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GAP ANISOTROPY IN THE ENERGY SPECTRUM OF SUPERCONDUCTORS

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I. FEATURES OF ENERGY SPECTRUM OF SUPERCONDUCTORS

THE microscopic theory of Bardeen, Cooper, and Schrieffer^[1] and of Bogolyubov^[2] explained superconductivity as being the result of the occurrence of a region of forbidden electronic states in the energy spectrum of the metal near the Fermi surface, this being connected with the appearance in the superconductor of electron pairs with opposite momenta and spins at a temperature below the transition temperature. Pair production is the result of the exchange of virtual phonons and occurs when the electron attraction connected with this electron-phonon interaction^[3] prevails over the Coulomb repulsion. The energy spectrum of the electrons in the metal is changed during the course of the superconducting transition in such a way, that a gap $2\Delta(T)$ appears in the electron spectrum of the superconductor; this gap depends in a special manner on the temperature (Fig. 1). The binding energy of a pair of quasiparticles at $T = 0^{\circ} K$ is equal to

$$2\Delta(0) \approx 4\Theta_D \exp\left[-\frac{1}{N(0)V}\right]$$

where Θ_D is the Debye temperature of the metal, N(0) is the density of the electron states on the Fermi surface in the normal state of the metal, and V is the matrix element of the quasiparticle interaction. For the superconductor to be excited at 0°K, it is necessary to break a pair of quasiparticles, and the minimum energy required for this is $2\Delta(0)$. In a superconductor, the energy of quasiparticles that obey Fermi statistics is E_q = $(\epsilon_q^2 + \Delta_q^2)^{1/2}$, where ϵ_q is the quasiparticle energy in the normal metal, measured from the Fermi level, and Δ_q is a parameter of the energy gap and depends in the general case on the direction of the quasiparticle wave vector **q** and on ϵ_q . Figure 2 shows the dependence of E_q in a superconducting state of a metal on the wave vector **q**. The density of the single-particle states in the superconductor is determined by the following relation:

$$\rho_s = N(0) E \left(\epsilon + \Delta_{\min} \frac{\partial \Delta_{\min}}{\partial \epsilon} \right)^{-1}$$

if $\Delta = \Delta(\epsilon_q)$, where Δ_{\min} is the smallest value of Δ_q .

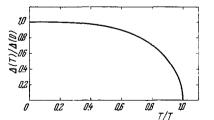
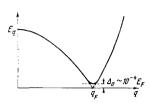


FIG. 1. Theoretical temperature dependence of the energy gap in the spectrum of a superconductor.

FIG. 2. Quasiparticle energy E_q in a superconductor vs. the quasiparticle wave vector q [⁵].



For an isotropic model, provided Δ does not depend on ϵ , the density of the single-particle states is $N(0)E/(E^2 - \Delta^2)^{1/2}$. The number of elementary excitations in the superconductor is determined by the Fermi distribution function $f(E) = [\exp(E/k_BT) + 1]^{-1}$, where k_B is Boltzmann's constant. At low temperatures, when $k_BT < \Delta(0)$, the number of elementary excitations that can accept energy from the outside is approximately proportional to exp $[-\Delta(0)/k_BT]$, making it possible to find the magnitude of the energy gap by experimentally investigating many excitation-dependent physical properties of the superconductor.

We note that the main properties of superconductors can be described by the simplest idealized model of a superconducting metal with an isotropic single-connected Fermi surface and an isotropic energy gap that does not depend on the wave vector q. However, many phenomena in a superconductor ("anomalies" of the low-temperature specific heat, anisotropy absorption of ultrasound and of electromagnetic oscillations, shift of T_c under the influence of an impurity, etc.) cannot be explained without taking into account the anisotropy of the physical properties and parameters of the metal. The point is that real metals are anisotropic and have in the normal state an intricate and multiply-connected Fermi surface and a complicated distribution of the electron velocities $v_{\mathbf{F}}$ on this surface. In such a case, the value of $\Delta_{\mathbf{q}}$ should depend not only on the energy ϵ_q and on the number of the branch (cavity) of the Fermi surface, but also on the direction of the wave vector of the quasiparticle, so that in a superconductor with a multiply-connected Fermi surface the corresponding values of the energy gaps are different.* In addition, in an anisotropic superconductor, the matrix element of the interaction of the quasiparticles $V_{\mathbf{q}\mathbf{q}'}$ is also an anisotropic quantity. It is precisely the combination of these circumstances which causes certain deviations from the predictions of the isotropic theory to be observed in a number of precise experiments, which will be described below.

It is natural for the additional singularity of the spectrum and in the energy of the gaps superconductors (see, for example, [6, 11-22]) to be of interest in the

^{*} The theory of anisotropic superconductors [⁶], in which account is taken of the overlap of the energy bands of the metal, shows that the gap vanishes at $T = T_c$ simultaneously on the entire Fermi surface (see also [⁷,¹⁰].

study of the structure of the Fermi surface of metals (one of the central problems of solid state physics); however, no detailed quantitative data on the gap anisotropy have been obtained as yet. The presently developing theory makes use of the following approaches to the solution of this complicated problem. First, it is possible to find the general laws common to all anisotropic superconductors, regardless of the origin and character of the gap anisotropy. In this manner, a number of general inequalities were obtained by Pokrovskii for the case of weak electron-phonon coupling.^[6] For example, whereas the isotropic theory of superconductivity gives a simple connection between the temperature of the superconducting transition and the magnitude of the gap at 0°K, namely $2\Delta(0) = 3.5 k_{\rm B} T_{\rm C}$ independently of the type of metal, it follows from Pokrovskii's theory

that the smallest gap equals $2\Delta_{\min}^{abs} < 3.5 k_{\rm B} T_{c}$.^[9] Another possible attempt at solving the problem is

to assume a concrete model of the gap anisotropy, as was done by Geilikman and Kresin, ^[14] by Markowitz and Kadanoff, ^[19] and by Clem, ^[22] and to calculate the gap. Geilikman and Kresin investigated the influence of the anisotropy of the shape of the Fermi surface on the anisotropy of the energy gap (in the case of an isotropic phonon distribution). They considered two models of the Fermi surface, closed ellipsoidal and open cylindrical, and showed that a considerable gap anisotropy results from any model, depending on the directions in the momentum space.

Finally, the third way, that of solving the problem of numerically under certain simplifying assumptions for at least one metal, was used by Bennett.^[15] In determining the gap anisotropy in superconducting lead, Bennett assumed the main source of the anisotropy to be the real phonon spectrum of this metal. He used the assumption that the electron-phonon interaction is constant, and that the strong coupling between the electrons in the lead causes the interaction to be effective in a wide energy layer near the Fermi surface. Since the latter causes a certain isotropization of the gap, Bennett introduces the assumption of a relatively weak gap anisotropy; this enabled him to carry the calculation through to conclusion. It turned out that at the same appreciable anisotropy of the gap on each of the cavities of the Fermi surface, the values of the gap in the minimal, maximal, and saddle points of different cavities were very close, so that there is practically no difference between these values for different cavities.* The regions of the Fermi surface near the boundaries of the Brillouin zone, as noted by Bennett, can have several different values of the gap and of its anisotropy, whereas the influence of the anisotropy of the electron-phonon interaction parameter, which was not introduced in the calculation, should add up with the obtained gap anisotropy on the entire Fermi surface.

For tin, likewise, Bennett obtained by calculation, under the same assumptions, approximately the same complicated picture of the anisotropy of the gap. However, the results are only qualitative, owing to an annoying error which has crept in the very beginning of the calculations: the smallest energy gap in the spectrum of superconducting tin was assumed to equal $3.05 \, k_B T_c$ in the direction of the two-fold axis, whereas the smallest gap in this superconductor, according to all data, is not oriented along the principal axes and apparently amounts to $2.7 \, k_B T_c$ (see the Appendix). In addition, inasmuch as lead is a superconductor with weak coupling, the entire assumed calculation scheme is less justified for this metal.

It is interesting to note that the temperature dependence of the effective interaction of the quasiparticles $V_{qq'}$ greatly influences the magnitude of the energy gap: a 5% variation of $V_{qq'}$ suffices to produce a change of the gap in the range $3.0 < 2\Delta/k_{\rm B}T_{\rm C} < 4.2$, depending on the momentum-space region that determines the interaction.^[233]

From the experimental point of view, several investigation methods have been developed and are extensively used at present; these yielded (and much less frequently—permitted a detailed study of) the anisotropy of the gap in the spectrum of superconductors. Among the most widely used indirect methods are investigations of the thermodynamic properties (heat capacity, thermal conductivity, critical magnetic field, variation of T_c under the influence of an impurity) and the study of the absorption of ultrasonic oscillations. Among the direct methods are investigations of the interaction of highfrequency electromagnetic oscillations with superconductors, and the tunnel effect.

The gap anisotropy, generally speaking, exerts different influences on the physical properties of superconductors.^[22] This influence on the thermodynamic properties near Tc turns out to be very weak, although the gap anisotropy a itself can be appreciable, and consequently these properties are determined by the gap $\Delta_{\mathbf{q}}$ averaged over all the directions, so that the magnitude of the mean-square gap anisotropy $\langle a^2 \rangle$ = $(\Delta_q - \overline{\Delta}_q)^2 / \overline{\Delta}_q^2$ characterizing the superconductor is approximately equal to 0.01 for most pure superconductors. On the other hand, a number of physical properties (including, above all, the absorption of ultrasound and the tunnel effect), which are determined by electrons gathered in one manner or another from definite regions of the Fermi surface, make it possible to investigate the orientation dependence of the gap and by the same token reflect the gap anisotropy a of the superconductor.

II. EXPERIMENTAL INVESTIGATIONS OF THE ANISOTROPY OF THE ENERGY GAP IN THE SPECTRUM OF SUPERCONDUCTORS

1. Electron Specific Heat

The microscopic theory of superconductivity yields the following expression for the electronic specific heat of an isotropic superconductor:

$$\frac{c_{es}}{\gamma T_{c}} = \frac{3}{2\pi^{2}} \left(\frac{\Delta}{k_{B}T_{c}}\right)^{3} \left(\frac{T_{c}}{T}\right)^{2} \left[3K_{1}\left(\frac{\Delta}{k_{B}T}\right) + K_{3}\left(\frac{\Delta}{k_{B}T}\right)\right],$$

where γT_c is the electronic specific heat of the metal in the normal state at $T = T_c$, and K_1 and K_3 are Bes-

^{*} The values of the gap (in meV) at the minimum is: band II (holes) -2.66 and 2.65, band III (electrons) -2.60 and 2.55; at the maximum: band II -2.86 and 2.77, band III -2.76; at the saddle points: band II -2.70 and 2.66, band III -2.71, 2.65, and 2.60.

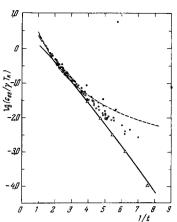
sel functions of the second kind.^[23] Calculations show that this expression can be reduced to the form $c_{es}/\gamma T_c$ $\simeq a \exp{(-bT_c/T)}$, and in the temperature interval 2.5 $< T_c/T < 6$ we have a = 8.5 and b = 1.44, whereas at temperatures $7 < T_c/T < 10$ we have a = 26 and b = 1.62.^[24] In the temperature region $T_c/T > 10$ we get the following relation:^[25]

$$\frac{c_{es}}{\gamma T_{c}} = 2.37 \left(\frac{T_{c}}{T}\right)^{3/2} \exp\left(-\frac{1.76T_{c}}{T}\right).$$

It is interesting to note that even before the appearance of the modern theory of superconductivity, Koppe obtained, [26] within the framework of the Heisenberg twofluid theory, ^[27] an approximately exponential temperature dependence of the thermal properties of superconductors. These were the results with which comparisons were made of low-temperature measurements of the thermal conductivity of Sn by Goodman,^[28] of the specific heat of Nb by Brown et al., and of the specific heat of V by Corak et al.^[30] It is probable that the study of V revealed experimentally, for the first time, the exponential temperature dependence of the specific heat, leading to the prediction of a gap $2\Delta \sim k_{\rm B} T_{\rm c}^{~\rm I~31}$ in the spectrum of this superconductor, just as in the study of the thermal conductivity of Sn by Goodman.^[28] On going to lower temperatures, the number of superconductors investigated increased (Table I), and following the appearance of the microscopic theory of supercon-ductivity, its conclusions were compared^[7, 32, 24, 33] with the results of the earlier experiments.

The experiments have shown that in certain superconductors (which included until recently A1,^[34, 35, 36] Zn,^[35, 37, 38] and Sn^[34, 39]) the temperature dependence of the electronic specific heat deviates at low temperatures from the predictions of the isotropic model (Fig. 3). A theoretical analysis by Abrikosov and Khalatnikov^[7] and by Cooper^[33] has shown that one of the most probable causes of this anomaly may be the anisotropy of the gaps of the superconductors. The point is that at very low temperatures their thermal properties are determined by the value of the smallest gap in the energy spectrum $2\Delta_{\min}^{abs}$, while at intermediate temperatures it is determined by a certain average value over the entire Fermi surface.*

In the general case it is impossible to determine from specific-heat measurements the direction or the section of the Fermi surface on which the experimentally obtained energy gap is located. However, an analysis of its possible anisotropy, made by Zavaritskii^[40] using the anomalies of the specific heat, has shown that FIG. 3. Temperature dependence of the electronic specific heat of aluminum, zinc, and vanadium and the theoretical dependences as obtained with the isotropic and with the two-fluid models of superconductivity [²⁴] solid line __BCS, dashed ---- $3(T_C/T)^2$, $\bigcirc = Al$, $\spadesuit = Zn$, $\triangle = V$.



this possible anisotropy should be appreciable (~30% for Zn and ~15% for Sn). This explanation of the lowtemperature specific heat may be confirmed by the results of experiments performed on aluminum by Geiser and Goodman^[41] and on lead by Keesom and Van Hoeven^[42] (in both cases they investigated pure metals and

Table I. Energy gap $2\Delta/k_{\rm B}T_{\rm C}$ at 0°K and its anisotropy in the spectrum of superconductors as obtained by measuring the electronic specific heat.

and s	conductor, purity, ingle-crystal status of the sample	Lowest tem- perature of investigation	Temperature dependence of the electronic specific heat $c_{es} \sim a \exp(-bT_c/T)$	$2\Delta/k_{\rm B}T_{\rm C}$, Gap anisotropy - α
Al:	34	0,15	a = 6.9, b = 1.3; deviation from exponential at T _c /T > 5	ahe
	99,99%, polycrystal ³⁵	0,2	a = 8,2. $b = 1,2$; deviation from exponential at $T_c/T > 5$	$2\Delta_{\min}^{abs}/k_BT_c = 3,12$ ⁴⁰ . Gap anisotropic
	99.998% 36	0,1	a = 7, 1, b = 1.34; deviation from exponential at T _c /T > 4	$2\Delta/k_{\rm B}T_{\rm c}=3,3$
	99,997% 41	$T_{\rm c}/T \leqslant 6$	a = 4.8, b = 0.82; deviation from exponential at low temperatures	$\begin{array}{l} 2\Delta_{\min}^{abs}/k_{\rm B}T_{\rm c}\sim2;\\ a\sim25\%, \qquad \text{impurity}\\ \text{decreases a} \end{array}$
Cd:	99,999%, single crystal ⁵⁰	0,1	a = 6, 2, b = 1.26	$2\Delta/k_{\rm B}T_{\rm c}=3.1$
Ga:	99,999% ³⁸ 99,999% ⁵⁰	0,35 0,1	a = 7, b = 1,35 a = 7,46, b = 1.39; no deviation from exponential	$2\Delta/k_{\rm B}T_{\rm c}=3.4$
Hg:	99.996%, polycrystal ⁵²	0,35	At $T_c/T < 4$ $a = 15 \pm 1$ $b = 1.64 \pm 0.1$	$2\Delta/k_{\rm B}T_{\rm c}=3.98$
In:	53 48 99.999%, single crystal ⁴⁹	1,6 0,4 0,1	a = 9.6, b = 1.6 b = 1.6	By analysis [⁵⁴] $2\Delta/k_BT_c = 3.3 - 3.7$ dependent on the interpretation
	xture of 95% hex. 5% fcc phases [⁵⁵]	2	a = 7.8, b = 1,56	$2\Delta/k_{\rm B}T_{\rm c}=3,6$
Mo:	>99.999% 56	$ T_{c}/T < 2.4$		$\begin{array}{ c c c } 2\Delta/k_{\rm B}T_{\rm c} = 3.4 \pm 0.15.\\ \hline \text{Possible anisotropy} \end{array}$
Nb:	⁵⁷ > 99,8%, single crystal ⁵⁸ 99,9%, single crystal ⁴⁵	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	a = 10, b = 1.63 a = 8.21, b = 1.52; deviation from exponential at T _C /T > 6 Superposition of two exponentials with a' = 7 and b' = 1.46 (T _C /T > 6) and a'' = 0.0065, b'' = 0.12 (T _C /T > 14).	$2\Delta/k_{\rm B}T_{\rm c} = 3.7$ $2\Delta'/k_{\rm B}T_{\rm c} \sim 3.5 \text{ and}$ $2\Delta'/k_{\rm B}T_{\rm c} \sim 0.3$

^{*} We recall that all the thermodynamic properties of superconductors near T_c are insensitive to the gap anisotropy (the errors are of the order of $\sim < a^2 > \sim 0.01$), because these properties are determined by the probability of quasiparticle excitation. At energies $k_BT \sim 2\Delta(T)$ this probability is appreciable for all orientations in momentum space. In addition, the strong electron-phonon coupling and the gap anisotropy affect the thermodynamic properties in opposite directions (for example, the strong coupling uncreases the gap $2\Delta(O)/k_BT_c$, causes a jump of the specific heat $\Delta c/\gamma T_c$, and leads to a temperature dependence of the critical magnetic field H_c/H_o , whereas the gap anisotropy decreases these quantities.) Since both effects are present in one form or another in most pure superconductors the interpretation of the experiment is a complicated matter (see, for example, [²²]).

and s	rconductor, purity, single-crystal status of the sample	Lowest tem- perature of investigation	Temperature dependence of the electronic specific heat $c_{es} \sim a \exp(-bT_c/T)$	$2\Delta/k_{\rm B}T_{\rm c},$ Gap anisotropy- $lpha$
Pb:	$>$ 99,999%, single crystal 42	0.3	At $T_c/T > 5$, superposition of two exponentials with a' = 10.7 and a'' = 0.1	$\frac{2\Delta'/k_{\rm B}T_{\rm c}}{2\Delta''/k_{\rm B}T_{\rm c}} \sim 4.1 \text{ m}$
Re:	99.98% 59	1.2	a = 11.6, b = 1.64	$2\Delta/k_{\rm B}T_{\rm c}\sim 4$
Sn:	34	0.15	deviation from exponential at $T_c/T > 5$	
	99,998%, single crystal ³⁹	0,2	b = 1,35; deviation from exponential at T _c /T > 5	$\begin{array}{l} 2\Delta/k_{\rm B}T_{\rm c}\approx 3.6,\\ 2\Delta_{\rm min}^{\rm abs}/k_{\rm B}T_{\rm c}=3.2,\\ a\sim 15\%^{40} \end{array}$
	99,999%, polycrystal ⁴⁸	0,4	a = 7,63, b = 1,41; no deviation from expo- nentials at low temperatures	$2\Delta/k_{\rm B}T_{\rm c}=3.43$
	99,999%, polycrystal ⁴⁹	$T_{\mathrm{R}}/T < 9$	a = 7.85, b = 1.42; no deviation from exponen- tials at low temperatures	$2\Delta/k_{\rm B}T_{\rm c}=3.45$
Ta:	< 99,9% 60	1,7	b = 1,49	$\frac{2\Delta/k_{\rm B}T_{\rm C}}{\rm ysis} \sim 3.5$ by anal-
	< 99,9% 61	1.3	a = 10, b = 1.5 as estimated in [³⁸]	
	45	0,35	Superposition of two exponentials	
Tl:	99.999% 54	1.1	a = 5.8, b = 1.3	
	99,991% 52	0.35	a = 9, b = 1.52 at $T_c/T < 4$	$2\Delta/k_{\rm B}T_{\rm c}=3,67$
V:	~ 99.8% 31	1.2	a = 9.17, b = 1.5	
	> 99.9% 62	0,8	a = 7, b = 1.34	$2\Delta/k_{\rm B}T_{\rm c} = 3.3$
	45	0,35	Superpostion of two exponentials	
	> 99.99% sin-	0,6	At low temperatures, a term c_{es} linear in the tem-	$2\Delta'/k_{\rm B}T_{\rm c}=3.2\div3.5,$
	gle crystal , $R_{290^{\circ} \rm K}/R_{4^{\circ} \rm K} = r = 140^{47}$		perature appears	$2\Delta''/k_{\rm B}T_c \sim 0.1$
Zn:	99,9999%, sin- gle crystal ³⁵	0.2	a = 2,3, b = 1.03	$\frac{2\Delta/k_{\mathbf{B}}T_{\mathbf{c}}\approx 3.5,}{2\Delta_{\min}^{\min}/k_{\mathbf{B}}T_{\mathbf{c}}\approx 2.7,}$ $a\sim 30\%^{-40}$
	99,999% 38	0.35	a = 6.4, b = 1.27	ω - 0070 ···
	single crystal ³⁷	0,15	a = 5.8, b = 1.22; deviation from exponential at T _C /T >4	

Table I (cont'd.)

their alloys with nonmagnetic impurities). If the deviation of the low-temperature specific heat of the superconductor from the theoretical predictions is actually connected with the anisotropy of the gap, then introduction of the impurity should, in accordance with the Anderson theory of "dirty superconductors,^[21] smooth out the anisotropy of the gap and lead to agreement with the theory. Effects of this type were possibly observed in aluminum and lead (Fig. 4), although no exact quantitative agreement with theory was obtained.^[43] According to these data the anisotropy of the gap of aluminum is $\sim 25\%$, and the temperature dependence of the specific heat of Pb can be represented in the form of two components with gap values $\sim 4.1 k_B T_c$ and $\sim 1.1 k_B T_c$.* An investigation of sufficiently pure Nb, Z, and Pa has also shown that temperature dependence of the specific

heat can be represented by a superposition of two exponentials with gaps $\sim 3.5 \, k_B T_c$ and $\sim 0.3 \, k_B T_c$ (for the case of Nb).^[45] The hypothesis advanced by Phillips and co-workers, namely that the specific heat is influenced by two gaps that are due to the overlap of the s and d bands on the Fermi surfaces of these transition metals, was confirmed theoretically in ^[46]. Subsequent investigations have revealed that in order to describe the temperature dependence of the specific heat of V it is necessary to assume that the large gap is itself anisotrpic ((3.2–3.5) $k_B T_c$).^[47]

The foregoing confirmation of the probable connection between the gap anisotropy of a superconductor and the anomaly of its low-temperature specific heat is not superfluous, because in recent papers by Keeson, Phillips, and co-workers, devoted to the study of Sn, $^{[\,48,\,49]}$ which is particularly convenient for investigations because of its high T_c and Θ_D , as well as of Ga, ^[50] revealed no deviation of the specific heat from an exponential variation, up to temperatures $T_c/T \simeq 9$ (for Sn, Fig. 5) and $T_c/T \simeq 5.5$ (for Ga).* In spite of the fact that the calorimetry was improved in these experiments (low temperatures were obtained by pumping off saturated He³ vapor, and not by adiabatic demagnetization), it is hardly possible to agree with Phillips (see the proceedings of the calorimetric conference [51], that the gap $2\Delta_{\min}^{abs}$ in these superconductors (and in Al and Pb) does not appear at all; it is more likely that the deviations of the specific heat are weaker than customarily assumed. Comparison of the experimental data of Keesom and Phillips and their co-workers^[48,49] with Clem's theory^[22] shows, in our opinion, that in Sn

2. Electronic Thermal Conductivity

we have $\langle a^2 \rangle \sim 0.03$.

The question of the thermal conductivity of superconductors was considered by Biondi and co-workers^[32] and by Douglass and Falicov.^[25] In spite of the fact

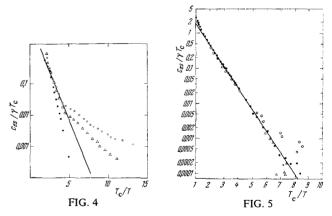


FIG. 4. Temperature dependence of the electronic specific heat of superconducting lead and of its alloy with indium [⁴²]. Line – BCS, O – pure PB, Δ – Pb + 1.76% In, \bullet – Pb + 5.93% In.

FIG. 5. Temperature dependence of the electronic specific heat of tin in the superconducting state $(\bullet, \Delta - [^{48}]; \bigcirc -data$ of Goodman $[^{34}], [^{48}].$

^{*} Unsuccessful attempts were made later to attribute the singularities of the specific heat of Pb to the temperature dependence of the electron effective mass brought about by the strong electron-phonon interaction [⁴⁴].

^{*} According to preliminary data of Phillips, there is no anomaly of the specific heat in aluminum [⁵¹].

that the theoretically investigated mechanisms of the electronic specific heat in scattering of electrons by impurities^[63,64] and by phonons^[65,66] are in fair agreement with certain experiments, this question has not been fully resolved.^[4] The point is that, besides the electrons, the thermal conductivity is governed also by the lattice, and each of these contributions is limited by different scattering mechanisms (this is precisely why in most experiments deviations are observed in the temperature dependence of the thermal conductivity from the exponential low). Nonetheless, for a number of superconductors (Table II) an exponential temperature dependence of the electronic specific heat was actually observed in a certain temperature interval (such a regularity was first observed by Goodman^[28] for Sn).

Further investigations by Zavaritskii have established a sharp anisotropy of the temperature dependence of the electronic specific heat of single crystals of $Ga,^{[67]}$ and Zn and $Cd^{[68]}$ (Fig. 6). A comparison with Khalatnikov's theory, ^[11] which takes into account the influence of the gap anisotropy on the thermal conductivity, has shown that the gap anisotropy in Ga and Zn

Table II. Energy gap $2\Delta/k_BT_c$ at 0°K and its anisotropy in the superconductor spectrum as determined by measuring the electronic specific heat.

and	erconductor, purity, single-crystal status of sample	Lowest inves- tigated tem- perature, °K	Temperature dependence of electronic specific heat $\kappa_{es} \sim \exp(-\beta T_c/T)$	$2\Delta/k_{\rm B}T_{\rm C}$, anisotropy of gap - α
Al:	99,99% 35	0,15	$\beta = 1.5$	$2\Delta/k_{\rm B}T_{\rm c} = 3.3 \pm 0.1$
	very pure 71	0.32	Impurity does not change the temperature dependence	$2\Delta/k_{\rm B}T_{\rm c} = 3.5$
Cd:	single crystal	0,1	Anisotropic temperature dependence	$\frac{2\Delta_{\min}^{\mathrm{afc}}/k_{\mathrm{B}}T_{\mathrm{c}}=2,7,}{\mathrm{anisotropic gap}}$
	75	0,3		$2\Delta/k_{\rm B}T_{\rm c}=3.4$
Ga:	99.999 и 99,9%, single crystal ⁶⁷	0.2	At $T_c/T < 4$ and $1.2 \le \beta \le 1.5$, depending on the orientation; the impurity does not change the temperature dependence	$2\Delta_{\min}^{a6c}/k_{B}T_{c} = 2.6,$ $\cdot 2\Delta_{cp}/k_{B}T_{c} = 3.5,$ $a \sim 30\%$
Hg:			-	$2\Delta/k_{\rm B}T_{\rm c}=4.1$ from analysis ⁷⁶
In:	pure 77	1.5		$\frac{2\Delta/k_{\mathbf{B}}T_{\mathbf{c}}=3.5}{2.7\pm0.4}$
	films with Sn impurity up to 5% [⁷²]	1.5		$2\Delta/k_{\rm B}T_{\rm c} = 3.7 \pm 0.1$ for all concentrations of Sn
Nb:	single crystal $r = 100^{-78}$	0,2		$2\Delta/k_{\mathbf{B}}T_{\mathbf{c}} = 3.5 \pm 0.2$
	98,5% 79	1.6		$2\Delta/k_{\mathbf{B}}T_{\mathbf{c}} = 3.5$
Pb				$2\Delta/k_{ m B}T_{ m C}=4.1$ from analysis 78
Sn:	~ 99,996%, single crystal 69, 70	0,2	Anisotropic temperature dependence	
	99.998%, single crystal ³⁹	0,15	$\beta = 1.45$	$2\Delta_{\min}^{a\delta c}/k_{B}T_{c} = 3.1$
	polycrystal 73	1.3	The results could not be connected with the gap anisotropy	$\begin{array}{l} 2\Delta/k_{\rm B}T_{\rm c} = 3.3 \\ ({\rm Sn} \ 99.999\%), \\ 2\Delta/k_{\rm B}T_{\rm c} = 3.9 \\ ({\rm Sn} \ \text{with impurity} \\ 0.01\%) \end{array}$
`a:sin	gle crystal $r = 50^{-78}$	0,2		$2\Delta/k_{\rm B}T_{\rm c}=3.8\pm0.2$
Zn:	single crystal 99,9999% 35	0,15	β=1.3	
	single crystal ⁶⁸	0.1	Anisotropic temperature dependence	$2\Delta_{\min}^{\text{afc}}/k_{\text{B}}T_{\text{c}} = 2.4,$ $2\Delta_{ep}/k_{\text{B}}T_{\text{c}} = 3.6,$ $a \sim 40\%$
	polycrystal ⁷⁵	0.3	Temperature dependence differs from the data of [⁶⁸], possibly as a result of the scattering centers (grain boundaries)	$2\Delta/k_{\rm B}T_{\rm c}=3.4$

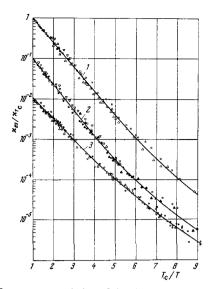


FIG. 6. Temperature variation of the electronic thermal conductivity of single crystals of Ga in the superconducting state. 1 – orientation of sample along the b and c axis. The samples contained 0.001% of impurity (P series) and 0.1% (D series) [⁶⁷]. Curves: 1) ∇ - a-1D, \bullet – 3D-a, Δ – a-2P, O – 2P-a; 2) ∇ – b-1D, \bullet – 3D-b, O – b-3P, \blacktriangle – 2P-b; 3) ∇ - 3D-c, O – c-3P, Δ – c-4P, \bullet – 2P-c.

is ~30 and ~40% respectively, and the gap can be approximated by an ellipsoid that is oblate along the c axis of Ge or in a direction perpendicular to the hexagonal axis of Zn and Cd. We note that the anisotropic temperature dependence of the electronic thermal conductivity of superconducting Sn, as a function of the orientation of single crystals, can, in accordance with the data of Laredo^[69] and Graham,^[70] also be interpreted as a manifestation of the gap anisotropy, but only Zavaritskiĭ's analysis of the thermal conductivity of Sn at very low temperatures,^[40] has shown that $2\Delta_{min}^{abs}$

= $3.1 k_B T_c$ (from these data, however, it is impossible to determine the section of the Fermi surface to which this value applies).

A surprising circumstance, from the point of view of Anderson's theory, ^[21] is the absence of any changes in the temperature dependence of the electronic specific heat of $Ga^{[67]}$ when its purity is varied in a wide range (from 99.999 to 99.9%). The presence of an appreciable gap anisotropy in the spectrum of this superconductor should have contributed to an effective smoothing of this anisotropy under the influence of the impurity (with an appropriate change in the temperature dependence in the thermal conductivity, since at low temperatures this property is determined by the smallest $gaps^{[11, 6]}$). Satterswaithe.^[71] investigating the electronic specific heat of pure Al and its alloys in the superconducting state, has shown that a change of the electron mean free path by 140 times has likewise not led to an appreciable change of this dependence (Fig. 7). Since very pure aluminum is the most convenient object for such investigations (it is subject to only one electron scattering mechanism, elastic scattering by static defects, in the entire temperature region owing to its high Θ_D and low T_c), Satterswaithe arrives at the conclusion that measurements of the specific heat are not a sufficiently sensitive method of determining the gap (and all the more its

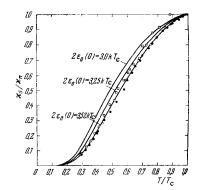


FIG. 7. Temperature dependence of the thermal conductivity of superconducting aluminum and its alloys. O - aluminum with 0.3% copper, residual electric resistance r = 26; \bullet – aluminum, r = 430; \Box – aluminum, $r = 3660 [^{71}]$.

anisotropy) in superconductors. The same conclusion is reached by Serin and co-workers, [72] who investigated the thermal conductivity of In films (thicknesses 1200-20 000 Å) containing up to 5% Sn impurity. Since the scattering by the boundaries decreases the mean free path of the electrons to a much lesser degree than that of phonons, the authors succeeded in measuring the ratio of the electronic thermal conductivity in the superconducting and normal states without excluding the lattice thermal conductivity. It turns out that the temperature dependence of this ratio is not sensitive to the composition of the films.*

Thus, in comparing the thermal methods of investigating the gap and its anisotropy in superconductors. preference should be given to results obtained by investigations of the specific heat, although some unanswered questions still remain in this case.

3. Critical Magnetic Field

The theoretical investigations of Pokrovskii^[6] and of Clem^[22,80] have shown that a careful measurement of the temperature dependence of the critical field H_c in superconductors can yield information on their meansquare gap anisotropy $\langle a^2 \rangle$. In the case of weak electron-phonon coupling, $\langle a^2 \rangle$ enters, for example, in the function of the deviation of H_c/H_0 from a parabolic dependence in the following manner:

$$D(t) = \frac{H_{c}}{H_{c}} - (1 - t^{2}) = -0.1317 (1 + 6.6 \langle a^{2} \rangle) (1 - t^{2})$$

 $+0.0986(1+3\langle a^2\rangle)(1-t^2)^2+0.0287(1+6.15\langle a^2\rangle)(1-t^2)^3+\ldots,$ where $t = T/t_{c}$.

Comparing with theory the temperature dependence of H_c (at not too low temperatures) of Ga^[81] (Fig. 8) and its change under the influence of an impurity in Sn, [82] Cochran and Reynolds and co-workers determined the values of $\langle a^2 \rangle$ of these superconductors (Table III). Further experiments, however, are necessary at low temperatures, since the only low-tempera-

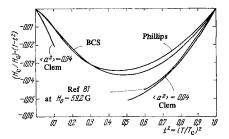


FIG. 8. Deviation of critical magnetic field from a parabolic temperture dependence. The figure shows the theoretical BCS and Clem curves, and data obtained by measuring $H_c[^{s_1}]$ and $c_{es}[^{s_0,s_1}]$ of gallium [^{s_1}].

Table III. Energy gap $2\Delta/k_{\rm B}T_{\rm c}$ at 0° in superconductor spectrum, and its anisotropy as determined by measuring the critical magnetic field.

Superconductor, purity, and single-crystal status	Ga, 99.9999%, single crystal	Hg, > 99.999% 83	In, 99.999%, single crystal ⁸³	Sn, 99.999%, single crystal
Minimum temperature of investigation	0.82	0.3	0,3	0,383
$\frac{2\Delta/k_{\mathbf{B}}T_{\mathbf{c}}}{\langle a^{2} \rangle}$	3.32 0.04	4.0	3,64	3.60 83 0.022 82

ture investigation of H_C known to us (to $0.3^{\circ}K$), that of Finnemore and Mapother^[83] has so far not yielded any significant results with respect to the anisotropy of the gap of Sn, Zn, and Hg.

4. Linear Lowering of T_c in Dilute Solid Solutions

Until recently, the manifestation of the anisotropy of the gap in the spectrum was taken to be a linear decrease of T_c as a function of the reciprocal of the electron mean free path l^{-1} (regardless of the type of im-purity) in dilute solid solutions of superconductors with nonmagnetic impurities (see, e.g., $l^{19,841}$). The idea that allowance for the isotropic scattering of electrons by impurity centers can lead to a smoothing of the anisotropy of the gap as the condition $l \sim \xi$ is approached (ξ -coherence length) was first proposed by Anderson.^[21] The very phenomenon of the linear lowering of T_{c} (Fig. 9) was observed following introduction of impurities (up to several tenths of a percent), introduction of vacancies, plastic deformation, neutron irradiation, etc., in a number of superconductors (Table IV contains data on the magnitude of the mean square gap anisotropy

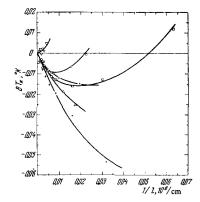


FIG. 9. Variation of T_c of indium under the influences of various impurities [85].

Apparently Reynolds et al. [74] are inclined to ascribe similar results of a study of the thermal conductivity of polycrystals of pure Sn and its alloys [73] to the pure-sample texture at which the minimal gap was measured; in this case the gap can increase with increasing impurity. A subsequent detailed investigation of single-crystal Sn^[234] revealed the influence of the gap anisotropy on the electronic thermal conductivity $(2\Delta/k_BT_c =$ 3.0 - 4.0).

Table IV. Mean square gap anisotropy $\langle a^2 \rangle$ in superconductor energy spectrum as obtained from data on the shift of T_C under the influence of an impurity and of plastic deformation.

Super- conductor	A1, 19	Hg, 96	In, 19,97	Pb, 98	Sn, 82	Ta, 99	T1, 86	V, 47	Zn, 94
$\langle a^2 \rangle$	0,011	0,005	0.021	0.004	0,023	0.011 estimate 47	0.001 0.04 ²⁴⁵	0.016	0.047

 $\langle a^2 \rangle$, obtained in accordance with the theory of Markowitz and Kadanoff,^[19] for all the superconductors investigated in this manner; the data for Tl were obtained by analyzing the variation of T_c following plastic deformation;^[86,245] the fact that T_c of Re remains unchanged^[87] may possibly be connected with the insufficient purity of the initial metal).

The results of investigation of Tl and Zn are particularly remarkable. To explain the absence of a linear displacement T_c in Tl under the influence of an impurity,^[88] two points of view were advanced. Lazarev and co-workers (see, e.g., [89]) proposed that this circumstance, together with the previously observed $^{[\ 90\]}$ singularity in the dependence of ${\rm T}_{\rm C}$ of T1 on the pressure (and the influence of impurity on this singularity) is connected with the decrease in the number of cavities of the Fermi surface of this metal.^[91]* In spite of the fact that such an electronic transition has been indeed observed also by a direct method $^{[\,93\,]}$ in Zn containing $\sim 0.1\%$ Cu impurities and in Cd at hydrostatic pressure of ~ 10 kbar (the de Haas-van Alphen effect and the angular dependence of the electric resistance in a magnetic field were investigated), it would be of interest to have for Tl, Re, and In also direct data on the change of the Fermi-surface topology. As another possible explanation, Gey^[86] proposed the sharp increase (under pressure) of the very weak anisotropy of the energy gap of T1: the change of $\langle a^2 \rangle$ from 0.0008 (without pressure) to 0.007 at a pressure of 4 kbar. Naturally, the electronic transition should also be accompanied by a change of the gap anisotropy, † but for a final determination of the cause of such a change, further experiments are necessary.

The appreciable shift of T_c of Zn under the influence of an impurity, in the opinion of Farrell et al., ^[94] points to a large gap anisotropy, which the authors attribute to the increase of the value of the gap for those regions of the Fermi surface, which overlap on the faces (002) of the Brillouin zone.

Recently Moskalenko and co-workers^[95]</sup> have notedthat allowance for the interband scattering of the electrons by impurities[‡] also can lead to a lowering of T_cof a superconductor, so that in real superconductors,the indicated effects are probably superimposed.</sup>

5. Electron Absorption of Ultrasound

The sharp decrease of absorption of ultrasonic os-

cillations when a metal goes over into the superconducting state was discovered by Bommel (for Sn) and by Mackinnon (for Pb)^[100] even before the development of a superconductivity theory capable of explaining this effect as being due to the sharp increase of the energy gap with decrease in temperature below T_c . Within the framework of the isotropic model, the ratio of the coefficients of the electron absorption of ultrasound in the superconducting and normal states when $kl \gg 1$ (k-wave vector of sound) is

$$\frac{\alpha_s}{\alpha_n} = 2 \left(1 + \exp\left[\frac{\Delta(T)}{k_{\rm B}T}\right] \right)^{-1}$$

Since the gap is anisotropic in real pure superconductors, let us stop to discuss the work of Pokrovskiĭ and Privorotskiĭ,^[12,13] who took this phenomenon into account. They have shown that greatest interest attaches to absorption of sound in the low-temperature region. If the temperature is "moderately" low, $1/k l < (T/var)^{1/2}$ (and this is the only case so far realized in experiments) and exp $(var \Delta/T) < k l (var \Delta/T)^{1/2}$ then the ratio is

$$\frac{\alpha_s}{\alpha_n} \sim \left(\frac{T}{\operatorname{var}\Delta}\right)^{1/2} \exp\left(-\frac{\Delta_{\min}}{k_{\mathbf{B}}T}\right),\,$$

where var Δ = $\Delta^{\rm abs}_{\rm max}-\Delta^{\rm abs}_{\rm min}$, and $(T/{\rm var}\;\Delta)^{1/2}\sim 1$ for an anisotropic superconductor. Inasmuch as metals are characterized by a sound to electron velocity ratio $v_s/v_F \sim 10^{-3}$, the only electrons effectively interacting with the sound waves are those moving parallel to the wave front, i.e., in the equal-phase planes. Therefore the formula for the absorption of ultrasound contains the minimal value of the gap Δ_{\min} on the strip $\mathbf{k} \cdot \mathbf{v}_{\mathbf{F}}$ = 0 of the Fermi surface. At extremely low temperatures, the ratio α_s / α_n turns out to be determined by the smallest energy gap Δ_{min}^{abs} on the entire Fermi surface. Pokrovskii and Toponogov^[16] have demonstrated the possibility of reconstructing the gap anisotropy from ultrasonic measurement data at not too low temperatures (for a singly-connected Fermi surface). Although all the foregoing pertains, strictly speaking, to the case $kl \gg 1$ and to longitudinal sound, further theoretical investigations^[65, 101, 102, 103] and numerous experiments have confirmed the applicability of this analysis to other conditions in a wider temperature interval, starting with a temperature somewhat lower than T_c . We confine ourselves, however, to the presented information in view of the fact that the energy gap and its anisotropy are determined in the lowtemperature region.

The possibility of investigating the orientational dependence of the gap in an anisotropic superconductor (the change of the orientation of k relative to the crystallographic axes of a single crystal leads to a change in the location of the strip $\mathbf{k} \cdot \mathbf{v}_{\mathbf{F}} = 0$ on the Fermi surface) has led to the fact that even the first detailed experiments, performed with longitudinal sound by Galkin and Morse and co-workers, ^[104] clearly demonstrated the presence of noticeable gap anisotropy in superconducting Sn (Fig. 10). Measurements of the absorption of transverse sound^[105, 106] also confirmed the anisotropy of the gap in the superconductor, and yielded gap values coinciding within the limits of experimental accuracy with the earlier data. As the result of our investigation

^{*} A similar conclusion was recently drawn also with respect to $In^{[92]}$ and $Re^{[235]}$ (see also the investigations of $B^{[236]}$, $Cd^{[237]}$, $In^{[238]}$, and $Zn^{[239]}$).

[†] This reasoning was first advanced by V. G. Bar'yakhtar.

[‡] Besides the anisotropy of the matrix elements of the electronelectron interaction, the anisotropy of the Fermi surface also comes into play here.

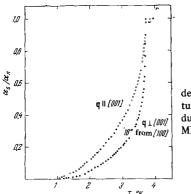


FIG. 10. Temperature dependence of the absorption of longitudinal ultrasound in superconducting tin (sound frequency 80 MHz [¹⁰⁴]).

in a wide interval of crystallographic orientations^{[107}, ^{108]}, we obtained a "map" of minimal gaps on the lines $\mathbf{k} \cdot \mathbf{v}_{\mathbf{F}} = 0$ of the Fermi surface of Sn (Fig. 11), constructed in such a way that to each point of the Fermi surface there is set in correspondence a point on a unit sphere, such that the normals at these points are parallel. Here, naturally, each line $\mathbf{k} \cdot \mathbf{v}_{\mathbf{F}} = 0$ of the Fermi surface corresponds to a great circle on the unit sphere. It is seen from the results that the orientational dependence of the energy gap in Sn has a complicated character, and the anisotropy of the gap is not less than 50%. (In a report of a tunnel investigation published by Zavaritskii^[109] simultaneously with our paper,^[107] the same value was obtained for the gap anisotropy of Sn.) Unfortunately, in connection with the fact that the Fermi surface of Sn is multiply connected, we are not certain of the part of the Fermi surface to which the measured values pertain, all the more since the detailed structure of the Fermi surface of this me metal has not yet been sufficiently well investigated. It it interesting to note the experiments of Claiborne and Einspruch,^[110] in which the decrease of the gap anisotropy (Fig. 12) in Sn (with impurities up to 0.1%) is regarded as a patent confirmation of Anderson's theory.^{[21]*} In an attempt to compare the experimentally obtained temperature dependences of the absorption of sound in pure superconducting tin with a formula that

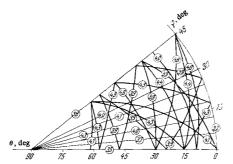


FIG. 11 Projections of the lines $\mathbf{k} \cdot \mathbf{v_F} = 0$ on the unit sphere for the investigated orientations of the wave vector of sound k in tin (conical equalinterval projection). Heavy lines-data of [107,108], thin lines-data of $[104^4]$ The point with coordinates $(\theta, \varphi) \sim (90^\circ, 0^\circ)$ corresponds to the direction of [001] of tin; $(0^\circ, 0^\circ) - [100]$; $(0^\circ, 45^\circ) - [110]$. The numbers show the values of the minimum energy gaps on the corresponding lines of the Fermi surface [108].

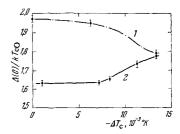


FIG. 12. Value of the gap Δ/k_BT_c of tin as a function of the displacement of T_c under the influence of the impurity.

takes into account several gaps on the Fermi surface, the authors obtained a result which they regard as clearly unphysical (e.g., $2\Delta'/k_BT_c \simeq 3$ and $2\Delta''/k_BT_c \simeq 9$ for k $\|[001]$.*

An appreciable gap anisotropy (~40%) was observed by Claiborne and Morse^[113] in a study of the absorption of transverse sound in superconducting Al, in spite of the closeness of its Fermi surface to the "almost-free" electron model. These investigations, however, cannot be regarded as complete, since the parameter kl, which is most important in such investigations, was larger in the investigation of a Dutch group,^[14] where no gap anisotropy was observed at all in Al. As shown by an investigation of Bezuglyĭ and co-workers,^[24] the anisotropy of the energy gap of Al is manifest also in the absorption of longitudinal ultrasound (the values of the gap for different orientations lie in the range (3.25– 3.7) k_BT_c.

Indications of a gap anisotropy are contained also in ultrasonic investigations of Ga, ^[115] Zn, V, ^[112] Nb, ^[116] Tl, ^[117, 118] Re, ^[119] In, ^[120, 121] and Mo^[228] (Table V lists all the data known to us concerning this question). Jones and Rayne^[119, 228] conclude, on the basis of the investigation of three orientations of single-crystal Re and Mo, that a direct connection exists between the slope of the curves representing the frequency dependence of the coefficient of electron absorption of ultrasound in the normal state of the metal and the values of the energy gaps in the superconducting state. Our more detailed investigations of Sn^[107, 108, 122] revealed no such simple correlation.

An ultrasonic investigation of the gap anisotropy of $TI^{[117]}$ and $In^{[123]}$ is made difficult by the dislocation (amplitude-dependent) absorption of sound, analogous to that observed earlier in Pb, $^{[124, 125]}$ but it should be noted that neither in pure Pb $^{[126]}$ nor in pure Hg $^{[128]}$ is an amplitude dependence of absorption observed (according to a preliminary communication by Willard and Shaw, $^{[118]}$ this effect is missing also in pure Tl). In an analysis of the results of an investigation of In, Bezug-lyĭ and co-workers $^{[121]}$ have proposed that the gap is isotropic on the second hole band of the Fermi surface of In, and the entire gap anisotropy is connected with the third electron band, the minimal gap belonging to the external contour of the central section of the third band, perpendicular to the [001] axis. This assumption,

^{*} A similar phenomenon, to be sure, can be observed also for $kl \rightarrow 1$, when the absorption of sound is determined by the electrons on the entire Fermi surface $[^{111}]$ (see also $[^{240}]$).

^{*} In the experiments of Claiborne and Einspruch [¹¹⁰] (as also earlier in V^[112] and in Sn^[107], deviations from an exponential temperature dependence of the sound absorption was observed at the lowest temperatures. This is possibly connected with the fact that in the region of rather low temperatures the absorption is determined not by the value of the minimum gap on the k-v_F = 0 strip, but by absolute minimum of the gap on the entire Fermi surface [^{12,3}].

Table V. Energy gap $2\Delta/k_{\rm B}T_{\rm c}$ at 0°K and its anisotropy in the spectrum of superconductors from measurements of ultrasound absorption.

	rconductor, purity, and -crystal status of sample	Minimum tem- perature, [°] K	Frequency f (MHz), type of sound, value of kl ; singularities of the temperature dependence of the ultrasound absorption coefficient α	Orientation of wave vector k, polari- zation s of ultrasound relative to the crystallographic directions	$2\Delta/k_B T_R^{},$ gap anisotropy – a
	99,9992%, single crystal 114 99,999%, single	0,4 0,33	f = 5 - 25, longitudinal and transverse, $kl \sim 10$; for transverse sound near T _c - sharp decrease of α $f = 16 - 50$,	$ \begin{array}{c} \mathbf{k} \parallel [100], \ [110] \\ \mathbf{k} \parallel [100], \ \mathbf{s} \parallel [110], \ [010], \\ \mathbf{k} \parallel [100], \ \mathbf{s} \parallel [111], \ [101], \ [100] \\ \mathbf{k} \parallel [100], \ \mathbf{s} \parallel [110] \\ \mathbf{k} \parallel [110], \ \mathbf{s} \parallel [010] \\ \mathbf{k} \parallel [110], \ \mathbf{s} \parallel [110] \\ \end{array} $	3.5 ± 0.1 for all orientations 2.4 ± 0.4
	crystal 113 single crystal $r = 10^4 241$	0,35	transverse, $kl > 1$, near T_c - sharp decrease of α $f = 175 - 225$, longitudinal $kl \gg 1$	$ \begin{array}{c} \mathbf{k} & [[110], \ \mathbf{s}] \\ \mathbf{k} & [[110], \ \mathbf{s}] \\ [110] \\ \mathbf{k} & \perp (100) \\ \mathbf{k} & \perp (110) \end{array} $	3.4 ± 0.4 2.4 ± 0.4 $a\sim40\%$ 3.5 ± 0.2 3.6 ± 0.2
				$ \begin{array}{c} \mathbf{k} \perp (111) \\ \mathbf{k} \perp (122) \\ \mathbf{k} \perp \text{ to plane } 5^{\circ} \text{ from}(110) \end{array} $	$\begin{array}{r} 3.25\pm0.2\\ 3.3\pm0.2\\ 3.7\pm0.2\\ \end{array}$
Ga:	$\frac{R_{290^{\circ} \text{K}}}{R_{4^{\circ} \text{K}}} = \frac{1}{r = 5 \cdot 10^4},$ single crystal ¹¹⁵	0.3	f = 10 - 100, longitudinal and transverse, $kl > 10$; no sharp decrease of α for transverse sound near T _c	k c₀ k b₀	3.5 3,9
Hg:	99.999999%, 1.05, single crystal ¹²⁷	1.05	f=10-250, longitudinal; frequency dependence of α in the entire temperature region, but no ampli- tude dependence	k [111], [110]	$3.5 (kl \sim 1) \ge 5 (kl > 10)$
in:	single crystal ¹²⁸		f = 210, longitudinal, amplitude dependence of α	k [001]	3.7±0,2
In:	99, 9999%, single crystal ¹²⁰		f = 150 - 270, longitudinal $kl > 100$; amplitude dependence of α	k [110] k [001] k [100]	3.1 ± 0.2 3.1 ± 0.2 3.2 ± 0.2
	99,9995%, single crystal ¹²¹	1,0	f = 227, longitudinal $ kl > 10$; amplitude dependence of α	$ \begin{array}{c} \mathbf{k} \perp (100), \ (111) \\ \mathbf{k} \perp (001) \\ \mathbf{k} \perp (110) \\ \mathbf{k} \perp (011) \\ \mathbf{k} \perp (023) \end{array} $	$\begin{array}{c} 3.45{\pm}0.1\\ 3.15{\pm}0.1\\ 3.35{\pm}0.1\\ 3.10{\pm}0.1\\ 3.25{\pm}0.15\\ \end{array}$
Mo:	r = 450, single	0.5	f = 240, longitudinal	k [100]	3.5 ± 0.2
	crystal ¹²⁹ $r = 6.10^3$, single crystal ²²⁸	0.4	f = 175 - 950, longitudinal $kl > 1$	k [100] k [110] k [111]	$3.30\pm0.2 \\ 3.50\pm0.2 \\ 3.10\pm0.2$
Nb:	99.7%, single crystal ¹³⁰	1.2	f = 135, transverse $kl < 1$; no drop of α near T _c	k [110], s [110]	3.5 ± 0.2 (underestimated because of oscillations of α [¹³¹]
	99.8%, $r = 520$, single crystal ¹³²	1.3	f = 220, longitudinal $kl < 1$	k [100], [110], [111]	3.63 ± 0.06 for all orientations
	r = 300, single crystal ¹¹⁶	2	f = 300 - 1280, longitudinal $kl > 1$	k [100], [110] k [111]	$ \begin{cases} 3.5\\ 3.6 \end{cases} f = 1280 \text{ MHz} \\ \sim 3.7 \text{ for all orientations at} \\ f = 300 \text{ MHz} \end{cases} $
	$r = 10^3$, single	1,65	f = 70 - 90, longitudinal $kl < 1$	k [100]	$3.5{\pm}0.1$
	crystal 133 $r = 10^3$, single	1.3	f = 30 - 70, longitudinal and transverse $kl < 1$	k [110]	3.7
	crystal ¹³⁸ r = 400, single crystal ¹³⁴	1.8	$f = 30 - 50$, longitudinal $kl \ll 1$; frequency dependence of α		~ 4
Pb:	99,997%, single crystal ¹²⁵	1.3	f = 10 - 70, longitudinal, $kl < 1$; amplitude dependence of α	k [100] k [110] k [111]	$< 5.1 \\ 4.0\pm0.1 \\ 4.1\pm0.1$
	very pure single crystal ¹²⁴	2	f = 10 - 110, longitudinal , $kl > 1$; no amplitude dependence of α , but frequency dependence	[100] [110]	$ \begin{vmatrix} 3.5\pm0.1\\ 3.3\pm0.1\\ >4 & \text{for all} \\ \text{orientations at} \\ kl \gg 1 \end{vmatrix} $
	99,9%, single crystal ¹³⁵	1.4	f = 50 - 1050, longitudinal, $kl < 1$	k [111]	~ 5
Re:	$r > 10^4$, single crystal ¹¹⁹	0,45	f = 250 - 870, longitudinal , $kl > 1$	k [0001] k [1010] k [1120]	$2.9\pm0.13.0\pm0.13.5\pm0.1$
Sn:	pure single crystals [¹⁰⁴]	1.0	$f \approx 80$, longitudinal , $kl > 10$	k [001], angle between k and [100] in (001) plane	3.2±0,1
				$\begin{array}{c} \varphi^{\circ} = 0 \\ 6 \\ 12 \text{ and } 30 \\ 18 \\ 24 \\ 45 \end{array}$	$\begin{array}{c} 3.5 \pm 0.2 \\ 3.7 \pm 0.2 \\ 4.0 \pm 0.2 \\ 4.3 \pm 0.2 \\ 4.1 \pm 0.2 \\ 3.8 \pm 0.2 \end{array}$
	$r = 5 \cdot 10^4$, single crystal ¹⁰⁵		f = 80, transverse, $kl > 1$	k [001] k [100] k [110]	$ \begin{array}{c} a \sim 30\% \\ 3.2 \pm 0.3 \\ 3.4 \pm 0.3 \\ 3.7 \pm 0.3 \end{array} $

			Table V (contrd.)		
Sur sing	perconductor, purity, and le-crystal status of sample	Minimum tem- perature, °K	Frequency f (MHz), type of sound, value of k/i ; singularities of the temperature dependence of the ultrasound absorption coefficient α	Orientation of wave vector k, polari- zation s of ultrasound relative to the crystallographic directions	$\frac{2\Delta/k_{\mathbf{B}}T_{\mathbf{C}}, \text{ gap}}{\text{anisotropy} - a}$
Sn:	99.9999%, $r^{-1} \sim 10^{-5}$, single crystal ^{107,108}	1.0	$f = 100 = 300$, longitudinal, $kl \gg 10$	$ \begin{array}{c} \mathbf{k} \perp (101) \\ \mathbf{k} \perp (111) \\ \mathbf{k} \perp (301) \\ \mathbf{k} \perp (112) \\ \mathbf{k} \perp (211) \\ \mathbf{k} \perp (113) \\ \mathbf{k} \perp (311) \end{array} $	$\begin{array}{c} 3.9 \pm 0.2 \\ 4.8 \pm 0.3 \\ 4.1 \pm 0.2 \\ 4.4 \pm 0.2 \\ 3.9 \pm 0.2 \\ 4.0 \pm 0.2 \\ 4.3 \pm 0.2 \\ a \sim 50\% \end{array}$
	99.999%, single crystal ¹⁰⁶	1.1	f = 30 - 70, transverse $kl > 10$, sharp drop of α near T _c	 k [001], s [100] k [100], s [010] k [100], s [001] at k [001] there is such an s that 	$\begin{array}{c} 3.4 \pm 0.2 \\ 3.7 \pm 0.2 \\ 3.3 \pm 0.2 \\ 2\Delta/k_{\rm B}T_{\rm c} = 4.3 \end{array}$
	> 99.9999%, single crystal ¹¹⁰	1.2	f = 50 - 460, longitudinal , $kl > 40$	k [001] k [110] k [100] in Sn with 0.1% In at k [001] and [110]	$\begin{array}{c} 3.26 \pm 0.02 \\ 3.96 \pm 0.04 \\ 3.62 \pm 0.04 \\ (\text{does not depend on } kl) \\ 3.5 - 3.6 \end{array}$
	$r := 10^4$, single crystal ¹³⁶	1.2	f = 70 - 165, longitudinal, $kl = 30$	k (111)	3.8 ± 0.1 (obviously underestima-
	$r = 10^4$, single crystal ¹³⁷	1.2	$f=75\pm165,\; ext{longitudinal}$, $kl\gg1$	k _L (111)	$\begin{bmatrix} \text{ted} [137] \\ 4,45 \pm 0.15; \\ \text{at} \ kl \sim 1 \\ \text{gap} \ \sim 3.3 \ k_{\text{B}}^{T} \text{c} \end{bmatrix}$
	single crystal ¹¹¹	0.8	$f = 40 - 290$, longitudinal, $kl \gg 1$	angle between k and [100] in (001) plane	b b c
				φ° = 9 27 36 k [310]	$\begin{array}{c} 3.78 \pm 0.08 \\ 4.04 \pm 0.05 \\ 3.80 \pm 0.06 \\ 4.25 \pm 0.04 \end{array}$
Ta:	99,9%, single crystal 138,130	1,2	$ \begin{cases} f = 340, \text{ longitudinal }, kl < 1, \\ f = 135, \text{ transverse } kl < 1; \\ \text{no drop of } \alpha \text{ near } T_{\text{C}} \end{cases} $	k [110] k [110], s [110] }	$3,5\pm0.2$ (underestimated because of oscillations of α [¹³¹]
T1:	single crystal ¹¹⁷	1.2	f = 60 longitudinal, $kl < 1j = 12 - 110$, transverse $kl < 1$	k [0002] k [10ī0] k [12ī0] k [0001], s [10ī0] k [10ī0], s [0001] k [10ī0], s [1210]	$ \begin{vmatrix} 3,76\pm0,04\\ 4,10\pm0,04\\ 4,00\pm0,04\\ 3,7\pm0,1\\ 3,75\pm0,1\\ 3,75\pm0,1\\ 3,9\pm0,1\\ \text{Accuracy overestimated,}\\ \text{since } \alpha_{n} \text{ is small and}\\ T>0.5 \ T_{c} \end{vmatrix} $
	99,999%, single crystal ¹¹⁸	0.5	f = 10 - 130, longitudinal	k [0001] k [1210] k [1010]	$\begin{array}{c c} 4.00\pm0.3\\ 3.62\pm0.1\\ 3.70\pm0.2\end{array}$
v:	99.95%, single	1.2	f = 100 - 380, longitudinal, $kl < 1$	k [110]	3.5±0.15
	crystal 140,130		f = 135 - 225, transverse $kl < 1$, no drop of α near T _c	k [110], s [110]	$3,6\pm0.2.$ (underestimated because of oscillations of α [¹³¹])
	$r \sim 130$, single crystal ¹¹²	1.2	f = 342, longitudinal, $kl > 1$	k [100] k [110] k [111]	$\begin{array}{r} 3,1{\pm}0.2\\ 3,4{\pm}0.2\\ 3.2{\pm}0.2\end{array}$
Zn:	99,9999%, single crystal ¹¹²		f = 233, longitudinal, $kl > 1$	k [1210] k [1010]	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$

Table V (cont'd.)

generally speaking, contradicts the existing theoretical notions, ^[14,15] all the more since it was assumed in the analysis of ^[121] that in the third band of the Fermi surface of In there are no electron tubes of α type; experiments^[246] and calculations^[247] show that this is not the case.

6. Relaxation of Nuclear Spins

....

In view of the fact that the nuclear and electron spin systems interact strongly in metals, the ratio of the rates of nuclear spin-lattice relaxation in superconducting and normal states of the metal, according to the isotropic model of superconductivity, turns out to be

$$\frac{R_s}{R_n} = 2 \int_{\Delta(T)}^{\infty} dE \left[\wp_s(E) \right]^2 \left[1 + \frac{\Delta^2(T)}{E^2} \right] \left[-\frac{\partial f(E)}{\partial E} \right].$$

In comparing this expression with experiment, Hebel and Slichter, $^{[141, 142]}$ in order to remove the logarithmic divergence at the lower limit as $T \rightarrow T_c$ and $\Delta(T) \rightarrow 0$, introduced a certain "smearing" of the density of quasiparticle states. If this "smearing" is related to the gap anisotropy of the superconductor, $^{[143]}$ then the results of measurements of nuclear spin relaxation of A1, $^{[143]}$ Cd, $^{[144]}$ and Ga $^{[145, 146]}$ might be regarded as a manifestation of a certain gap anisotropy in the spectrum of these superconductors. In spite of the fact that introduction of an impurity in Al decreases the "smearing" of the state density, $^{[147]}$ and the gap and its anisotropy itself apparently also decrease with increasing dimensions of the investigated superconducting particles and films $^{[148, 149]}$ (characteristic dimension $\leq \xi$), the proposed explanation of the indicated "smearing" is not the only possible one. A similar one, unfortunately, can be obtained in a superconductor by the interaction between the quasiparticles and the thermal phonons^[150] (Fig. 13). More unique results can be obtained in investigations of nuclear spin relaxation at very low temperatures, where the absolute minimum of the gap should appear.^[22]

7. Interaction of Electromagnetic Radiation with Superconductor

Work in this interesting field of research on superconductivity began rather long ago^[151,152] and was stimulated by the hypothesis^[153,26] that an energy gap exists in the electron spectrum of the superconductor (for details see ^[154]). As the high-frequency techniques progressed, it was possible to cover in the mid-sixties the frequency range corresponding to photon energies $\hbar \omega \sim 3 k_{\rm B} T_{\rm c}$.^[155] Table VI contains the values of the energy gap and its anisotropy, obtained in the study of threshold effects ($\hbar \omega \ge 2\Delta$), and the main results of the investigations of the absorption of low-frequency electromagnetic oscillations in superconductors. We note, that according to the data of Abrikosov, Gor'kov, and Khalatnikov,^[156] the experimental results are in good agreement with the theory,^[156, 157] especially at high frequencies; here, as shown by Pokrovskiĭ and Ryvkin,^[158] allowance for the gap anisotropy leads to a decrease of the values of the gap (by 10%) compared with the values listed in Table VI and obtained from investigations of threshold effects.

The first gap anisotropy was obtained in a study of threshold effects by Richards^[163] in a spectroscopic investigation of single-crystal Sn in the wavelength range 0.5-3 mm.* Unfortunately, the absorption edge is strongly smeared out (Fig. 14), making it impossible to determine the value of the gap in samples of different orientations. Estimates by Richards^[163] have shown that in his experiment he measured certain average

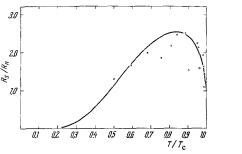


FIG. 13. Temperature dependence of the ratio of the relaxation rates of nuclear spins in aluminum. $\bullet, X - experiment [1^{41}, 1^{43}]$, curve—theory (owing to a numerical error, the theoretical curve should pass somewhat lower) [150].

Table VI. Energy gap $2\Delta/k_{\rm B}T_{\rm c}$ at 0°K and its anisotropy as obtained by investigations of the interaction of electromagnetic radiation with the superconductors.

Superconductor, purity	Measurement method; frequen- cy f (wavelength λ) of electro- magnetic radiation	Study of orientation of single crystals	2∆/k _B T _c , gap anisotropy -a
Al: 171	Change of surface resistance, $\lambda = 3 - 20 \text{ mm}$	Polycrystal	3.2 ± 0.1
99,9999%, single crystal ¹⁶⁹	Absorption of electromagnetic radiation, $\lambda = 3 \cdot 20 \text{ mm}$	Planes: (100), (111), (110) at polariza-	(3.15 and 3.44)±0.03 (3.18 and 3.50)±0.04
		tion: E [100] E [110]	$\begin{array}{c} (3,08 \text{ and } 3,37) \pm 0.04 \\ (3,04 \text{ and } 3,37) \pm 0.05, \\ a \sim 20\% \end{array}$
Hg: 160, 172	Reflection of radiation from bulky metal,	Polycrystal	$4,6\pm0.2;$ structure of absorption edge at energy lower than $2\Delta/k_{\rm B}T_{\rm C}$ ("fore- nunner peak")
In: 173	Transparency of thin film in	Polycrystal	3,9±0.3
172	IR region Reflection of radiation from bulky metal,	» »	$4.1{\pm}0.2$
242	$\lambda = 0.1 - 2 \text{ mm}$ Absorption of IR radiation at 1°K	Film (9000Å)	$3.69{\pm}0.04$
La: 95% fcc, 5% hex ¹⁶⁷	Reflection of radiation from bulky metal	Polycrystal	2.85 ± 0.24 . At energy $5.7k_{B}T_{c}$ structure of absorption
fcc phase ¹⁷⁴	Measurement of surface resistance, $f = 30 - 150$ GHz	Annealed polycrys- talline film (6 · 10 ⁴ Å)	edge 2,87±0,1
Nb: 172	Reflection of radiation from bulky metal, $\lambda = 0, 4-2 \text{ mm}$	Polycrystal	2,8±0.3
175	Temperature dependence of depth of penetration of magnetic field; $f = 0.8$ and 4.4 MHz	»	~ 3,52
242	Absorption of IR radiation at 1°K	Film (2500 Å)	$3.6{\pm}0.2$
Pb: 176, 172	Reflection of radiation from bulky metal, $\lambda = 0.1 - 2$ mm.	Polycrystal	4.1±0.2; "forerunner peak"
Pb: 173	Transparency of thin film in IR region	Polycrystal	4,0±0.5; "forerunner peak"
177	Measurement of depth of pene- tration of magnetic field, f = 2 MHz	*	\gg 4,9
pure and alloys with Tl, Bi, Sn 178	Reflection of radiation from bulky metal, $\lambda = 0, 1-2$ mm	*	4,14±0,1 (pure Pb); the absorp- tion edge in the alloys is sharp, but a "fore- runner peak" is present
161	Simultaneous investigations of reflection and transparency of thin films in IR region	*	$4,5 \pm 0.1;$ no "forerunner peak"
162	Absorption of IR radiation	Polycrystalline films of thickness 1400, 6000, 54000 Å	no "forerunner peak"
242	Absorption of IR radiation at 1° K	Film (10000 Å)	4.28±0.02 and 4.65± ±0.02. Gap anisotropy
Sn: 179	Change of surface resistance, $\lambda = 1-4 \text{ mm}$	Polycrystal	~ 3,5
173	Transparency of thin film in IR region	Ŋ	3.3 ± 0.2
172	Reflection of radiation from bulky metal, $\lambda = 0.1-2$ mm	»	$3,6{\pm}0,2$
180	Investigation of depth of pene- tration of magnetic field	n	~ 4,2

^{*}After Tinkham and co-workers observed in Pb and Hg [^{159,160}] a fine structure in the absorption edge of the infared radiation at a photon energy lower than the energy corresponding to the gap ("forerunner peak") this phenomenon was taken to be a manifestation of the gap anisotropy in the spectrum of Pb and Hg. Many papers were published concerning the 'forerunner peak,' and only recently (in the 13th paper!) did Palmer and Timkham [¹⁶¹], by measuring simultaneously the passage and reflection of infrared radiation in thim films of Pb (making it possible to determine the optical constants without theoretical premises), did not find it at all. The absence of a "forerunner peak" was confirmed also by investigations of the surface resistance of Pb films [¹⁶²].

Superconductor, purity	Measurement method; frequen- cy f (wavelength λ) of electro- magnetic radiation	Study of orientation of single crystals	$2\Delta/k_{\rm B}T_{\rm c}$, gap anisotropy
single crystal ¹⁶³	Reflection of IR radiation from bulky metal; absorbed edge smeared (considerable anisotropy of energy gap)	Planes (110), (001), (100)	Average gap for (110) larger than for (001) and (100); structure of absorption edge in all samples at energy (4.2 - 4.5 kgT _C , impurity does not destroy it, but the absorption edge becomes sharper
164	Surface resistance near T _C (estimates of gap inaccurate) $\lambda \sim 2 mm$	Polycrystal	3.5; 4.3?; 5.5? in pure Sn; ~ 3.6 for electrons moving para- lel to [001]; ~ 3.6 in alloys with in, distinct absorption edge
Sn: 99,9999% 105	Surface resistance $f = 23$ GHz	single crystal	Possible presence of two gaps in this spectrum
single ₁₆₆ crystal	Surface impedance $f=3$ GHz	Sample axis parallel to [001], [100], [110]	In direction [100] ~ 2,9; [001] π [110] ~ 3,7; <i>a</i> ~ ~ 30%
181	Reflection and absorption of radiation by film (thickness 50Å); f = 22 - 72 GHz	Polycrystal	~ 2.8
242	Absorption of IR radiation at 1° K	Film (3500 Å)	$3,58\pm0.04$ and $3.86\pm\pm0.08;$ gap anisotropy
Ta: 172	Reflection of radiation from bulky metal, $\lambda = 0.1-2$ mm	Polycrystal	≪3,0
242	Reflection of radiation from bulky metal,	Film (7500 Å)	$3.5{\pm}0.2$
V: 172	Reflection of radiation from bulky metal, $\lambda = 0.1 - 2 \text{ mm}$	Polycrystal	3.4 ± 0.2
242	Absorption of IR radiation at 1°K	Film (2500 Å)	3.4 <u>±</u> 0.1
Zn: 99,999% 169	Reflection of radiation from bulky metal, $\lambda = 3 - 20 \text{ mm}$	c axis of single crys- tal parallel to sample surface	3,0±0,15; possible gap anisotropy
99, 999% 182	Reflection of radiation from bulky metal, f = 50-75	Polycrystal	3.01 ± 0.09

Table VI (cont'd.)

values of the gap, for electrons from a Fermi-surface strip ($\sim 30^{\circ}$) parallel to the surface of the sample and shifted somewhat away from the central section of the Fermi surface, took part in the interaction with the unpolarized radiation. Attention is called to the fine structure of the absorption edge, observed in all the Sn samples at photon energies $(4.2-4.5)k_{\rm B}T_{\rm C}$ (i.e., at an energy higher than the average gap, unlike Pb and Hg). Although Richards refrains from speculating on the nature of this anomaly, his data show that addition of 0.1% In to pure Sn has no great influence on the anomaly, whereas the main absorption edge becomes sharper and its energy locations cease to depend on the crystallographic orientation of the samples. The latter is regarded by him as a manifestation of the isotropization of the gap,^[21] all the more since a further increase of the impurity content does not cause noticeable changes in the picture of the phenomenon. Indirect confirmation of the anisotropy of the energy gap in Sn may be the measurement data of Adkins,^[164] Lewis,^[165] and Waldram,^[166] who were forced, in the analysis of the temperature dependence of the surface resistance of single crystals of various orientations (in the case of $\hbar \omega$ $< 2\Delta(0)$), to introduce into the calculations an appreciable gap anisotropy for this superconductor. Leslie et al.,^[167] in a study of the reflection of elec-

Leslie et al.,^{LNTJ} in a study of the reflection of electromagnetic radiation in bulky La (face-centered cubic phase), found a fine structure at energies double the energy corresponding to the value of the main gap.* In a paper by Biondi and co-workers,^[169] devoted to

a direct measurement of the energy gap in superconducting Al using polarized radio waves in the range 20-3 mm, data are presented indicating a noticeable anisotropy of the gap in the energy spectrum of this superconductor. The results of an investigation of threshold absorption, obtained by the authors at 0.34°K in pure single crystals oriented along the principal crystallographic directions, are shown in Fig. 15. All the surface-resistance curves are characterized by two sharp changes of the slope at definite photon energy values; this is attributed by the authors to the gap anisotropy, which may be connected with the presence of different gaps on different parts of the Fermi surface. However, as indicated by the authors, with a reference to W. Harrison, inasmuch as the electrons on all parts of the Fermi surface of aluminum are almost free, it is more probable that one energy gap belongs to the undistorted sections of the Fermi surface, which are far from the boundaries of the Brillouin zone, whereas the other corresponds to the distorted sections. (That paper contains preliminary data on the investigation of single-crystal Zn, whose energy gap is also anisotropic.) A recent investigation of infrared absorption in thick Pb and Sn film has revealed two gaps in each of these superconductors.^{[242]†}

8. Tunnel Effect

T

In 1960, Giaever^[183] observed that a system con-

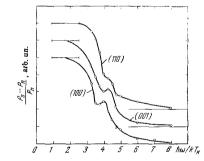


FIG. 14. Frequency dependence of the relative reflection of electromagnetic radiation from the surface of single-crystal tin of the indicated orientation at 1.2° K [¹⁶³].

* The authors were inclined to ascribe this structure to the gap anisotropy connected with the possible presence of a narrow f-band in La, located somewhat higher than the Fermi surface and exerting a strong influence on the superconductivity of this metal [¹⁶⁸]. We note however, that investigations of the specific heat of La, made by Finnemore and Johnson (see the Proceedings of the Calorimetric Conference [⁵¹]) apparently do not confirm the indicated mechanism of superconductivity of La.

[†] Since we are not considering the influence of the magnetic field on the energy gap, we only mention an interesting investigation of pure aluminum, in which Budzinski and Garfunkel [¹⁷⁰] observed a unique gap anisotropy caused by an external magnetic field.

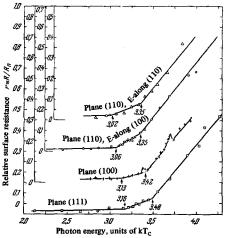


FIG. 15. Dependence of the relative surface resistance on the energy of electromagnetic radiation in single crystals of aluminum at $t = T/T_c = 0.34^{\circ}$ K ($T_c = 1.175^{\circ}$ K). The figure indicates the orientations of the crystals and the polarization of the high-frequency electric field E relative to the crystallographic directions; for the (100) plane of aluminum E || [100]; for the (111) plane E || [110] [¹⁶⁹].

sisting of a superconductor and a normal (superconducting) metal, separated by an insulator, is capable of conducting electron current as a result of the tunnel effect. The dependence of the tunnel current I (or of di/dV) on the potential difference V applied to such a sandwich is not linear, and the gap in the energy spectrum of the superconductor can be determined from these characteristics (theoretical considerations are given in [184,186]). Since most experiments were made on films of thickness smaller than the coherence length, it is natural that no manifestation of the gap anisotropy was seen in these investigations, all the more since the films always contained lattice defects and impurities. Equally averaged values of the gap were obtained in investigations of bulky Nb^[187, 188] and Ta^[188-190] (Table VII contains data obtained with the aid of the tunnel effect; the metals investigated in bulky state are specially noted). Zavaritskiĭ,^[109, 191] in investigations of single-crys-

Zavaritskiĭ,^[109,191] in investigations of single-crystal Sn was the first to demonstrate the dependence of the tunnel effect on the crystallographic orientation, namely, a smearing of the plot of I_S/I_n against V, frequently with several steps (Fig. 16), was observed on the current-voltage characteristic at definite orientations. Zavaritskiĭ proposed that this may be due to the

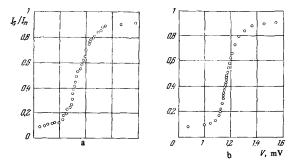


FIG. 16. Relative conductivity I_s/I_n vs. V for tunneling between a tin film and a bulky sample, the normal to the surface of which makes the following angle with the [001] axis: a)60°, b) 22° [¹⁹¹]. (The same abscissa scale is used for a) and b).)

Table VII. Energy gap $2\Delta/k_{\rm B}T_{\rm c}$ at 0°K and its aniso-
tropy in the spectrum of superconductors from tunnel-
effect data.

effect data.						
Superconductor, state, purity	Second element of pair (film); state of pair	Minimum temper _o ature, K	2∆/k _B T _c , gap anisotropy – a			
Al: film ²⁰⁵	Pb; superconductor- superconductor, s – s	0.8	2.7 \pm 0.3; T _c smeared out			
(1 ÷ 3)·103 Å 185	Pb, Sn, In, s – s	0.9	3.2 ± 0.3 at 1°K			
10 ⁻⁵ cm ²⁰⁶	Pb, Sn, In (10^{-5} cm) , s - s	0.1	3.37 ± 0.1			
207	Pb, $s - s$	0.8	2.5 ± 0.3			
208	Sn, s $-$ s	0.87	3.3 (thickness of aluminum film 400 A°)			
16·10 ³ Å ¹⁹⁵	Al (100 – 200 Å), s – s	1.14	Noticeable gap anisotropy			
Bi: amorphous film 700 Å 209	Al, Sn, s – s	1	~4.1			
film ²¹⁰	Al, s – s	1.0	4.6			
(1000 Å) ²³¹	Al film, s – s	1.13	4.60 ± 0.05			
Ga: mixture of phases	Al, Sn, Pb films	1.4	4.2 (amorphous Ga)			
film,	s – s	:	4.1 (y-Ga)			
500 – 2000 Å	3 – 3	i i	3.8 (β - Ga)			
single- crystal, r = 31 000 ²⁴³	Pb, s – s		3.63 – 3.94 depending on orientation			
Hg: film ²¹²	A1, s - s	1.07	4.6 ± 0.11 (thickness of 1500 Ű)			
In: 187,185	Al, s – s	~1	3.63 ± 0.10			
10 ⁻⁵ sm ²⁰⁶	Al, (10^{-5} sm) , s – s	0.1	3.45 ± 0.07			
207	Sn, s - s	0.8	~ 3			
168	Mg, superconductor – normal metal s – h	0.3	3.36 ± 0.1			
5.10 ³ Å ¹⁹⁵	A1 (100 - 200 Å), s - s	1.14	Noticeable gap anisotropy			
thin film ²¹³	Pb, film, s – s	1.2	3.87 ± 0.08			
La: film, $14 \cdot 10^3 R$, fcc phase $(\le 5\%)_{214}$ hex.),	Al, $s - s$, Mg, $s - h$ (5.10 ³ Å)		1.65 ± 0.15 (underestimated because of incorrect determi- nation of T _c [²¹⁵]			
La: (3 ÷ 10)·10 ³ Å 215	Al (10^3 Å) , s – s	1.19	3.2 (in some film structure of $I - V$ characteristics)			
99.9% bulky 198	Nb bulky, s – s	2.7	Hexagonal phase of La – gap anisotropy: $2\Delta/k_BT_c$ = 3.3 ÷ 3.9. Fee phase $2\Delta/k_BT_c$ = 3.9			
Nb: polycrystal	Pb, s s	1.9	≈ 3.59			
Ditto 188	Sn, s – s	1.1	3.84 ± 0.06			
film, 10 ³ Å 216	Sn, s – s	1.8	3.6			
single – crystal r = 750 230	In – film, s – s	0.9	Along directions: $[110] \sim 2.84 \pm 0.02 \text{ meV}$ $[311] \sim 3.22 \pm 0.03 \text{ meV}$ $[111] \sim 3.2 \text{ meV}$ $[110] \text{ and } [112] \sim 3.10 \pm 0.05 \text{ meV}$ $a \sim 15\%$			
Pb: film ¹⁸³	Al, s – h	1.6	4.2±0.1			
205	Al, $s - s$	0.8	4.35 ± 0.1			
187, 185	Ditto	~1	4.33 ± 0.1			
206	Ditto	0.1	4.26 ± 0.08			
207	Pb, Sn, $s - s$	0.8	4.04 ± 0.1			
188	Al, Pb, s – s	0.3	4.33 ± 0.1			
217	Ge bulky	2	4.4			
188	Ta bulky , s – s	1.1	4.30 ± 0.08 (2.67 meV) and 4.67 (2.90 meV), $a \approx 10\%$			

		1	·····
Superconductor, state, purity	Second element of pair (film); state of pair	Minimum tempera- ture, K	$2\Delta/k_{\rm B}T_{\rm c}$, gap anisotropy – a
thick tex- tured films, [111] per- pendicular to surface (grain $5 -$ 10μ) [¹⁹⁶]	Al, s – s	1	two values of gap
film 5400 Å ¹⁹⁹	Ditto	1.1	2.62 and 2.82 meV. In alloys with T1 (3 - 13%) one gap at 2.66 meV.
218 5·10 ³ Å ²⁰⁰	Ditto Al (10 ³ Å), s – s	1	4.8 2.99, 2.71 and 2.44 ± 0.02 meV considerable gap anisotropy
2.10 ³ Å 219	P b, s – s	1.9	4.29 ± 0.04 (2.69 meV)
$\geq 3.10^3 \text{ Å}^{201}$	Pb (≥2·10 ³ Å), s – s	1.2	2.11 2.99 meV, con- siderable gap anisotropy
Pb: thick (>3·10 ³ Å) polycrystal-	Films of Al (≤ 1000 Å), Films of Pb (≥2000 Å), s - s	1.0	$V_c, meV \ 2\Delta_c, meV \ 2\Delta/k_BT_c$
line film ²⁰²			2.11 3.40 2.23 3.60 2.33 3.76 2.39 3.85 2.44 2.44 2.52 2.55 4.11 2.61 2.97 2.99 4.81
$\lim_{1 \mu^{232}} 0 and$	film Al, s h	1.5	4.42 ± 0.04
$1 \mu^{232}_{2000} \text{ Å}^{229}_{229}$	Film Sn. (≽ 2000 Å), s – s	1.5	Additional structure of $dV/dI - V$ characteristics at $2V \approx 3.2, 3.4, 3.5, and 3.7$ meV.
Sn: Film 185 206 207 188 >99.999%, single crys- tal 109,191	Al. s - s Ditto Pb. In. s - s Nb bulky. s - s Sn. s - s	0.9 0.9 0.8 1.1 1.36	3.46 ± 0.1 3.47 ± 0.07 3.10 ± 0.05 3.51 ± 0.18 2.7 - 4.3 depending on orientation, $a = 50\%$
film (11 thous. Å) 208	A], s —s	0.87	3.65 ± 0.2
textured films (3 μ), [001] perpendicular surface ¹⁹⁴	Al (0.05µ) s – s	1.1	1.2, 1.1 and 1.4 meV; no. 1.02 meV (contained in 109,191)
thin film ²¹³	Films of Sn, s – s	1.2	3.67 ± 0.07
film	Pb film, (≥2000 Å),	1.5	Additional structure of $dV/dI - V$ characteristics at $2\Delta/k_BT_c = 4.05$; 3.7; 3.48; 3.15 and 3.0
Ta: bulky 189	Pb , s – s	1.6	3.72
188 single crystal 190	Ditto Ditto	1.1 2	3.6 ± 0.1 3.65 ± 0.05 at surface orienta- tion (100), (110), (210), (211)
film	Ditto	1.8	3.5
Ta: single crystal 197			3.6; state-density singularity dependent on the purity
Tl: film ²²⁰	A1, 5 – 5	0.3	3.57 ± 0.05
textured films, c axis perpen- dicular to the surface 221	Ditto	0.8	3.2 - 3.3
V: film ²¹⁶	Pb, s – s	1.8	~ 3.4
Zn: film ²²²			3.2 ± 0.1
2n: 111m	Al, s - s	0.1	3.2 ± 0.1

Table VII (cont'd.)

presence of several gaps in the spectrum of this superconductor, it being bound that the anisotropy of the gap is ~50% (values of $2\Delta/k_{\rm B}T_{\rm C}$ from 2.7 to 4.3). Recognizing that the greatest contribution to the tunnel current is made by electrons moving near the normal to the interface of the sandwich, the author attempted to explain the complicated character of the gap anisotropy of Sn (Fig. 17) as being due to singularities of the Fermi surface, using a simplest model, in which the gap is assumed to be constant on each of the cavities, and the gap anisotropy is connected with different gaps at different cavities. Within the framework of such a hypothesis, certain regions of gap values ($\sim 3.55 k_{\rm B} T_{\rm c}$ and $3.75 k_{\rm B} T_{\rm c}$) could be set in correspondence with the regions of the Fermi surface of Sn, constructed on the basis of the almost-free electron model^[192] (the first range of values is similar to the third hole surface, the second to the fourth hole surface, and probably to the fifth electron surface), whereas others ($\sim 4.3 \ k_{\rm B} T_{\rm C}$ and $3.1 k_{\rm B} T_{\rm c}$) deviate greatly from this model.* The interesting question of the possible identification of the smallest observed value of the gap $(2\Delta_{min} = 2.7 k_B T_c)$ within the framework of the assumed model, can unfortunately not be solved. (The gap anisotropy of Sn is dealt with also in [194, 195, 229].)

Indication of a gap anisotropy was subsequently observed in the investigations of the tunnel effect in Pb, ^[188, 196] Ta, ^[197] La, ^[198], Al, In, ^[195] and Nb, ^[230] and it was found that addition of Tl impurities to Pb destroys the fine structure of the I-V characteristic, as a result of the smearing of the gap anisotropy. ^[199] Rochlin and Douglass, ^[200, 201] and Rochlin^[202] have recently investigated the tunnel effect in thick films of Pb. The fine structure of the I-V (and of the dV/dI-V) characteristics, connected with the gap anisotropy, becomes manifest not only at a potential difference cor-

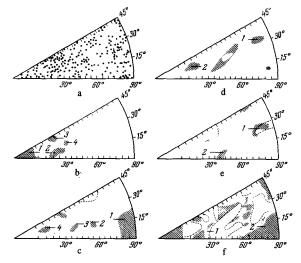


FIG. 17. a) Orientation of investigated tin samples on a conical equalangle projection of a sphere; the shaded regions denote the values of the gap $2\Delta/k_{\rm B}T_{\rm c}$: b) 4.3, c) 3.1, d) 3.4, e) 3.55, f) 3.7-3.8. At $(\theta,\varphi) = (58^{\circ}, 18^{\circ})$ and $(67^{\circ}, 6^{\circ})$ the gap is $2\Delta/k_{\rm B}T_{\rm c} = 2.7$ [¹⁹¹].

*Unfortunately, the Fermi surface of Sn, according to present-day notions [¹⁹³], differs from that used in the analysis of [¹⁹¹]; the changes occur in the bands II - VI.

responding to 2Δ of Pb, but also at a smaller potential difference (Fig. 18). A detailed analysis of the first of the indicated regions of characteristics has made it possible to relate values of the gap $2\Delta_c = 3.93 \text{ k}_B T_c$ and $4.11 k_{\rm B} T_{\rm c}$ with saddle points, and $4.8 k_{\rm B} T_{\rm c}$ and $4.21 \, k_{\rm B} T_{\rm C}$ with the maximum and average values of the gap on the entire Fermi surface of Pb (no minimum value of the gap was observed). The singularities of the characteristics at a smaller potential difference correspond to "subharmonics" V_c/n (up to n = 7, $1 \le k \le 8$), where $eV_c = \Delta'_c + \Delta''_c$ are the critical values of the gap in the sandwich films (concerning the mechanism of this fine structure, see also [203]). Although some of the obtained eight critical values of V_C (see Table VII, in which the middle values of the Pb gap, 2.71-2.75 MeV, have been omitted), are possibly averages of other (in spite of the fact that there are no values of $V_{\rm C}$ between known gaps, for example $3.93 \text{ k}_{\text{BT}_{\text{C}}}$ and $4.11 \text{ k}_{\text{BT}_{\text{C}}}$), the authors call attention to their large number, whereas the Fermi surface of Pb consists of only two rather smooth but greatly differing cavities (hole-in the second band and electron-in the third; the first band is filled; Fig. 19). The much greater anisotropy of the energy gap in the spectrum of this superconductor, than is called for by Bennett's theory^[15] (Fig. 20), is con-nected by the authors of $[^{201}, ^{202}]$ with the anisotropy of the electron-phonon interaction parameter, which was not taken into account in the development of the theory.

A brief communication of Yoshihiro and Sasaki^[243] presents data on the gap anisotropy of superconducting Ga, observed in a tunnel investigation of single crystals. $2\Delta = 3.63 \text{ k}_{B}\text{T}_{c}$ in the [001] and [100] directions, and (3.78-3.94) k_{B}T_{c} near [010], and the temperature dependence of the tunnel effect in the [110] direction near T_{c} of Ga can be described by a gap $3.78 \text{ k}_{B}\text{T}_{c}$ ($2\Delta = 3.63 \text{ k}_{B}\text{T}_{c}$ at $\text{T}/\text{T}_{c} < 0.55$). The great discrepancy

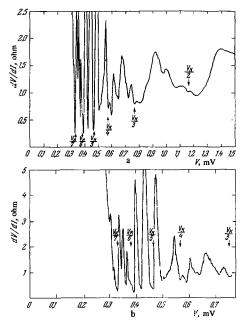


FIG. 18. Dependence of dV/dI on V at T = 1.18° K, for a sandwich consisting of thick Pb films separated by an insulator. One of the series of V_c/n is indicated for V_c = 2.31 MeV [²⁰²]. Pb₁: 2700Å, Pb₂: 1800Å; Pb-I-Pb junction 301-E, 1.18° K, H = 30 Oe.

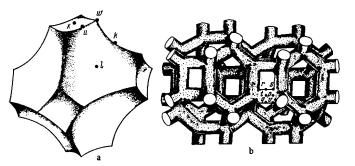


FIG. 19. Fermi surface of lead in accordance with the almost-free electron model. a) Hole surface in the second Brillouin zone; b) electron surface in the third zone (scheme of repeating zones) [²⁴⁴].

between these results (the character of the anisotropy and the magnitude of the gap) and the data obtained by measurements of the thermal conductivity^[67] and ultrasound absorption^[115] makes a further investigation of Ga very urgent.

It should be noted that the main shortcoming of the tunnel procedure is the fact that the obtained information characterizes a relatively small surface layer of matter (not deeper than ξ), and may not be typical for the superconductor as a whole.* In addition, the fine structure of the characteristics may be due to "traps" (impurity metallic atoms, oxygen-ion vacancy) in the dielectric layer between the elements of the pair.^[204]

III. CONCLUSION

From a general review of all the papers devoted to the investigation of the gap in the energy spectrum of superconductors—the gap being one of the few fundamental characteristics of the superconducting state of the metal—and to a determination of this gap, we can draw the following conclusions:

1. The presence of a temperature-dependent energy gap in the spectrum of the superconductor leads to important singularities in many of its physical properties, both thermodynamic and kinetic.

2. A superconductivity theory operating with an

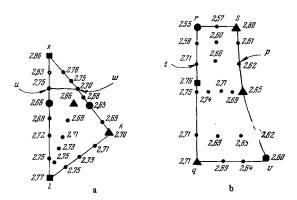


FIG. 20. Energy gap (in MeV) in superconducting lead: a) on the hole surface (second zone); b) on the electron surface (third zone). The Latin letters pertain to corresponding points of the Fermi surface of Fig. 19. The squares, triangles, and circles denote the values of the gap at the maxima, saddle points, and minima $[^{15}]$.

 16 This probably explains the scatter in the values of the gap obtained by various authors for the same superconductor (see Table VII).

idealized model of the metal with an isotropic singlyconnected Fermi surface and with an isotropic gap describes sufficiently well the main properties of superconductors.

3. Experimental investigations recently performed by various methods have established that the energy gap in the spectrum of pure superconducting aluminum, vanadium, gallium, indium, cadmium, lanthanum, molybdenum, niobium, tin, rhenium, lead, tantalum, thallium, and zinc is anisotropic.

4. The presently developing theory of anisotropic superconductors relates the appreciable anisotropy of the gap with the anisotropy of the Fermi surface of metals and with the anisotropy of their phonon spectrum. The value of the gap depends here not only on the energy of the quasiparticle and the number of the cavity of the Fermi surface, but also on the direction of the wave vector of the quasiparticle, and the gap anisotropy is appreciable within each of the cavities of the Fermi surface.

5. There are no published quantitative theoretical data on the local connection between the gap and the Fermi surface of superconducting metals or on the influence exerted on it by the real phonon spectrum (such results were obtained only for lead) and on the anisotropy of the parameter of the electron-phonon interaction.

6. In spite of the large number of experimental papers, no detailed ideas have been obtained as yet concerning the orientational dependence of the energy gap in real superconductors (with the exception of the relatively noncontradictory "map" of the gap in superconducting tin as obtained from data on the tunnel effect, ultrasound absorption, and surface resistance).

Thus, to gain a better idea concerning the superconducting state of real metals it is necessary to perform both further theoretical investigations of concrete superconductors, and detailed experimental studies of the superconductors, especially at low temperatures, preferably by selective methods.

The author is grateful to Academician of the Ukrainian Academy of SciencesB. G. Lazarev, to Professor V. L. Pokrovskiĭ, and to Doctor A. J. Bennett for interesting discussions.

APPENDIX

In view of the fact that the anisotropy of the energy gap of superconducting tin has been investigated in greater detail by direct methods, it is meaningful to attempt to compare the obtained results.* Account must be taken here of the difficulties of such an analysis, due to the specific features of the procedures, since the values of the gap measured in each of the procedures are not quite identical. For example, one of the difficulties in a quantitative comparison of the data of the most selective procedures—the results of ultrasonic investigations [104, 107, 108] of the energy gap of bulky superconducting tin (see Fig. 11) and of the data of tunnel measurements [109, 191] in the surface layer of this metal (see Fig. 17) is the fact that a contribution to the sound ab-

sorption can be made by the electrons of the bridges of the Fermi surface and of its section near the boundaries of the Brillouin zone, ^[224] where the velocity is $v_F \sim 0$,* whereas electrons, as one might assume, do not take any part in the tunnel effect. Furthermore, it is not quite clear how close the results of the near-surface (not deeper than ξ) investigations (tunnel effect) should be to volume measurements (absorption of ultrasound, and also the investigation of thermodynamic properties and threshold effects†);^[225] apparently, an additional difficulty lies in the fact that the singularities of tunnel characteristics (disregarding the possible influence of "traps" in the nonconducting layer of the sandwich^[204]) may be due not only to the gap anisotropy, but also to the energy dependence of the gap.‡

In spite of the fact that qualitatively the data on the energy gaps of tin are very similar, from the quantitative point of view there are slight differences between the extremal quantities—a systematic shift, the cause of which is still unclear, by approximately 15% (the values of the gap obtained by the tunnel procedure are smaller than those obtained by ultrasonic measurements). From a comparison of Figs. 11 and 17 we can conclude that the gap $2\Delta/k_{\rm B}T_{\rm C} \sim 3.1-3.2$ is located on the Fermi surface near the [100] direction (a similar conclusion is reached also by Waldram⁽¹⁶⁶⁾ in an analysis of the data of the surface impedance of superconducting tin; see Table VIII, which contains a summary of the values of the gap in tin obtained by various methods).

The second value $2\Delta/k_{\rm B}T_{\rm c} \sim 3.75$, obtained for this direction from data on the tunnel effect, differs greatly from the results of other procedures. We note that from symmetry considerations the value $2\Delta/k_{\rm B}T_{\rm c} \sim 3.1-3.2$ cannot be the absolute minimum of the gap in tin; in addition, from tunnel measurements, the smallest value $2\Delta/k_{\rm B}T_{\rm c} = 2.7$ belongs to two points on Fig. 17, with coordinates (θ , φ) ~ (58°, 18°) and (67°, 6°); the latter value, to be sure, differs from the values of the gap obtained by the same author^[40] from the thermal conductivity and the specific heat of tin at very low temperatures ($3.1k_{\rm B}T_{\rm c}$ and $3.2k_{\rm B}T_{\rm c}$). Inasmuch, as follows from the theory^[7, 11, 33], as the smallest gap should be manifest in these properties, the question of the exact value of $2\Delta_{\rm min}^{\rm abs}/k_{\rm B}T_{\rm c}$ in the spectrum of su-

perconducting tin remains open. As to the orientation, it is clear that the absolute minimum does not lie along

the principal crystallographic directions of the tin.

The magnitude and location of $2\Delta_{max}^{abs}/k_BT_c$ in tin are apparently not yet clear. It is seen from the ultrasonic data that the largest of the observed gaps, $4.8k_BT_c$, does not lie along the principal axes; furthermore, this value cannot be an absolute minimum, since the latter quantity does not enter in the formula for the absorption coefficient of sound and cannot be deter-

^{*} The data on the mean-square anisotropy of the gap of tin, $\langle a^2 \rangle \sim 0.02 - 0.03$, obtained by measuring the temperature dependence of H_c and ces and the shift of T_c under the influence of the impurity, are only qualitative in character.

^{*} In such a situation, probably, the ultrasonic measurements give not the miminal values but the effective values of the gap on the lines $k \cdot v_F = 0$.

 $[\]dagger$ Inasmuch as an appreciable depth of penetration of the electromagnetic field in the superconductor follows from the uncertainty relation near threshold [²²³].

[‡] The author is indebted to V. L. Pokorvskii for the last remark.

Measurement method	2∆/k _B T _c	$2\Delta_{\min}/k_{B}T_{c}$	Note
Electronic specific heat	3.6 ³⁹ 3.4 ^{48,49}	3.2 40	Measurement down to 0.2° K Value of gap to 0.4° K
Critical magnetic field	3.683		Value of gap to 0.3° K
Electronic heat conductivity	3.9 ⁶⁸	3.1 ⁴⁰ 3.0 ²³⁴	Measurement down to 0.2° K Measurement down to 1.0° K
Absorption of ultrasound	3.2 - 4.8 ^{104,110}	3.2 104, 105, 110	Measurement down to 1.0° K
Infrared absorp- tion at temper- atures at 1.4°K	$3.3^{173}, 3.6^{172}$ $4.2 - 4.5^{163}$		Structure of reflection edge
Infrared absorp- tion 242	3.58 ± 0.04 and 3.86 ± 0.08		Measurement at 1° K
Surface resis- tance near T_c , f = 140 GHz	3.6; 4.3?; ≥ 5.0? ¹⁶⁴		In direction of [001] $2\Delta/k_{\rm B}T_{\rm C} = 3.6$
Reflection and absorption of radiation f = 22 - 72 GHz	2.8 ¹⁸¹		Measurements down to 2° K
Surface impedance at temperatures to 2.5° K, f = 3 GHz	~2.9;~3.7 ¹⁶⁶	~2.9	In direction of [100] $2\Delta/k_BT_c \sim 2.9$ In direction of [001] and [110] $2\Delta/k_BT_c \sim 3.7$
Depth of penetra- tion of magnetic field	4.2 ¹⁸⁰		
Tunnel effect	$3.1^{207}, 3.7^{213} \\ 2.7 - 4.3^{109}, ^{191}$	2.7	Measurements down to 0.8° K Measurements down to 1.3° K

Table VIII.	Energy gap of superconducting ti	n as		
obtained by various measurements.				

mined. The largest value $4.3 k_{\rm B} T_{\rm c}$, in the [001] direction, obtained by tunnel investigations, differs from the results of the study of the surface resistance of super-conducting tin made by Adkins^[164] and Waldram.^[166] The values of the gap measured by these authors in the [001] were respectively $3.6 k_B T_c$ and $3.7 k_B T_c$ (according to Adkin's statement, there is only the single indicated value in this direction). The second value $3.8\,k_{\rm B}T_c,$ which was obtained in tunnel measurements for the [001] direction, agrees best with data obtained by other procedures; the ultrasonic measurement data can be treated in such a way that the gap in the considered direction lies in the range $(3.5-4.0)k_{\rm B}T_{\rm c}$ and apparently not larger than the upper value.* A certain indication that the value of the gap is $\sim 5.0 k_{\rm B} T_{\rm c}$ was obtained by Adkins; [164] in a study of the reflection of infrared radiation from the surface of single crystals of tin, Richards observed, for all orientations, a fine structure of the reflection edge at photon energies up to $4.5 k_{\rm B} T_{\rm c}$.^[163] It is quite probable that a further investigation of this structure will make it possible to refine the value of $2\Delta_{\min}^{abs}$ of tin.*

There is no disagreement with respect to the value of the gap in the region of the Fermi surface of tin near the third principal direction [110], namely, the gap amounts to $(3.7-3.8) k_B T_c$ as obtained by ultrasonic investigations, by surface-resistance data,^[166] and from the tunnel effect.

As to the "reconciliation" of the obtained values of the gap with the Fermi surface of tin, such a procedure is premature, first because the detailed structure of this surface is complicated (Fig. 21) and has not yet been sufficiently well studied; a slight change in this structure leads to an appreciable change of the orientation of v_F , i.e., of those regions of the Fermi surface, whose electrons take part in the tunnel effect and in the absorption of ultrasound. In addition, the assumption made in tunnel investigations of tin, ^[109, 191] namely, that the anisotropy of the gap in this superconductor is connected with the presence of strongly differing gaps on each of the cavities of the Fermi surface (with weak variation of the gap along each of them) contradicts the contemporary theoretical notions that the gap has an appreciable anisotropy within the limits of each of the cavities of the Fermi surface.[14,15]

Summarizing, we can assume that the results of the measurements of the energy gaps in superconducting tin, obtained by various methods, agree sufficiently well with one another and make it possible to assume with assurance that the gap anisotropy in this superconductor exceeds 50%.[†] To establish the local connection

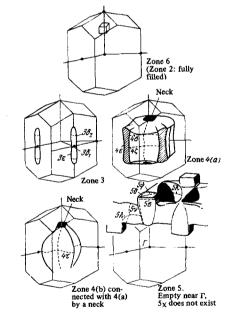


FIG. 21. Systematic representation of the Fermi surface of tin. The first and second zones are filled, zones 4(a) and 4(b) are connected with a bridge [¹⁹³].

^{*} It is interesting to note that in a review of Douglass and Falikov $[^{25}]$, based on sketchy data of earlier work, they advance the correct opinion that the smallest gap in tin should be less than 3.1 kBT_c, and the largest greater than 4.3 kBT_c; it seems that in all other respects the analysis of the gap of tin made by these authors belong with the prediction of the orientation of the extremal values of the gap along the principal axes, is inaccurate.

^{*} Owing to the large anisotropy of the gap in tin, the main absorption edge is strongly smeared out, making it impossible to determine the $2\Delta \hat{m}_n/k_B T_c$.

[†]Such an appreciable anisotropy can apparently lead to a better agreement between theory [^{18,226}] and the experimentally observed decrease of T_e of Sn under the influence of impurities [²²⁷].

between the values of the gap and the entire Fermi surface of tin, further theoretical and experimental research is necessary.

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Notes added in proof: 1(p. 696). As shown in a recent investigation of T1 (T. A. Ignat'eva, V. I. Makarov, and N. S. Treshina, Zh. Eksp. Teor. Fiz. 54, 1617 (1968) [Sov. Phys. - JETP 27, 865 (1968)], the meansquare gap anisotropy $\langle a^2 \rangle \approx 0.058$ remains practically unchanged in the pressure interval 0 = 1.7 kbar. 2(p. 697). According to ultrasonic data (A. C. Sinclair, Proc. Phys. Soc. 92, 962 (1967), the energy gap in In is anisotropic: $2\Delta/k_BT_c = 2.0 - 3.4$.

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