that any existing anisotropy would appear for $ql > 1$. A frequency dependence of just this kind has been observed by Dobbs and Perz[6] in Nb.

The present experiments were performed using standard single-ended pulse-echo techniques.[7] Results for $\vec{q} \parallel [100]$ are shown in Fig. 1 for ultrasonic frequencies of 11, 71, and 112 Mc/sec along with the BCS curve for $2\Delta(0) = 3.5kT_c$. The data have been analyzed utilizing Eq. (1) in the normal manner except that in the case of the 112-Mc/sec run the zero-point attenuation $\alpha_S(0°K)$ is determined from the essentially flat part of the curve below 6°K. Similar results have been obtained for sound along [110] and at two angles between [100] and [110] in the (110) plane. The data at low frequencies differ very little from the BCS isotropic model, giving values of the zero-temperature energy gap of $(3.5 \pm 0.1)kT_c$ for [100] propagation and $(3.3 \pm 0.1)kT_c$ along [110]. As the frequency increases, however, considerably larger apparent gaps occur until finally

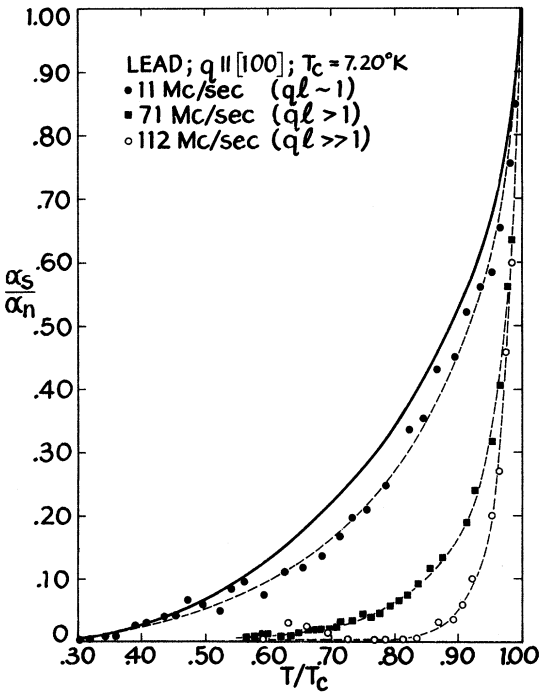

FIG. 1. Normalized compressional wave attenuation in Pb along the [100] direction for ultrasonic frequencies of 11, 71, and 112 Mc/sec. The solid curve represents the BCS expression for a zero-temperature energy gap of $3.5kT_c$.

the attenuation falls off so rapidly below T_c that analysis with the BCS equation does not seem meaningful. Since the ultrasonic frequency is the only variable changed to obtain the three experimental curves in Fig. 1, it is obvious that the shape of the α_s/α_n curves varies as a function of ql. In order to establish approximate values of ql for the various frequencies, several determinations of l between 4.2 and 7.2°K were made using high-field attenuation techniques described earlier.[8] The mean free paths evaluated for $\vec{q} \| [100]$ and $\vec{H} \| [010]$ in this manner utilizing free-electron theory are very approximate but represent an average over essentially the same parts of the Fermi surface responsible for the superconducting attenuation for $\vec{q} \| [100]$. Because of the superconductivity of Pb, it was necessary to use the relative attenuation at the critical field as the comparison base for the calculations of l. The values of l and ql are given in Table I as a function of temperature. It is apparent that the large deviations from BCS behavior occur when the electron mean free path becomes large compared to the sound wavelength.

It appears that the discrepancies observed in the ultrasonic attenuation can be understood relatively well on the basis of similar anomalous behavior seen in the thermal conductivity of the strong-coupling metals Pb and Hg in the superconducting state.[9] It is found that when phonon scattering is predominant, the ratio of the thermal conductivities in the superconducting and normal states, k_s/k_n, falls off much more rapidly just below T_c than is predicted by weak-coupling theory.[10] This anomaly can be explained satisfactorily when the strong-coupling theory[11] of Pb is considered in the derivation of the expression for k_s/k_n.[12] The major factors responsible for the abnormal behavior in Pb as given by Ambegaokar and Woo[12] are (1) the large value of $2\Delta(0) \sim 4.2kT_c$ found experimentally for Pb as contrasted to average values of approximately $3.5kT_c$ for weak-coupling materials; (2) the more rapid decrease of quasiparticle lifetime with phonon frequency in Pb than in weak-coupling materials because of the small density of low frequency phonons in Pb; and (3) the decrease in the ratio of the normal to superconducting quasiparticle lifetime for Pb when T decreases below T_c. These factors, when taken together, account rather well for the experimentally observed thermal conductivity of Pb.

The possible existence of a correlation between ultrasonic attenuation and thermal conductivity at low temperatures has been proposed by Chaudhuri[13] but the suggested relationship $\alpha_s/\alpha_n = k_s/k_n$ seems to be an oversimplification. The present data imply the empirical relationship $\alpha_s/\alpha_n \propto \exp(k_s/k_n)$. In any case, there is an evident similarity between the mechanisms responsible for both ultrasonic attenuation and thermal conductivity. Since the important thermal phonons have wavelengths of about 10^{-7} cm, the condition $ql \gg 1$ is easily satisfied in the pure samples of Pb used in the thermal conductivity experiments. This suggests that the condition for observation of a similar anomaly in ultrasonic attenuation would be $ql \gg 1$, which would explain the frequency dependence of Fig. 1. In conclusion, on the basis of the likeness of the two anomalies, it is felt that the anomalous behavior of α_s/α_n in Pb at high frequency is just a manifestation of the strong-coupling character of Pb and can be accounted for with an analysis similar to that suggested by Ambegaokar and Woo.[12]

Attempts in our laboratory to find a frequency dependence of α_s/α_n in single crystals of Sn and In have shown no such effect, and to our knowledge no frequency dependence similar to the present has been reported in the literature for weak-coupling materials. These facts lend support to the conclusion that this effect probably will be observed only in the

Table I. Approximate mean-free-path values determined from high field attenuation measurements in Pb for $\vec{q}$ along [100] and $\vec{H}$ along [010].

Temperature (°K)	l (cm)	ql(11 Mc/sec)	ql(71 Mc/sec)	ql(112 Mc/sec)
4.2	0.0087	2.8	18	28
5.3	0.0042	1.3	8.0	13
6.0	0.0022	0.7	4.4	7.0
7.2	0.0014	0.4	2.8	4.4

strong-coupling superconductors Pb and Hg.

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SUPERCONDUCTIVITY IN CERAMIC, MIXED TITANATES*

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We have observed superconductivity in semiconducting specimens of the mixed compounds $(Ba_xSr_{1-x})TiO_3$ and $(Ca_ySr_{1-y})TiO_3$, when $x \leq 0.1$ and $y \leq 0.3$. Some of the insulating compounds are ferroelectrics; reduced specimens are semiconductors. This work was prompted by the recent developments concerning superconductivity in semiconductors.[1-3] Cohen's theoretical treatment[1] indicates that the occurrence of superconductivity depends on a strong electron-phonon interaction; both the effective mass m^* of the charge carriers and the dielectric function $\epsilon(\omega, q)$ play an important role. The latter function contains the static dielectric constant ϵ_0 of the lattice (without electrons).

In order to investigate the effect of these parameters on the superconducting transition temperature T_c, it is desirable to change the symmetry or the lattice parameter of the solid. This can be achieved either by pressure (uniaxial or hydrostatic) or by substitution. Replacement of the Sr ion in $SrTiO_3$ by Ba or Ca gives rise to small, but gradual, changes in the lattice constant[4,5]; at the same time the static dielectric constant ϵ_0 is drastically modified.[4,6,7]

Previous work of this laboratory concerned with the semiconductivity and superconductivity of reduced $SrTiO_3$ has been performed on single crystals of the compound.[8,3,9] We realized that studies of the systems $(Ba_xSr_{1-x})TiO_3$ and $(Ca_ySr_{1-y})TiO_3$ would be greatly facilitated if ceramic samples could be used. Initial measurements on reduced ceramic specimens of pure $SrTiO_3$ indicated superconductivity at transition temperatures about equal to those of single crystals of the same carrier concentration.[9,10] Encouraged by this result, we decided to use only ceramic samples in this study of mixed titanates.

Samples were prepared by pressing and were then subjected to a final sintering at ~1650°C. The high sintering temperature is necessary to produce grains larger than the penetration depth.[11] Samples containing 0-20% Ba and 0-100% Ca were prepared and reduced in hydrogen. The Ba and Ca content was checked by determining the lattice parameter[4,5] from x-ray measurements. The substituted amounts deduced from these experiments are shown in Table I beside the nominal values. The composition appeared to be quite homogeneous