AN INVESTIGATION OF ENERGY GAP ANISOTROPY IN SUPERCONDUCTING TIN [1)]

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New experimental data are presented on electronic absorption of ultrasound up to 300 Mc in pure tin single crystals at 1—4° K. The directions of the acoustic wave vectors are perpendicular to all the crystallographic planes of lowest indices. The values thus obtained for the energy gap in the electron spectrum of superconducting tin are used to map the anisotropy of the gap on the Fermi surface. A comparison of all experimental data indicates ~70% anisotropy of the energy gap for this superconductor.

1. INTRODUCTION

ONE of the fundamental characteristics of a superconductor in the BCS microscopic theory is the energy gap in the electron spectrum.[1] This theory accounts satisfactorily for the basic properties of superconductors by using an isotropic model.[2] However, detailed experiments[3-7] indicate an appreciable anisotropy of the energy gap resulting from anisotropy of the Fermi surface and of electron-phonon interaction. According to the theory of anisotropic superconductors developed by Khalatnikov,[8] Pokrovskiĭ,[9,10] and Privorotskiĭ,[11] the energy gaps of real superconductors should exhibit considerable anisotropy.

The investigation of the electronic absorption of ultrasound is one of the most fruitful methods of studying the electron spectrum of metals in both the normal and superconducting states. When $kl \gg 1$ (where k is the acoustic wave vector and l is the electron mean free path), ultrasonic attenuation in superconductors makes it possible to determine the minimum energy gaps on certain regions of the Fermi surface. (This applies, of course, only to pure substances, where the gap anisotropy is not "smeared" by an impurity effect,[12,13] i.e., there is a coherence length $\xi_0 \ll l$.) Unfortunately, the study of ultrasonic attenuation, like other methods, does not determine the largest energy gaps in semiconductors.

The energy spectrum of tin is one of the most throughly investigated among semiconductors. Approximately 30% anisotropy of the energy gap in tin has been indicated by the study of ultrasonic attenuation.[5,6,7] Privorotskiĭ[14] showed in a theoretical analysis based on symmetry considerations that the smallest energy gap of superconducting tin has not yet been determined and that it is not located along one of the principal crystallographic directions. A value of about 50% for the energy gap anisotropy in tin was obtained by one of the present authors from ultrasonic attenuation,[15,16] and by Zavaritskiĭ from the tunnel effect.[17,18]

A number of theoretical studies[9-11,19,20] have pointed to the need of obtaining an experimental "map" of the energy gap anisotropy on the Fermi surface. We have therefore investigated ultrasonic attenuation in superconducting tin for acoustic wave vectors oriented perpendicular to all crystallographic planes of the lowest indices. The existence of detailed data on the energy spectrum of a superconductor can, as we know, further the development of the theory of superconductivity.[13,21,22]

The present article presents results obtained by investigating experimentally the temperature dependence of absorption in several new directions of ultrasonic propagation within superconducting single crystals of tin.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

1. Our samples were spherical single crystals of pure tin grown by the Obreimov-Shubnikov method. The original tin, containing under 10^{-4}% impurities, was characterized by the electrical resistivity ratio $R_{4.2^\circ K}/R_{300^\circ K} \sim 10^{-5}$. The orientations of the single crystals were determined goniometrically from the reflection spot pattern following etching. The samples were cut

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parallel to the required crystallographic planes by the electroerosion method; the surfaces were then polished accurately by hand and the stressed layer was removed by etching. Highly accurate plane parallel surfaces of the tin samples and of the quartz crystals were required for work at high ultrasonic frequencies.

Ultrasonic pulse absorption was measured in the range 100—300 Mc.[23] Rf pulses of a few hundred volts and of 1-μsec duration were fed from the pulse generator to the quartz driver crystal. The X-cut quartz piezoelectric transducers 0.15—0.3 mm thick that were used to excite ultrasound in the samples were themselves excited by the radio pulses to oscillate at higher longitudinal harmonic frequencies. Complex crystal oscillations were then possible in general; however, the temperature dependence of the electronic absorption of high-frequency ultrasound in a superconductor at low temperatures is determined by the minimum energy gap along the corresponding line on the Fermi surface. The transmission of ultrasound from the quartz crystals to the samples, which encounters difficulties at low temperatures, was performed through a thin vacuum-cooked layer of a rubber and vaseline mixture. Ultrasonic vibrations traversing a sample excited the quartz receiver, which then sent pulses to a superheterodyne receiver for amplification and detection. A comparison pulse traveled at the same time, with a regulated delay, from a standard generator tuned to the working frequency, through a continuous attenuator to the receiver. The receiver output was connected to an oscilloscope; the screen displayed the comparison pulse and a series of pulses corresponding to multiple ultrasonic reflection from the parallel surfaces of the sample. The comparison pulse was rendered equal to the investigated signal by means of the continuous attenuator, whose readings indicated relative absorption in the sample.

The evacuation of liquid helium vapor in the cryostat lowered temperatures to the 1—4° K range, in which the temperatures were measured from the pressure of saturated helium vapor and the readings of a carbon thermometer. A detailed description of the apparatus has been given in[24].

3. EXPERIMENTAL RESULTS AND DISCUSSION

The accompanying table gives the investigated orientations of tin single crystals, characterized by the direction of the acoustic wave vector with respect to the crystallographic planes, the highest ultrasonic frequencies used in the measurements,

Orientation of acoustic wave vector k with respect to crystallographic planes of tin	Maximum frequency f, Mc	Electronic absorption in normal state α_n, dB/cm	Minimum energy gap on corresponding Fermi surface belt for tin, $2\Delta_0/kT_C$
$k \perp (101)$	257	58.5	3.9
$k \perp (111)$	252	52.5	4.8
$k \perp (112)$	257	69.5	4.4
$k \perp (211)$	276	65.5	3.9
$k \perp (301)$	257	80.5	4.1
$k \perp (113)$	257	75.0	4.0
$k \perp (311)$	215	66.2	4.3

and the electronic absorption coefficients α_n in the normal state (at the given frequencies). Since nonelectronic ultrasonic attenuation in the given temperature interval is known[23,25] to be independent of temperature, α_n was defined as the difference between absorption at the superconducting transition temperature and at 1° K. (It is noteworthy that the electronic absorption was tens of times greater than the neglected non-temperature-dependent fraction of ultrasonic absorption associated with scattering by lattice defects, and with losses in the quartz crystals, in the layer be-

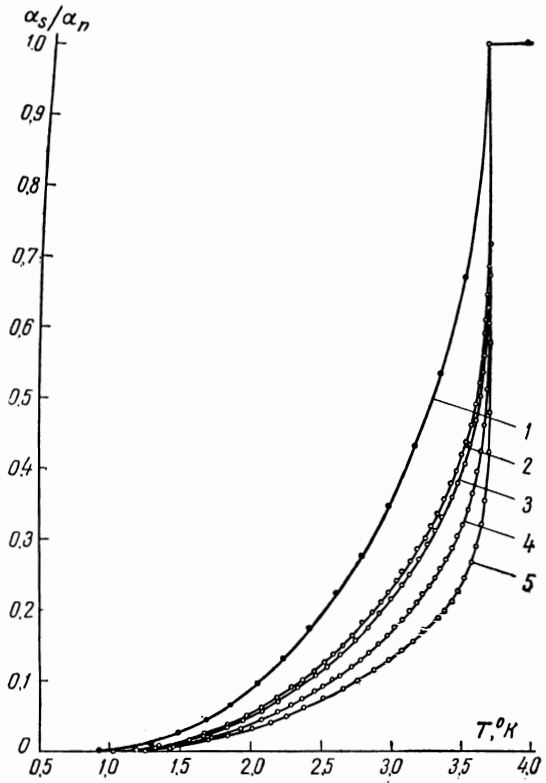

FIG. 1. Ratio of ultrasonic attenuation coefficients in superconducting and normal tin versus temperature. 1 – isotropic model; [1] 2 – acoustic wave vector $k \perp (211)$, ultrasonic frequency f = 276 Mc; 3 – $k \perp (113)$, f = 257 Mc; 4 – $k \perp (311)$, f = 215 Mc; 5 – $k \perp (112)$, f = 257 Mc.

tween samples and quartz crystals etc.) As expected, since $kl \gg 1$, the α_n were linearly dependent on the ultrasonic frequency.

Figure 1 shows the experimental data regarding the temperature dependence of the ratio α_s/α_n between the attenuation coefficients of superconducting and normal tin, for the newly investigated directions of ultrasonic propagation, along with the theoretical curve for an isotropic gap of 3.53 kT_c.[1]

According to recent theoretical studies[10,11] the temperature dependence of electronic attenuation of ultrasound in superconductors at low temperatures is associated with the minimum energy gap on a Fermi surface belt satisfying the condition $\mathbf{k} \cdot \mathbf{v}_F = 0$, where $\mathbf{k}$ is the acoustic wave vector and $\mathbf{v}_F$ is the electron velocity on the Fermi surface.

The curves in Fig. 1 were extrapolated to 0° K (assuming the absence of electronic absorption at 0° K) to obtain a straight low-temperature segment of the curve for log α_s versus T_c/T.[7] (Inaccurate extrapolation, changing the value of the gap by $\pm 0.1\ kT_c$, produces an appreciable departure from the straight line.) The extrapolated attenuation coefficients have been denoted by α_s^* and α_n^*.

Figure 2 is a semilogarithmic plot of

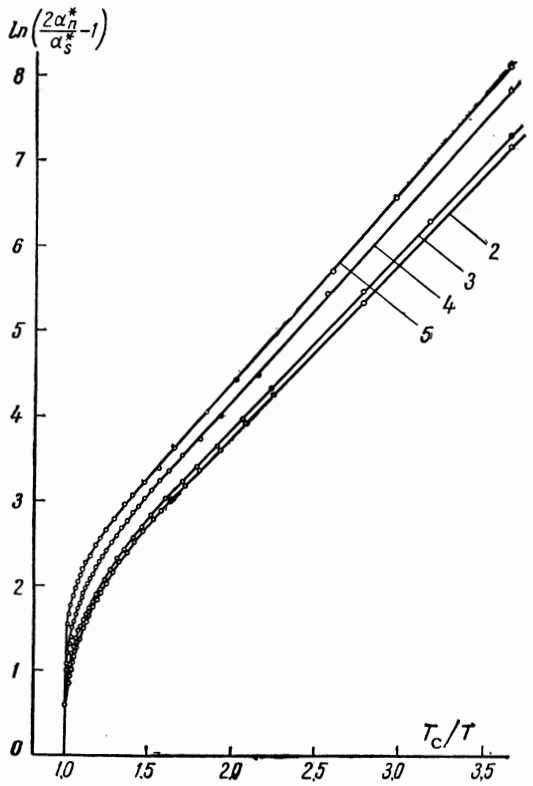

FIG. 2. ln $(2\alpha_n^*/\alpha_s^* - 1)$ versus T_c/T for ultrasound in tin. Curve 2 – $k \perp (211)$; 3 – $k \perp (113)$; 4 – $k \perp (311)$; 5 – $k \perp (112)$.

$(2\alpha_n^*/\alpha_s^* - 1)$ versus T_c/T. Here the slope at low temperatures, according to the BCS formula:[1]

$$\alpha_s^*/\alpha_n^* = 2[\exp(\Delta/kT) + 1]^{-1}$$

can be used to determine the minimum energy gaps at 0° K on the corresponding Fermi surface belts. (We note that with each calculation $[\ln(2\alpha_n^*/\alpha_s^* - 1]^{-1}$ versus $(T_c/T)^{-1}$ was plotted; this provided an additional control of the extrapolation, because the straight segment of this plot should pass through the coordinate origin.)

For the direction of the wave vector k perpendicular to the (112) plane we obtain $2\Delta_0/kT_c = 4.4$. Other results are: for $k \perp (211)$, ~3.9; for $k \perp (113)$, ~4.0; for $k \perp (311)$ ~ 4.3. The error of these values, taking into account the possible error in the orientation of the acoustic wave vector with respect to the crystallographic planes, is at most 5%. The accompanying table gives all our experimental values of the energy gaps in superconducting tin at 0° K.

The following appropriate comment can be made regarding the temperature dependence of ultrasonic attenuation in superconductors. Because of the observed deviation of the temperature dependence of the energy gap at high temperatures from the BCS prediction,[1] attempts have been made to relate this discrepancy to the ultrasonic attenuation contribution near T_c of several gaps on the Fermi surface,[26,15,27] and to the finite lifetimes of quasiparticles.[28,29] It does not seem possible to explain the discrepancy uniquely on the basis of the ultrasonic attenuation data (with the phonon energy $\hbar\omega \ll \Delta$).

Figure 3 is an equidistant conic projection of the spherical region containing the investigated orientations of the wave vector k with respect to crystallographic directions in tin. (The data were obtained from other ultrasonic investigations[5-7,16] as well as the present work.) The point $(\theta, \varphi) \sim (90°, 0°)$ corresponds to the direction of

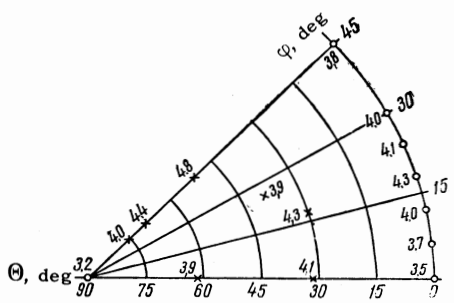

FIG. 3. Investigated orientations of acoustic wave vector k with respect to crystallographic directions in tin (equidistant conic projection of a sphere). × – present investigation; o – [5-7].

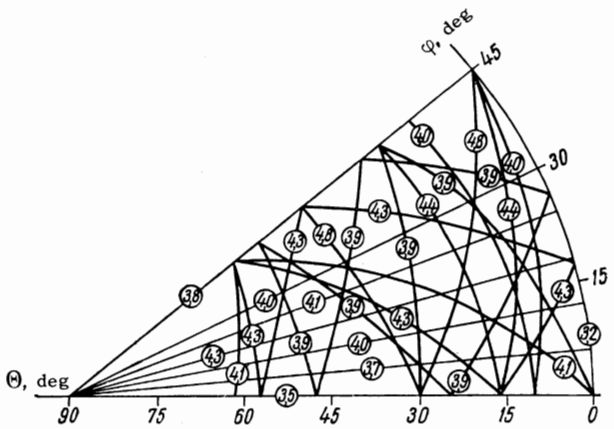

FIG. 4. Projections of the lines $\mathbf{k}\cdot\mathbf{v}_F = 0$ on a unit sphere for the investigated directions of the wave vector k (equidistant conic projection). Heavy lines – present investigation; thin lines – [5-7]. The circles contain values of the minimum energy gap $2\Delta_0/kT_C$ on the corresponding lines of the Fermi surface.

the fourfold [001] axis of tin, (0°, 0°) corresponds to the [100] twofold axis, and (0°, 45°) to the plane diagonal [110]. Each direction of k is characterized by a minimum energy gap in the electron spectrum of superconducting tin for the corresponding line on the Fermi surface. (These values of $2\Delta_0/kT_C$ are shown in Fig. 3.)

If each point on the Fermi surface is associated with a point on a unit sphere such that the normals at these points are parallel, a large circle on the unit sphere will correspond to each line $\mathbf{k}\cdot\mathbf{v}_F = 0$ on the Fermi surface. Figure 4 shows these circles for all the investigated directions of the wave vector k. The anisotropy of the energy gap is seen to be complex. Unfortunately, the Fermi surface of tin is multiply connected and it is not clear to which part the measured values belong; furthermore, the energy gap is probably anisotropic on each region and its values are continuous. Further investigations, both experimental and theoretical, will evidently enable us to determine the local relationship between the Fermi surface and the energy gap of a superconductor.

We note the following information regarding the energy gap anisotropy of superconducting tin: 1) The minimum energy gap ($3.2\,kT_C$) determined by the ultrasonic method, is probably not the absolute minimum (from symmetry considerations); 2) the maximum energy gap ($4.8\,kT_C$) obtained using the same technique is not the highest value, since the latter cannot be determined (it does not appear in the formula for the attenuation coefficient); 3) the smallest value ($2.7\,kT_C$) of the energy gap was obtained by Zavaritskiĭ[18] using the tunnel effect.[2)]

All the foregoing discussion indicates 70% anisotropy of the energy gap in superconducting tin. Data regarding the surface resistance of superconducting tin[27,33] can also be treated assuming a highly anisotropic energy gap.

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152