

which scientific and technical problems have been solved and the results put into practical operation. This can be explained only by the close and friendly contact between science and technology, which is possible under our government. It is possible mainly because in our socialist country there is only one all-powerful landlord, and that landlord is the people. Under capitalism, where industry is in private hands and companies are often competing against one another, scientific organizations are largely left to their own devices. The coordinated activity of all scientific and industrial resources, which is naturally and simply achieved in a socialist country, is under capitalism impossible.

The rate of growth of Soviet physics, and of all branches of science, is nevertheless influenced by our contacts with foreign science. We all believe that the basic task of science is the understanding of nature, and the basic purpose of this understanding is the conquest of nature for the benefit of mankind.

Scientific truth is one, and the more rapidly it is discovered and the more intensively science is developed the greater the benefit to all mankind. Nowhere in the history of human culture has international co-operation given such great benefits to humanity as in the field of science.

We are very happy that in all these years our journal has not only been widely read here in the Soviet Union but has also had a wide foreign circulation. We welcome the recent appearance of the "Journal of Experimental and Theoretical Physics" overseas in an English translation.

International professional contacts between scientists are valuable not only to progress in science. Understanding between scientists leads also to understanding and trust between countries. Peaceful co-existence, so necessary for happy and prosperous human life, is impossible without trust between peoples. Physicists more than anybody else should now be concerned for peace, since they have the responsibility before mankind for putting into our hands weapons of annihilation which if carelessly handled could lead to misery on an unprecedented scale.

Translated by F. J. Dyson

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INVESTIGATION OF THE THERMAL PROPERTIES OF SUPERCONDUCTORS

1. TIN (DOWN TO 0.15°K)

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Measurements have been made of the thermal and thermometric conductivities of several samples of tin in the range from 0.15 – 4°K. These make it possible to determine the specific heat of tin down to 0.15°K. It has been found that, below 0.45°K, the specific heat is due to the lattice and varies according to Debye's law, with $\Theta_D = 202 \pm 3^\circ\text{K}$. Above 0.45°K, the specific heat of the electrons appears, which depends on temperature as $c_{eS} = A(T) \times \exp(-\alpha T_C/T)$. The free energy of the superconducting electrons below 3°K, determined on the basis of these measurements, can be represented as $F_{eS} = BT^n \exp(-\alpha T_C/T)$, where $B = 8.7 \times 10^{-4}$ joules/g-mole-deg, $n = 2.5 \pm 0.5$, $\alpha = 1.35 \pm 0.1$. The thermal conductivity of tin below 0.3°K for all specimens is due to the heat transfer by the phonons; one of the samples exhibited a reflection effect of the phonons from the mirror surface. For higher temperatures, the thermal conductivity of the electrons varied for all samples as $K_{eS} = \text{const} \cdot \exp(-\beta T_C/T)$, $\beta = 1.45 \pm 0.05$. The results are discussed from the point of view of the presence of an energy gap in the excitation spectrum of superconductors.

AS is well known, the analysis of data on the thermal properties allows us to obtain a number of indications concerning the energy excitation spectrum in solids. We can obtain the most definite conclusions in this case on the basis of the analysis of the specific heat of bodies over a wide range of temperatures,

extending to the lowest temperatures possible. This latter is connected with the fact that the strictest theoretical considerations of the phenomenon are usually successfully carried through only in the region close to absolute zero, where the number of excitations is small. At the present time, information on the specific heat of bodies in this temperature region is limited. This also applies to the phenomenon of superconductivity. Fundamental measurements of the specific heat of superconductors¹⁻⁴ have been made only in the temperature range down to $T_c/T = 3$, and do not allow us to draw any unique conclusions as to the character of the energy excitation spectrum. Furthermore, experiments⁵⁻⁷ recently carried out in the temperature interval down to $T_c/T = 4$ have shown that the temperature dependence of the specific heat of superconductors discussed earlier does not correspond to reality.

The problem of the thermal conductivity is much clearer at present; at least, completely substantiated results have been obtained in a number of works⁸⁻⁹ down to $T_c/T = 10$.

The aim of the present research was the investigation of the thermal properties of superconductors over the widest temperature range possible. Since the critical temperature for most superconductors amounts to a few degrees, measurements of the specific heat down to temperatures of a few tenths of a degree are necessary for the solution of the problem. At these temperatures, the specific heat of most substances is negligible, which poses difficulties in the application of the direct method of measurement of the specific heat. As a consequence of this fact, an indirect method has been chosen for the measurements, based on a calculation of the specific heat of a body from its thermal conductivity K and its thermometric conductivity $a^2 = K/c\rho$. The methods worked out at the present time permit us to measure the

thermal conductivity of materials with relative ease at temperatures down to a few tenths of a degree, and the value of the thermometric conductivity can be determined by the method of temperature waves, already suggested by Angstrom.¹⁰ The idea of this method is as follows. If the periodic variation of the temperature is $T(0, t) = A \cos \omega t$ at the point $x = 0$ of an infinite specimen, then a temperature wave

$$T(x, t) = Ae^{-kx} \cos(\omega t - kx), \quad (1)$$

will be propagated, where

$$k = (1/a) \sqrt{\omega/2}.$$

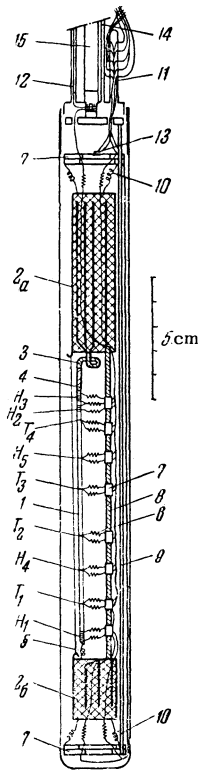


FIG. 1. Apparatus for the determination of thermal conductivity and temperature conductivity, (1) Sample under investigation; (2a, 2b) blocks of ferric ammonium alum; (3) copper heat conductors; (4) thermal resistance (bronze, of diameter 2 mm); (5) spring to draw lower end of sample with caprone thread; (6) coil of tinned constantan; (7) plexiglass blocks for fastening the leads; (8) copper rod for fastening the low-temperature components of the apparatus; (9) supporting frame (it consists of three bronze guide rods of 1.5 mm diameter and brass rings to which the salt is attached. All joints are sliding with stop screws); (10) spring for suspending the salt; (11) terminals of conductors from the apparatus by means of platinum sealed into the glass; (12) tube for the exit of conductors from thermometers T_2 and T_3 ; (13) carbon thermometer; (14) tube for evacuating and filling the apparatus with helium; (15) steel tube for fastening the apparatus; T = thermometers; H = heaters.

Thus, for the measurement of the thermometric conductivity, it suffices to determine either the propagation velocity of the temperature wave, or the law according to which its damping takes place. Until recently, the method of temperature waves has been applied only in the region of high temperatures;¹¹ very recently, it has been used in the region of liquid helium temperatures.¹² For low temperatures, this method takes on a number of specific peculiarities which are brought about by the sharp decrease in the specific heat, and correspondingly by an increase in the thermometric conductivity. As a consequence, while the length of the temperature wave for room temperatures amounts to centimeters at frequencies of hundreds of cycles, at helium temperatures these frequencies amount to thousands of cycles, which permits the use of standard radio methods in the measurements.

Tin was chosen as the object of investigation for the following reasons. In the first place, the new method of measurement of the specific heat is most successful on material whose specific heat has been

sufficiently well measured by generally accepted methods, if only in a narrow range of temperatures.^{1,13,14} Second, the specific heat of the lattice and the superconducting electrons in the chosen material must be comparable in order to obtain even a preliminary indication as to the character of the change of both these quantities from analysis of the data.

METHOD OF MEASUREMENT

The apparatus used to determine the thermal and thermometric conductivities of samples at temperatures below 1.5°K is shown in Fig. 1. Cooling of the sample 1 was accomplished by two blocks of ferric ammonium alum 2a and 2b, the temperature of which was lowered by adiabatic demagnetization. To switch from isothermal magnetization to adiabatic demagnetization we used a method based on the absorption of residual gas by the salt.¹⁵ The quantity of residual gas in the apparatus was controlled by heating the carbon thermometer 13, which is suspended on thin constantan conductors. The sample was cooled by means of the copper rod 3 of 2 mm diameter, the end of which, flattened out into a band of about 3 cm width, was pressed into the salt. A bronze rod 4 was sealed in between the sample and the copper heat conductor. The thermal resistance of this rod could be used to heat the sample up to one degree relative to the salt. For measurement, we used a coated carbon resistance thermometer. Thermometers T_2 and T_3 served to measure the thermometric conductivity of the sample, while thermometers T_1 and T_4 were used both to measure the thermal conductivity and to determine the temperature of the sample. These thermometers were calibrated in the course of each experimental run. Determination of the temperature was carried out by means of the susceptibility of the alum. To change from magnetic to absolute temperature, we used the data of Cook et al. of 1956.¹⁶

Several heaters were located on the sample. Heaters H_1 , H_2 and H_3 were prepared from manganin wires, H_1 and H_2 being used in the measurement of the thermal conductivity of the sample and H_3 serving to increase the temperature of the sample above the temperature of the salt. The film heaters H_4 and H_5 were used in experiments on measurement of the thermometric conductivity of the sample. The electrical wiring inside the apparatus was accomplished by means of constantan wires coiled in springs. These wires were of diameter 50μ , and were initially plated with a superconducting layer. To reduce electrical induction in measurements of temperature conductivity, the wires from the thermometers and the heaters were led separately through the salts 2a and 2b respectively.

The arrangement for the measurement of thermal conductivity did not differ from that used by us earlier¹⁷ in the measurements at much higher temperatures. The mean error amounted to about 5% for a temperature gradient along the sample of several percent of the mean temperature. The accuracy of determination of the thermal conductivity was limited in this case not only by errors in the measurements of the temperature gradient along the sample or the power consumed in heating, but also by errors connected with the determination of the absolute temperature of the specimen. As a consequence of the fact that the thermal conductivity changes sharply with temperature, an error of 1% in the determination of the temperature is equivalent to three to eight times greater error in the thermal conductivity. On the other hand, it is hardly possible to determine an absolute temperature lower than 1°K by the generally accepted method of the susceptibility of a paramagnetic salt with an accuracy better than one percent.

Determination of the thermometric conductivity a^2 was carried out by means of the phase shift $\Delta\varphi$ of the temperature oscillations at two points of the specimen, the amplitude of which in all measurements did not exceed a few per cent of the mean temperature. As is easily seen from (1), $\Delta\varphi = k\Delta x$ for an infinite specimen, where Δx is the distance between the points at which the measurement is made, and

$$a^2 = \Delta x^2 \omega / 2 \Delta \varphi^2. \quad (2)$$

The method of temperature waves, which is simple in principle, requires a number of precautions. Above all, the temperature oscillations of the film thermometer, in spite of its minute dimensions, do not coincide with the temperature oscillations of the sample (the thickness of the coating of the carbon thermometer does not exceed 0.20 mm).

These phenomena are probably connected both with the small thermometric conductivity of the carbon and with the presence between the thermometer and the sample of a layer of BF₂ dope of about 10μ thickness, which serves as an electrical insulation of the thermometers from the sample. As a consequence, if φ is the phase shift of the temperature oscillation of the sample at the location of the thermometer relative to the signal from the generator, then the measured phase shift is $\xi = \varphi + \psi$, where ψ depends

on the construction peculiarities of the given thermometer. Correspondingly, the measured phase difference between the signals will be

$$\Delta\zeta = \varphi_1 - \varphi_2 + \psi_1 - \psi_2.$$

Here, the quantity $\psi_1 - \psi_2$ can reach 30% of the quantity $\varphi_1 - \varphi_2$. However, since ψ does not depend on the direction of the temperature wave, $\psi_1 - \psi_2$ can be eliminated if we make use in the measurements of the temperature waves which are propagated in the two opposite directions. Actually,

$$\Delta\zeta^+ - \Delta\zeta^- = \varphi_1^+ - \varphi_2^+ + \varphi_2^- - \varphi_1^-,$$

where the plus and minus refer to the waves in different directions. We can obtain the actual value of the phase shift along the sample only if

$$\varphi_1^+ - \varphi_2^+ = \varphi_2^- - \varphi_1^-,$$

i.e., the law of phase change along the specimen is the same for waves of both directions. This holds either for an infinite specimen or when an identical reflection of the wave takes place from the ends of the sample. In the latter case, however, the connection of the phase shift and the thermometric conductivity is complicated, which makes the treatment of the results difficult. For example, as is easy to show, for thermal insulation of the end of the sample, $\varphi(x) = \arg \cosh k(1+i)x$, where x is the distance from the end of the sample, and correspondingly

$$\Delta\varphi = \arg \cosh k(1+i)x_1 - \arg \cosh k(1+i)x_2. \quad (3)$$

Therefore, it is always desirable to have conditions in which the effect of the reflected wave is negligibly small.

In the work the measurement of the phase shift was carried out between thermometers placed in the central part of the sample, so that the distance to each of the ends of the sample exceeded by two the distance between them.

TABLE I. Phase shift $\Delta\varphi$ of the temperature wave along finite and infinite specimens.

Ratio of the distance between thermometers to the wavelength	$\Delta\varphi_\infty$ in radians	$\Delta\varphi_{\text{fin}}$ for $2x_1 = 3x_2\Delta\varphi$, in radians
0.1	0.314	0.408
0.12	0.376	0.500
0.15	0.472	0.600
0.20	0.628	0.690
0.225	0.706	0.735
0.25	0.795	0.792
0.30	0.940	0.930
0.375	1.178	1.168
0.500	1.571	1.571

If we compare $\Delta\varphi_\infty$ for the infinite specimen and $\Delta\varphi_{\text{fin}}$ computed according to (3) for the chosen geometry, for various ratios of the distance between the thermometers $\Delta x = x_2 - x_1$ to the length of the temperature wave $\lambda = 2\pi/k$, then it turns out (see Table I) that for $\Delta x/\lambda \geq 0.25$, the difference between the phase shifts $\Delta\varphi_\infty$ and $\Delta\varphi_{\text{fin}}$ does not exceed 1%. In actuality, this is the upper limit of possible deviation, since only one end of the sample is thermally insulated. At the point of connection of the sample with the bronze, only partial reflection of the wave takes place. We can estimate the magnitude of the amplitude of the reflected wave in terms of data on the thermal conductivity and specific heat of the bronze and the tin. For equal diameters of the sample and the bronze rod, it amounts to about 90% of the amplitude of the incident wave for 1°K, and to about 30% for 0.3°K.

Reflection of the temperature wave also takes place from inhomogeneities in the cross section of the specimen, especially from the thermometers and heaters located on the sample. This effect could play an especially important role for temperatures of a few tenths of a degree, where, because of the different temperature dependence of the specific heat of the tin and the copper wires leading to the thermometer, the specific heats of the thermometer and of the cross section of the sample which it occupies are equal. It is also easy to compute the reflection of the wave from the thermometer, under the assumption that it takes part as a whole in the temperature oscillations of the sample. If the dimensions of the thermometer are much smaller than the wavelength of the temperature wave, then the ratio of the reflected wave to the incident is

$$\gamma \approx \frac{c_t \pi \Delta}{c_s \lambda},$$

where c_s and c_t are respectively the specific heat of the sample and the thermometer; λ is the length of the temperature wave, Δ is the width of the thermometer. Assuming that the specific heat of the thermometer is equal to the specific heat of the cross section of the sample, it is easy to obtain that for $\Delta = 0.2$ mm, at wavelengths greater than 4 cm, $\gamma \approx 10^{-2}$. In reality, the amplitude of the reflected wave

from the thermometers and the heaters is still smaller, since the temperature oscillations of the thermometer, especially at high frequencies, are much less than the temperature oscillations of the specimen. In particular, this appears as a sharp decrease in the signal from the thermometer for increase of the frequency of the temperature oscillations (in a frequency change from 40 to 800 cps, the signal decreases by a factor of 20). All that has been pointed out above shows that the effect of reflection of the temperature wave from the thermometer cannot have a material effect on the measurements. This is further confirmed by the absence of the effect of the mutual location of the thermometers and heaters on the results of the measurement of the thermometric conductivity (see below).

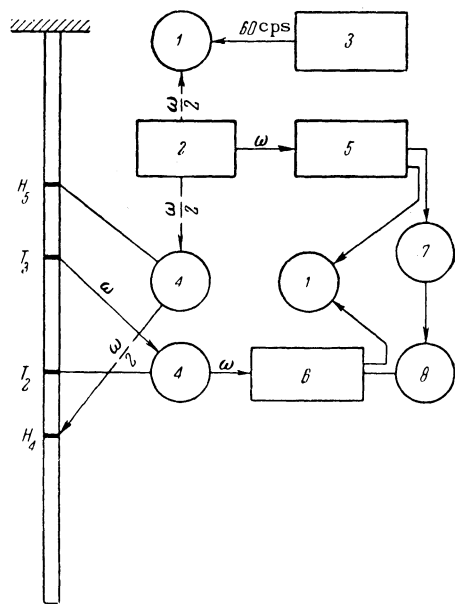


FIG. 2. Circuit for measurement of thermometric conductivity. 1—oscillograph, 2—generator, 3—quartz generator, 4—switch, 5—tuned filter, 6—tuned amplifier, 7—phase shifter, 8—phase detector.

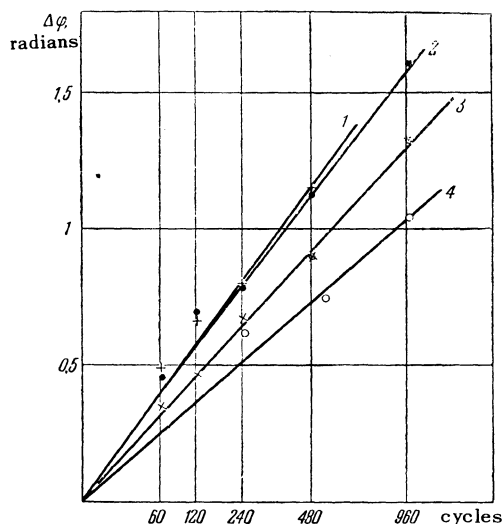


FIG. 3. Dependence of the phase shift on the frequency f of the oscillator. Sample Sn 2; distance between thermometers 23.2 mm, length of sample 100 mm. 1— $T = 4.35$; 2— $T = 0.558$; 3— $T = 0.730$; 4— $T = 1.12^\circ\text{K}$. Abscissa is plotted in terms of $f^{1/2}$.

A block diagram of the apparatus used for the measurement of the phase shift is shown in Fig. 2. The signal from an oscillator of frequency $\omega/2$ is applied to the heaters H_4 or H_3 . Since the heat liberated in the heater is proportional to I^2R , a temperature wave of frequency ω is propagated along the sample. The signal from thermometer T_2 or T_3 is fed to a tuned amplifier of center frequency ω and with a bandwidth of 10% of the center frequency. From the output of the amplifier, the signal is fed to an oscilloscope which serves as a control of the amplitude of the signal from the amplifier and to a cathode follower which is connected to a phase lag detector.¹⁸ A signal is also applied to the phase detector through a calibrated phase-shifter from a separate generator of frequency ω . In order to increase the stability of the circuit against possible changes in the frequency, this signal was passed through a filter exactly the same as that used in the amplifier. The measurements were carried out by a null method. Successive measurements were made of the phase angle between the signals from thermometers T_2 and T_3 and from the generator, which made it possible to determine the phase shift between the signals from the thermometers. In this case, by this method of measurement, one of the signals on the phase lag detector was of a strict definite frequency ω , and the whole circuit was little sensitive to a stray electric pickup. The error in the determination of the angle between the signals from the thermometers did not exceed 0.01 radian ordinarily, and was governed with the accuracy of calibration of the phase shifter. The measurements were carried out at several frequencies, multiples of 60 cps — the frequency of the quartz generator which served for testing the frequency of the fundamental generator. Before the measurements the oscillator was usually turned on and the dc current through the thermometers left turned off to check whether the thermometers picked up any extraneous signals.

The typical dependence of the phase shift of the temperature wave along the sample $\Delta\varphi = (\Delta\xi^+ - \Delta\xi^-)/2$ on the frequency of the oscillator $f = \omega/2\pi$ is plotted in Fig. 3. For sufficiently high frequencies, even in an infinite sample, $\Delta\varphi$ is proportional to $f^{1/2}$; in the region of much lower frequencies, there are observed significant departures from the proportionality of $\Delta\varphi$ and $f^{1/2}$, which is in qualitative agreement with the calculation of the effect of the reflected temperature wave from the end of the sample, carried out above. Therefore, the fundamental measurements were carried out only at frequen-

K in W/cm-deg

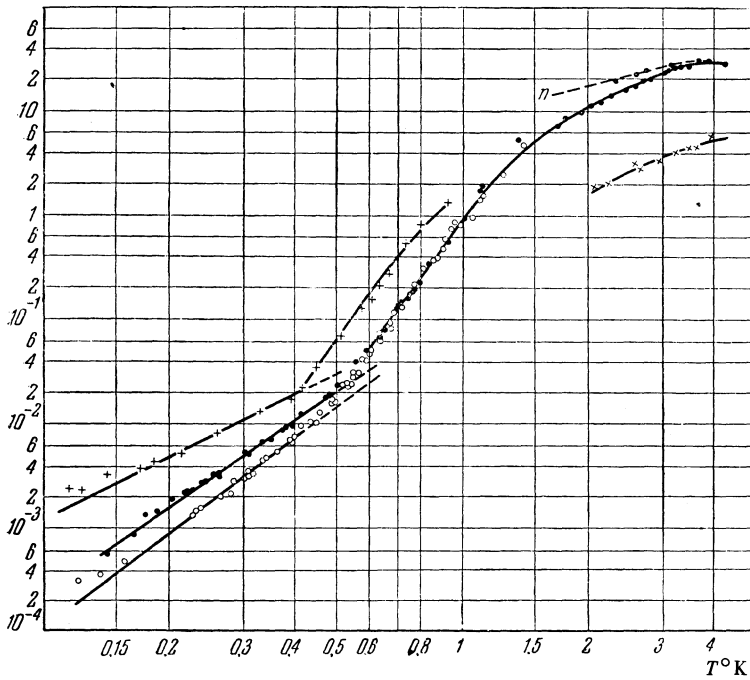


FIG. 4. Thermal conductivity of investigated samples of tin. n — thermal conductivity of tin in normal state. × — sample 1, ● — sample 2, ○ — sample 3, and + — sample 4.

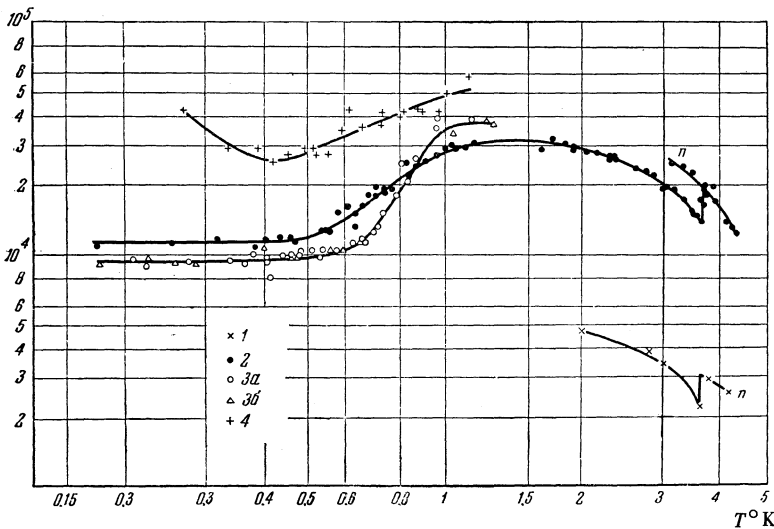
 α^2 in cm^2/sec 

FIG. 5. Thermometric conductivity of investigated samples. 1, 2, 3, 4 — number of samples, n — tin in the normal state; 3a and 3b — measurements for different reciprocal positions of thermometers and heaters; a — distance between thermometers 15.6 mm, from thermometer to nearest heater 15 mm; b — distance between thermometers 20 mm, to heater 5 mm.

TABLE II. Characteristics of samples

Number of sample	Percentage impurity	State of surface	Angle between axis of sample and (001) direction	Diameter mm
Sn 1	0.1	polished	—	1.89
Sn 2	0.002	rough	30°	1.72
Sn 3	0.002	rough	70°	1.40
Sn 4	0.002	polished	45°	1.81

cies for which the phase shift ≥ 0.8 radian and for which we can make use of Eq. (2) in the calculation of the thermometric conductivity.

For testing the reliability of the method selected, the measurement of the heat capacity was carried out on several samples with different thermometric conductivities. The characteristics of the samples studied are plotted in Table II. The samples were placed in a vacuum in a thin walled capillary of plexiglass; right after the casting, monocristallization of the sample took place. The glass was usually removed by etching with hydrofluoric acid. For preparation of the specimen Sn 4, such a thin wall capillary was chosen that after casting of the tin, the glass cracked and fell off the specimen without external action.

RESULTS OF MEASUREMENT

The results of the measurement of thermal conductivity of the samples are given in Fig. 4. The measurement of each of the samples extended over several days, with interruptions sometimes lasting several months.

The average scatter of points amounted to about 5%. A connection was observed between the mean error and the character of the change of conductivity with temperature. In the range $T > 0.5^\circ\text{K}$, where a much sharper change of thermal conductivity takes place with change in temperature, it does not exceed 4%. All this is in agreement with the analysis of errors worked out above.

In Fig. 5, results are given for the measurement of the thermometric conductivity of all samples studied.

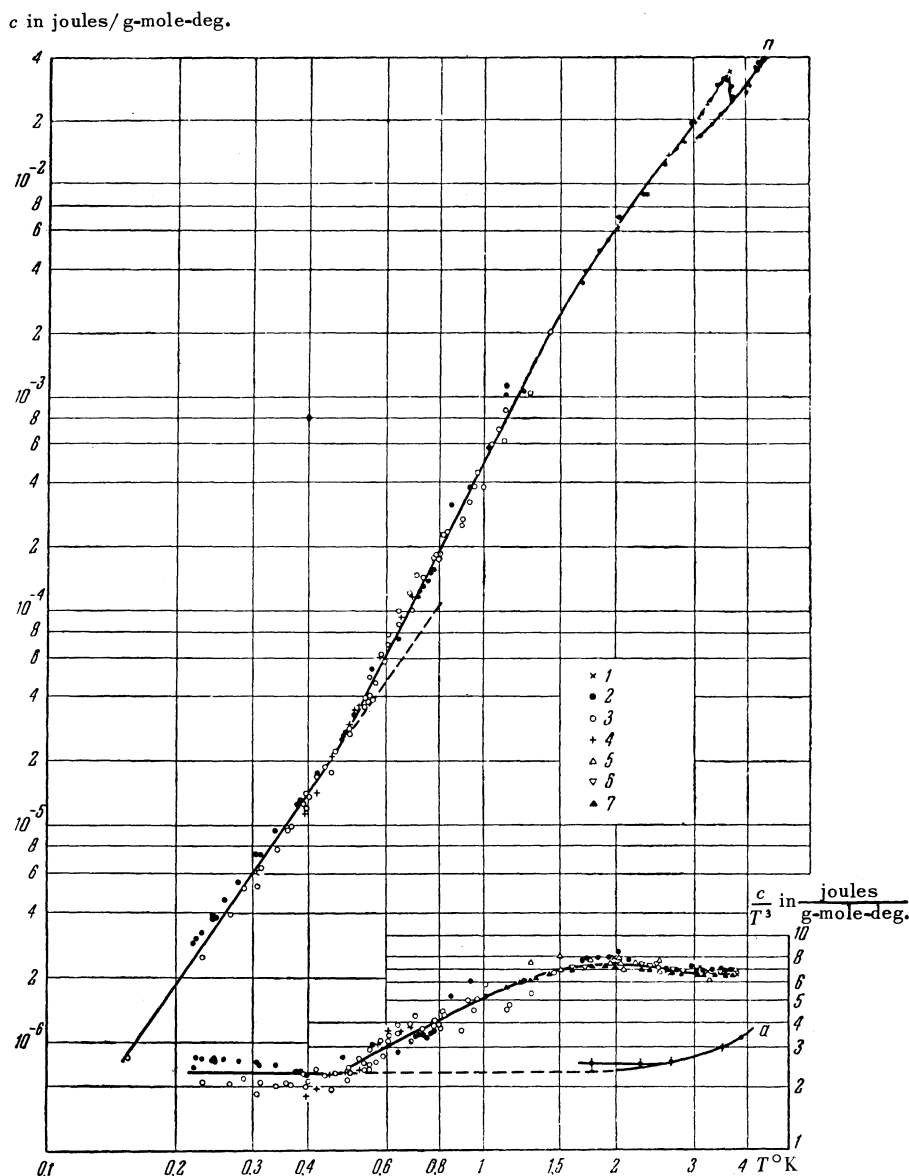


FIG. 6. Heat capacity of tin. 1, 2, 3, 4 — our measurements, n — normal state, 5, 6, 7 — calorimetric measurements; 5 — from the data of Ref. 1, 6 — from the data of Ref. 13, 7 — from the data of Ref. 14; a — heat capacity of the lattice from Ref. 14. The ordinate is plotted in terms of $(c/T^3) \times 10^4$.

thermal and thermometric conductivities of the samples studied differ in absolute value (up to 8 times), the temperature dependence of the heat capacity is the same for all samples. This is an additional confirmation of the reliability of the method of measurement employed. We note that in the region of helium temperatures the values of the heat capacity we obtained are, within the limits of accuracy, in agreement with the results of their determination by calorimetric methods.^{1,13,14}

* The results of measurement of the thermal conductivity of sample Sn 4 at $T > 0.8^\circ\text{K}$ are not very reliable, since even for the highest frequency $\omega = 1.22 \times 10^4$, the phase shift along the sample for several measurements did not exceed 0.8 radian. These data were not used in the determination of the heat capacity.

As in measurements of thermal conductivity, measurement of each sample was extended over several days, between which the arrangements of thermometers and heater on one of the samples (Sn 3) was completely changed. The mean error in the determination of the thermal conductivity does not exceed 2.5%, which agrees with the characteristics which apply to a radio circuit.*

The results of the calculation of the heat capacity of the samples from their thermal and thermometric conductivities are given in Fig. 6. In this case, at temperatures above 1.7°K , where the thermometric conductivity is more strongly changed than the thermal conductivity, the mean value of the thermal conductivity and the exact thermometric conductivity were used; for temperatures lower than 1.7°K — conversely — we used the mean value of the thermometric conductivity and the exact thermal conductivity. The mean scatter of the values of the heat capacity for temperatures below 1°K amounted to about 7% and at temperatures higher than 1.5°K to about 2%, which is in agreement with the accuracy of measurement of the thermal and thermometric conductivity. We note that the value of the heat capacity obtained can differ systematically from the true value by 3–5% because of possible errors in the determination of the geometric dimensions of the samples and the distance between thermometers.

If we compare Figs. 4, 5, and 6, it is easy to note that while the

DISCUSSION OF RESULTS

Heat capacity. As is well known, superconductivity is connected with the excitation of a new state of the electrons, in which they can move through the metal without the transfer of heat. At absolute zero, evidently, all the electrons are in this state, while at temperatures different from zero, some of the electrons pass over into the excited state, which is perhaps close to the state of the electron in the normal metal. It is natural that the electrons carry a contribution to the heat capacity of the superconductor c_{es} , connected perhaps with the change in the number of excitations with temperature.

Results of measurement show (Fig. 6) that in the interval from 0.2 to 0.45°K the heat capacity of tin in the superconducting state is proportional to T^3 , i.e., just the same as the heat capacity of dielectrics for

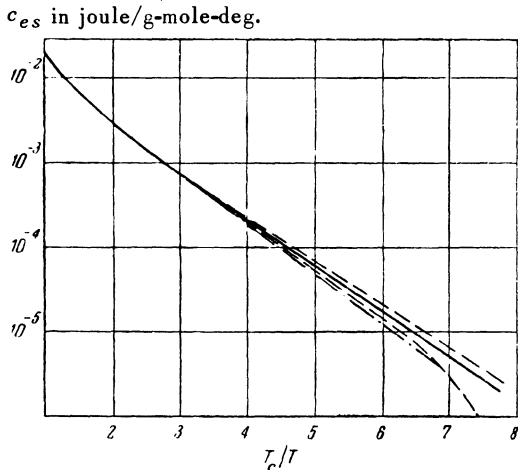


FIG. 7. Electronic heat capacity in tin in the superconducting state. The dashed lines represent the mean error, the dot-dash is $c_{es} = A \exp(-1.5 T_c/T)$.

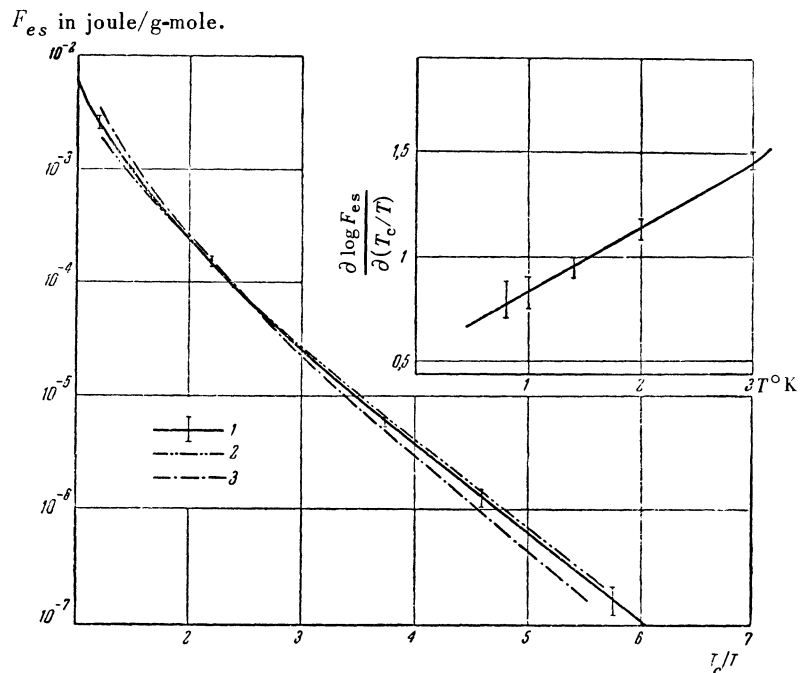


FIG. 8. 1 — Free energy of the electrons in tin in the superconducting state and the temperature dependence of its logarithmic derivative; vertical lines indicate mean errors; 2 — $F_{es} = 1.2 \times 10^{-3} T^2 \exp(-1.45 T_c/T)$; 3 — $F_{es} = 5.3 \times 10^{-4} T^3 \exp(-1.25 T_c/T)$ joule/g-mole.

sufficiently low temperatures. Therefore, it is natural to assume that below 0.45°K the heat capacity of tin is due in general only to the lattice. In this case, although the absolute value of $c/T^3 = 2.36 \pm 0.10 \times 10^{-4}$ joule/g-mole-deg⁴ (this corresponds to $\Theta_D = 202 \pm 3^\circ\text{K}$)

is 10% smaller than the limiting value of c_p/T^3 (c_p = heat capacity of the lattice), obtained from the analysis of the heat capacity of tin in the normal state,¹⁴ it is not excluded that in actuality this difference is due to an insufficiently accurate determination of c_p above 1°K, and the heat capacity of the lattice in the normal and the superconducting states agree with one another, changing with temperature in accord with the curve denoted by the dashed line in Fig. 6. The entire difference between c and c_p from this point of view is due to the heat capacity of the electrons.

The dependence of the heat capacity on T_c/T is plotted semi-logarithmically in Fig. 7. It can be represented in the form of the expression $c_{es} = A(T) \exp(-\alpha T_c/T)$. It should be emphasized that if in the heat capacity which is not connected with the lattice, a term is present which is proportional to T^3 , as follows from a series of theoretical researches,^{19,21} then its value at the critical temperature does not amount to 5% of the total electronic heat capacity. It should be noted that recently a series of experimental researches^{6,14} reached conclusions on the change in the heat capacity of superconductors according to the much simpler law $c_{es} = \text{const} \exp(-1.5 T_c/T)$. These results show that the erroneous results were probably connected with an insufficiently wide interval of measurement of the heat capacity (the measurements were carried out only down to $T_c/T = 4$).

From the analysis of the dependence $c_{es} = \Phi(T_c/T)$, it could be established only that the factor of the exponent is some polynomial function of T . However, it could be expected that on the basis of ther-

modynamic functions it will have a simpler form. We therefore determined by double integration the part of the free energy of the electrons in the superconductor depending on the temperature [F_{ES} (Fig. 8)]. The temperature independent part of the free energy F_{ES0} can be obtained from the equality of the free energy of the electrons in the normal and superconducting states at the critical temperature. Under the assumption of the equation for the free energy of the electrons in the normal state $F_{en} = \frac{1}{2}\gamma T^2$, where $\gamma = 1.75 \times 10^{-3}$ joule/g-mole-deg is a constant in the linear law of variation of the heat capacity, $F_{ES0} = (5.8 \pm 0.4) \times 10^{-3}$ joules/g-mole, which corresponds to the critical magnetic field for 0°K , $H_{C0} = 301 \pm 6$ oersted. This value, within the limits of accuracy of determination, agrees with the results of direct measurements of the critical magnetic field.

If the multiplier of the exponential in the free energy depends on temperature, then this manifests itself primarily in the change in the value of $\partial \log F_{ES} / \partial (T_C/T)$. Thus, if $F_{ES} = B T^n \exp(-\alpha T_C/T)$, then

$$\frac{\partial \log F_{ES}}{\partial (T_C/T)} = \frac{1}{2.3} \left(\alpha + n \frac{T}{T_C} \right),$$

which lets us determine both the quantity α and also n . Analysis of the dependence of $\partial \log F_{ES} / \partial (T_C/T)$ on the temperature in the interval from 0.8 to 3°K (Fig. 8) shows that $\alpha = 1.35 \pm 0.1$; $n = 2.5 \pm 0.5$ and correspondingly, $B = 0.7 \pm 3.4 \times 10^{-4}$ joule/g-mole-degⁿ (of course, all these quantities are in functional relation). As an illustration of the character of the change in the quantity F_{ES} in its dependence on n and α , we have also drawn $F_{ES} = \psi(T_C/T)$ in Fig. 8, under the assumption of the most extreme values of n and α .

It should be noted that the exponent n characterizes only the general change of the factor before the exponent, which can actually have a more complicated form.

Thermal conductivity. As is well known, the thermal conductivity of a metal can be represented as the sum of electron and lattice conductivities. In the case of a superconductor, we can thus consider separately the thermal conductivity of the electrons K_{ES} and of the lattice K_{PS} . As studies have shown, in the region of sufficiently low temperatures, the lattice plays an essential role in the transfer of heat. Let us consider our results from this point of view.

The thermal conductivity and heat capacity of the lattice are related: $K_p = \frac{1}{3} \ell u c_p$, where ℓ is the mean free path of the phonon, u is the mean velocity of sound, c_p is the heat capacity. As is known, in perfect dielectric crystals at temperatures below $\Theta_D/30$ (Θ_D is the Debye temperature) the mean free path is determined by the dimensions of the sample and by the condition of its surface. In samples with a rough surface, from which phonons are reflected diffusely, the path length does not depend upon the temperature, coinciding with the diameter of the sample. At temperatures below 0.45°K , this is observed in the samples Sn 2 and Sn 3 investigated by us. Thus, the free path length in these samples is shown to be equal to 1.45 mm and 1.18 mm, respectively, which, taking into account the approximate character of the method of determination of this quantity, we can consider reasonably satisfactory agreement. However, while the path length does not change with temperature in Sn 3 ($K_p \sim T^3$), in Sn 2, a certain increase in the free path length takes place upon decrease in temperature in Sn 2 ($K_p \sim T^{2.9}$). Evidently this is connected with the presence of reflection of the phonons from the surface of the sample. This effect is especially sharp in the sample Sn 4, which possesses a polished surface, the thermal conductivity of which below 0.4°K changes proportionally to T^2 , appreciably exceeding the thermal conductivity of samples with a rough surface. Actually, as is easily shown,²² the specular reflection of n phonons from the surface of the specimen leads to an increase in the mean free path by $(1+n)/(1-n)$. The value of n increases upon lowering of the temperature as a consequence of the increase of the wavelength of the phonon, up to a value comparable with the inhomogeneities of the surface of the specimen. Experiments with etching of the surface of sample Sn 4 (which led to a decrease in its thermal conductivity for $T < 0.4^\circ\text{K}$ to the value of the thermal conductivity of samples Sn 2 and Sn 3) confirm this point of view.

A similar reflection was observed in the study of the thermal conductivity of a series of dielectrics.^{22,23*} Thus, from the point of view of the essential representation of the thermal conductivity of dielectrics it proves possible to explain both the absolute value of the thermal conductivity of tin below 0.4°K , and also its temperature change. This result agrees entirely with the conclusions of previous investigations of the thermal conductivity of superconductors at temperatures below 1°K .^{8,9}

* According to a private communication from D. Shoenberg, reflection of phonons from a surface of tin has also been observed by Graham at Cambridge.

Everything that has been said above permits us to connect the sharp change in the temperature dependence of the thermal conductivity of Sn 2, Sn 3 and Sn 4 at 0.57, 0.5 and 0.42°K, respectively, with the appearance of the electronic thermal conductivity K_{es} , which can itself be determined under the assumption of the constancy of the laws of change of the lattice thermal conductivity even for temperatures above 0.5°K. A similar assumption, as the measurements of Laredo show, is valid up to 0.8–1°K. Above these temperatures, the thermal conductivity of the lattice begins to fall off sharply, because of the scattering of the phonons by electronic excitations. The value of this conductivity reaches a negligible value for

helium temperatures, which allows us to determine K_{es} in this region of temperatures also. The dependence of K_{es} on T_c/T , obtained by the method described above, is shown in Fig. 9. As is easy to see, the change in the thermal conductivity with temperature is determined for all the samples studied by one and the same exponential term

$$K_{es} = \text{const} \cdot \exp(-\beta T_c/T),$$

where $\beta = 1.45 \pm 0.05$. All the results known to us of the determination of the electron thermal conductivity of tin below 1°K^{8,24} do not contradict this dependence.

The dependence on the temperature of the electronic thermal conductivity of the superconductor in the region of temperatures where the number of excitations is small, is determined primarily by the change of the number of

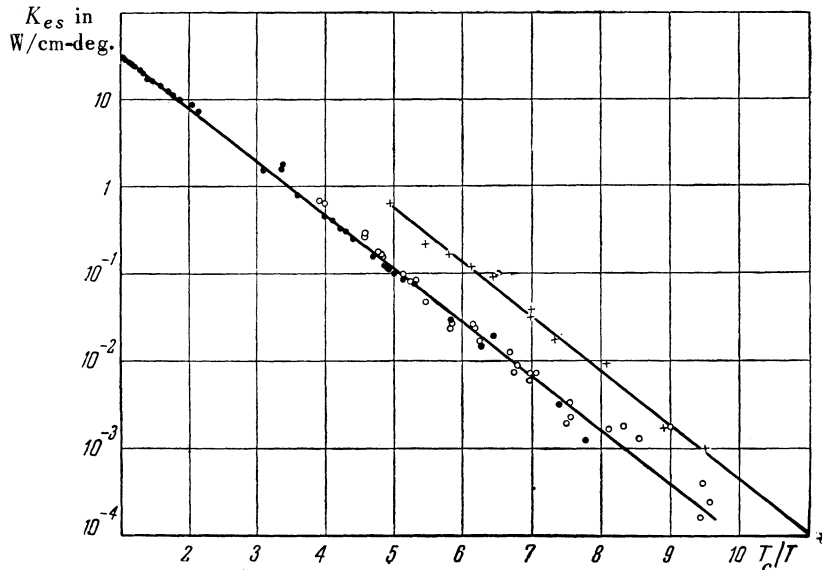


FIG. 9. Electronic thermal conductivity in tin in the superconducting state ● — Sn 2; ○ — Sn 3; + Sn 4.

excitations with temperature. The length of the free path of the excitations at these temperatures is evidently the same as in the normal metal, depending only on the chemical and physical purity of the sample, and does not change with the temperature. From this viewpoint, the character of the temperature dependence of K_{es} points out the exponential change with temperature of the number of excitations in the superconductor.

This position could be verified also by the temperature dependence of the normal conductivity in the superconductor, the depth of penetration of the magnetic field in the superconductor, the absorption of ultrasound in the superconductor, but the measurement of all these quantities at sufficiently low temperatures has not been carried out.

The results of the measurement both of the thermal conductivity and the heat capacity show the fundamental temperature change of these quantities is determined by the exponential factor. This testifies to the fact that the excited state of the electrons in the superconductor is distinct from the basic energy gap. Actually, similar representations (see Ref. 25) lead at once both to the presence of the exponent in the free energy of the electrons and to an exponential change of the number of excitations with temperature. From this viewpoint, most attention attaches to the measurement of the value of the energy gap by different methods. The fact is that the exponent in αT_c is, generally speaking, only proportional to the width of the energy gap Δ . The coefficient of proportionality is connected with the character of the appearance and annihilation of the excitations or, more precisely, with the location of the Fermi surface at the middle of the gap as, for example, in semi-conductors, $\alpha T_c = \Delta/2$. However, at the present time, direct measurements which would permit the determination of Δ with sufficient accuracy are lacking, although qualitative observations of the transparency of films of tin²⁶ in the region of high frequencies show that possibly αT_c is actually close to $\Delta/2$.

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