INVESTIGATION OF THE THERMAL PROPERTIES OF SUPERCONDUCTORS. II

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The specific heat, thermal and temperature conductivity of aluminum and zinc have been measured between 1.5 and 0.15°K by the temperature wave method described in Ref. 1. Results of measurement of the normal-state specific heat are identical with those obtained at higher temperatures. The temperature dependence of the electron specific heat in the superconducting state is given by Eq. (2), where $\alpha = 1.2$ for Al and $\alpha = 1.03$ for Zn. The heat conductivity of electrons in a superconductor also depends exponentially on the ratio T_k/T. In this case, in contrast to the electrons of normal metals, K_{es}/c_{es} depends on the temperature. The results obtained are compared with the results of measurement of the specific heat of other superconductors and with the results of the microscopic theory of superconductivity.[2,3]

RECENTLY, it has been shown in a series of papers[1,4-7] that the specific heat of electrons in a superconductor depends exponentially on T_k/T. However, it is still not clear whether this dependence is general for all superconductors, and whether one can speak of a law of corresponding states for their properties. To clarify these questions, a study was undertaken of the thermal properties of aluminum and zinc — metals which possess relatively low temperatures of transition to the superconducting state.

A study of these metals is also of interest from the viewpoint of the possibility of direct measurement of the specific heat and thermal conductivity of electrons. Thus, while in tin the specific heat of the electrons at the critical temperature amounts to only about 60% of the total specific heat, in aluminum and zinc it amounts to 98%.

The method of measurement was not fundamentally different from that used to investigate the thermal properties of tin.[1] The thermal conductivity and the thermometric conductivity $a^2 = K/c\rho$ were determined by direct measurements, from which the specific heat was calculated. Cylindrical specimens with diameters of about 1.5 mm and length 100 mm were employed. The zinc samples were single crystals, grown in thin glass capillaries. The angle between the (001) direction and the axis of the sample was about 30°. The aluminum crystals consisted of large crystals with the length of the sample equal to several times the diameter. Before the investigation, the aluminum was annealed in a vacuum at ~600°C for 4 hours.

The results of the direct measurement of the thermal and thermometric conductivities are shown in Figs. 1 – 4. Experiments with each of the speci-

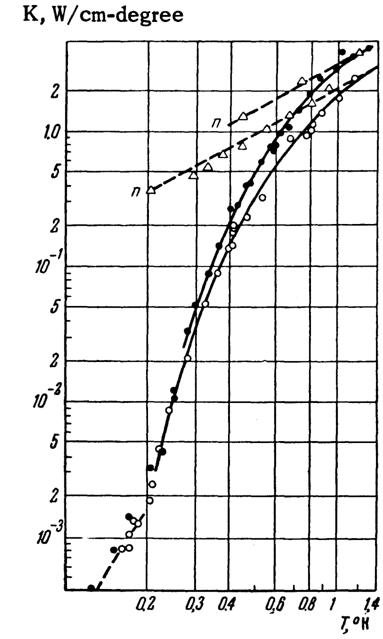

FIG. 1. Thermal conductivity of aluminum. ● – Al-1; ○ – Al-2; n – thermal conductivity in the normal state, Δ – measurements in a magnetic field.

mens were carried out over a period of several days. The mean spread of the results amounted to 10 and 4%, respectively, for the thermal and temperature conductivities. On lowering the temperature to 0.2°K and in the region of a strong dependence of the thermal conductivity on the temperature, the accuracy of the determination of the thermal conductivity was decreased. This condition was connected with the fact that at reduced absolute temperature the errors in its determination increased, reaching 3 — 4% near 0.2°K. In the

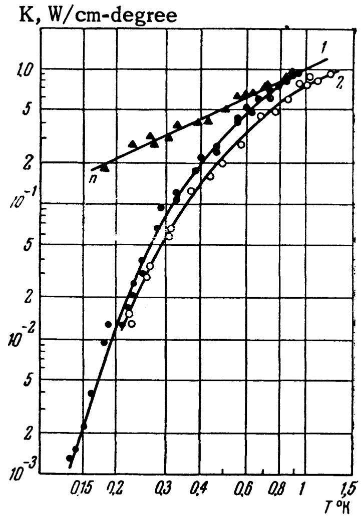

FIG. 2. Thermal conductivity of zinc. 1 – Zn-1; 2 – Zn-2; ▲ – measurements in a magnetic field.

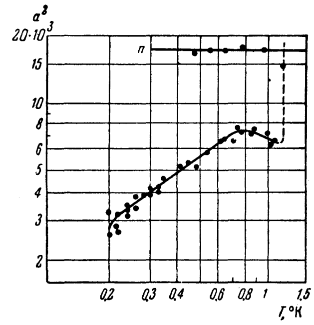

FIG. 3. Temperature conductivity of aluminum. Sample Al-2; n – normal state.

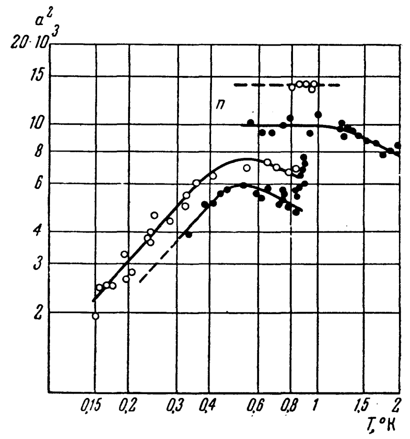

FIG. 4. Temperature conductivity of zinc. o – Zn-1, • – Zn-2; n – normal state.

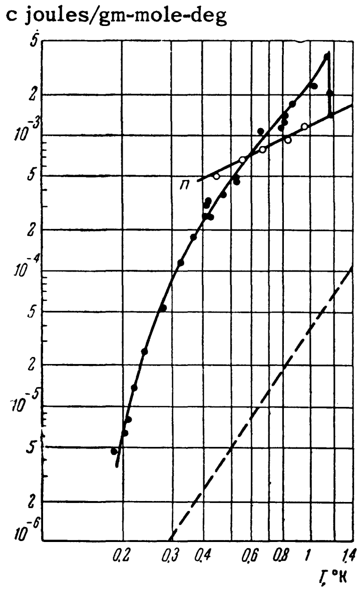

FIG. 5. Specific heat of aluminum; n – normal state, dashed line – lattice specific heat.

case of a strong change in the thermal conductivity with temperature, this is equivalent to the presence of a several times larger error in the magnitude of the thermal conductivity also.[1] Since such errors are determined in fact by the accuracy of establishing the absolute temperature, they always impose a certain limit on the determination of the temperature dependence of physical quantities beyond the dependence on the methods of their determination.

Measurements of the specimens in the superconducting state were carried out in a magnetic field which was compensated to 0.2 oersted. As in the investigation of the properties of tin, control experiments showed that the results were independent of whether the transition from the normal to the superconducting state took place in this same magnetic field or in a field ~ 10 oersted, perpendicular to the axis of the specimen. In the normal state, at temperatures below critical, measurements were carried out in a field parallel to the axis of the specimen and amounting to 115 oersted for Al and 60 oersted for Zn.

The specific heat of aluminum is shown in Fig. 5. The calculation was carried out in terms of the thermal and thermometric conductivities of the sample Al-2. The plotted points were obtained by calculation on the curve of Fig. 3, and from the results of measurement of the thermal conductivity of Fig. 1. The specific heat of zinc is plotted in Fig. 6. Calculations were carried out on the curves of Figs. 2 and 4 for each of the samples studied; the results led to numbers agreeing within the limits of error (~ 10%).

DISCUSSION OF THE RESULTS

Specific Heat

We first consider the results of the measurement of the specific heat in the normal state. As is well known, for sufficiently low temperatures, the specific heat of metals can be represented as

$$c_n = \gamma T + 1944\,(T/\Theta)^3 \quad \text{joule/g-mole-degree,} \qquad (1)$$

where Θ is the Debye temperature. The first term is due to the specific heat of the electrons, the second is due to the specific heat of the lattice. The value of the linear term for Al and Zn, ob-

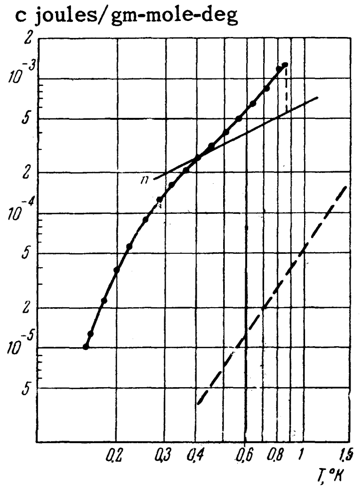

FIG. 6. Specific heat of zinc; n – normal state, dashed line – lattice specific heat.

tained on the basis of our measurements, is shown in Table I. For Zn, this value agrees, within experimental error, with the results of measurement at temperatures above 1.5°K; for aluminum, it is somewhat smaller than the literature value, although the deviation is also at the limit of the accuracy of measurement.

The thermometric conductivity a^2 of zinc in the normal state changes with temperature, as is seen from Fig. 4. Evidently this is connected with the specific heat of the lattice. Actually, since the thermal conductivity of metals is directly proportional to the temperature, we have

$$a^2 = D/(1 + qT^2),$$

where D is a constant and $q = 1944/\gamma\Theta^3$. Analysis of the resultant data shows that $q = 0.07 \pm 0.02$ for Zn; this corresponds to $\Theta = 340 \pm 20°$. This value of Θ agrees within experimental error with the results of measurement for temperatures above 1.5°K (see Table I). All these results are of interest from the point of view of confirming the validity of Eqs. (1) down to temperatures ~ 0.5°K.

TABLE I. Characteristics of metals studied

Sample	Per cent impurity	Results of measurement		Literature values		Reference
		$\gamma \cdot 10^3$, j/g-mole-deg²	K_0, W/cm-deg²	$\gamma \cdot 10^3$, j/g-mole-deg²	Θ, °K	
Al-1	0.01		3.02±0.08	1.44±0.05	408	[8]
Al-2	0.01	1.27 ±0.1	2.17±0.08	1.37±0.05	375	[9]
				1.40±0.07		[5, 12]
Zn-1	0.0001	0.67 ±0.04	1.02±0.05	0.654	321	[10]
Zn-2	0.0001	0.645±0.04	0.75±0.04	0.66	296	[11]

Earlier investigation[1] of the thermal properties of tin has shown that in the transition to the superconducting state only the specific heat of the electrons undergoes a significant change; the specific heat of the lattice remains practically unchanged. This allows us, by making use of data of the specific heat of the lattice in the normal state, to estimate its contribution to the total specific heat, and to separate the specific heat associated with the electrons. For both aluminum and zinc, the lattice specific heat is a relatively small quantity, not exceeding 10% of the total specific heat in the entire interval.

The transition of the metal into the superconducting state is accompanied by a discontinuity in the specific heat Δc. The relative magnitude $\Delta c/c_n(T_k)$ of the discontinuity can be determined from a measurement of the thermometric conductivity for the critical temperature. Specifically, inasmuch as the heat conductivity in the normal and superconducting states are the same at T_k,

$$\Delta c / c_n(T_k) = (a_n^2 - a_s^2) / a_s^2.$$

Analysis of the results of the measurement (Figs. 3 and 4) show that $\Delta c/c_n(T_k) = 1.60 \pm 0.15$ for Al and $\Delta c/c_n(T_k) = 1.25 \pm 0.15$ for Zn. These values practically coincide with the values of $\Delta c/\gamma T_k$ for Al and Zn, since the specific heat of the lattice in these cases amounts to less than 3% of the total specific heat (at T_k).

The dependence of the specific heat of the electrons c_{es} on T_k/T is plotted in semilogarithmic scale in Fig. 7. For $T < 0.7\ T_k$, it can be writ-

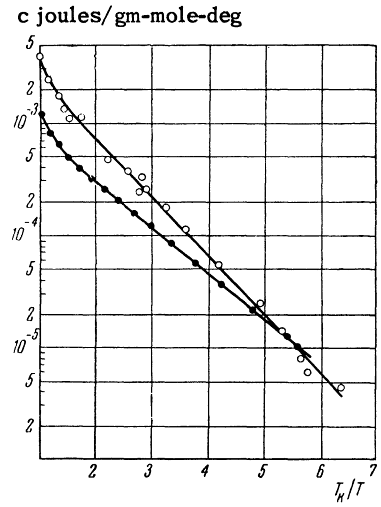

FIG. 7. Specific heat of electrons: o – aluminum, ● – zinc.

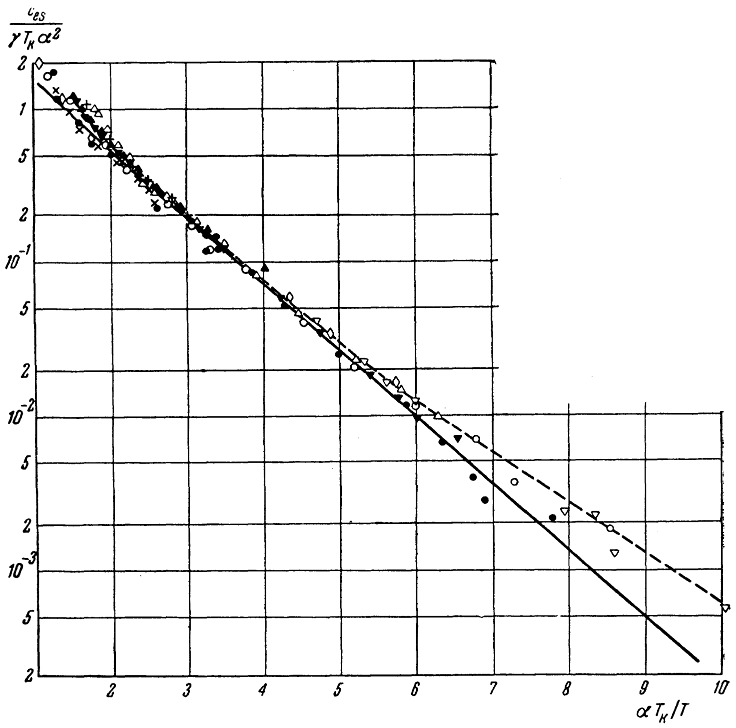

FIG. 8. Specific heat of electrons in superconductors. △ – Nb; ▼ – V; ▲ – Ta; + – In; × – Tl; ◊ – Zn; ---, ▽ – Sn; ●, ○ – Al (---, ● – measurements of author; ▽, ○ – measurements of Goodman[12]). Solid line – Eq. (2). Values of γ, T_k, α are given in Table II.

ten as

$$c_{es} = A \exp(-\alpha T_k / T),$$

where $A = (8.2 \pm 1) \times 10^{-3}$ joule/gram-mole-degree, $\alpha = 1.20 \pm 0.08$ for Al and $A = (2.3 \pm 0.3) \times 10^{-3}$ joule/gram-mole-degree, $\alpha = 1.03 \pm 0.08$ for Zn, under the assumption of $T_k = 1.17$°K for Al and $T_k = 0.84$°K for Zn (the errors in A and α are functionally related). The value of α obtained for Al differs somewhat from the value of 1.28 established by Goodman[5] by analyzing the results of direct calorimetric measurements of the specific heat of Al down to 0.25°K; however, new data by Goodman[12] also agree better with $\alpha = 1.20$ (see Fig. 8). There is a systematic deviation of about 10% in the absolute magnitude between the results obtained and the data of Goodman (see Table I).

The exponential dependence of the specific heat of the electrons, which was first discovered in vanadium, is also observed in tin, aluminum, and zinc. Probably, this dependence is a characteristic of all superconductors. However, the quantity α, which determines the dependence of c_{es} on the relative temperature, changes from one metal to another. By the same token, if a law of corresponding states is established for the specific heat of superconductors, the quantity α ought to appear in it along with γ and T_k.

From this point of view, we have analyzed all the results of the investigations which are suitable for the determination of the dependence of c_{es} on T_k/T in a sufficiently wide temperature range, in particular, for Nb, V, Ta, Sn, In, Tl, Al, and Zn. In all these metals, there exists a clearly delineated region of exponential dependence of c_{es} on T_k/T. In this region, in first approximation,

$$c_{es} = 4\gamma T_k \alpha^2 \exp(-\alpha T_k / T). \quad (2)$$

The values of γ, T_k, α are given in Table II. Thus, while the absolute values of c_{es} in the various superconductors at T_k differ by as much as a factor of 500, the expression $c_{es}/\gamma\alpha^2 T_k$ does not change by more than ~10% (Fig. 8). This variation can be ascribed in significant measure to errors in the determination of γ, c_{es}, α. Of course, the presence of a general relation among c_{es}, γ, T_k, α for all superconductors is due to the thermodynamic connection between the thermal properties in the normal and superconducting states of the metal. We note that deviations from a simple exponential law (2) possibly exist not only close to the critical temperature for $T > 0.7\, T_k$, but also in the region of very low temperatures,[1] for $T < 0.2\, T_k$ (see Fig. 8).

The difference in the dependence of the thermal properties of superconductors on the relative temperature T/T_k is defined by the quantity α. This quantity changes from one superconductor to another in a systematic manner. It is likely that some sort of relation exists between α and T_k/Θ of the superconductor (Fig. 9a), although the small number of metals for which α can be compared makes this conclusion not very trustworthy. Close

TABLE II. Characteristics of thermal properties of superconductors

Metal	$\gamma \cdot 10^4$, j/g-mole-deg	Θ, °K	T_k, °K	α	Reference
Nb	8.54	252	8.7	1.80	[13]
V	9.26	338	5.03	1.50	[4,14]
Ta	5.44	231	4.4	1.49	[14]
Sn	1.75	200	3.72	1.50	[1, 6]
In*	1.81	109	3.4	1.60	[15]
Tl*	2.55	86.6	2.36	1.30	[7]
Al	1.27	390	1.17	1.20	
Zn	0.65	340	0.84	1.03	

*One must regard the thermal characteristics of these metals with some caution, since their electron specific heat over the whole range of measurement amounted to only a small fraction of the total specific heat. This especially applies to Tl, for which the γ obtained on the basis of calorimetic measurements is substantially different from the value of 1.53 determined on the basis of magnetic measurements.[16]

to the critical temperature, the thermal properties are determined by the size of the discontinuity in the specific heat for the transition from the normal state to the superconducting. A comparison of the relative discontinuity $\Delta c/\gamma T_k$ shows that the change in this quantity is apparently also connected with T_k/Θ (Fig. 9b). In this case, since calorimetric measurements in a narrow range of temperatures close to T_k can also be used for the determination of the quantity $\Delta c/\gamma T_k$, the number of superconductors whose properties can be compared according to this characteristic is increased. A significant deviation from the general dependence of $\Delta c/\gamma T_k$ on T_k/Θ is observed only for thallium, if we make use of γ obtained from calorimetric measurements (see note on Table II). In the presence of a general law for the change in the specific heat of the electrons in the superconductor with the temperature, $\Delta c/\gamma T_k$ and α are probably interrelated. From this viewpoint, the data of Fig. 9b serve as additional proof of the presence of a connection between the quantity α and T_k/Θ.

It is natural to compare all these results in the first place with the recently developed[2,3] microscopic theory of superconductivity. In first approximation, the theory describes the change in the specific heat of superconductors with temperature with sufficient accuracy. The theoretical values $\Delta c/\gamma T_k = 1.4$, $\alpha = 1.44$ also agree with the experimental values. However, according to the theoretical model, these quantities should be constant for all superconductors; in reality they vary considerably. This change could be corrected, for example, with the appearance of an anisotropy in the electron spectrum in the real metal, from which the specific heat at sufficiently low temperatures will be determined by the change of the sums of exponents. Here, however, one would expect a connection between α and the crystallographic structure of the metal, a relation which has not as yet been discovered. Moreover, only the decrease of α in comparison with α_{theor} could be explained in this way, whereas, for a series of metals, $\alpha > \alpha_{theor}$. All this shows that a further refinement of the model currently considered is necessary to explain quantitatively the properties of superconductors. Since the value of α is connected with the temperature dependence of the value of the energy gap Δ, then the experimental data (Fig. 9) should be regarded as indicative of the presence

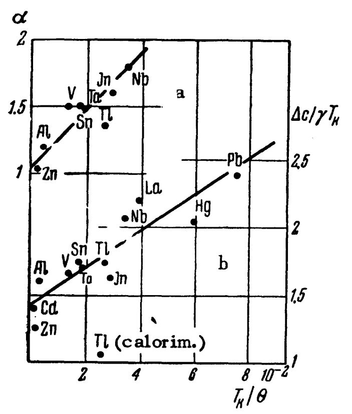

FIG. 9. (a) α and T_k/Θ of superconductors. The researches involved are enumerated in the text; (b) $\Delta c/\gamma T_k$ and T_k/Θ of superconductors. For Cd,[17] and especially for La,[18] the data are not very trustworthy; for Hg,[16,19] the data are from magnetic measurements; for Pb, the data of Refs. 20, 21 are used, for the other metals, the results of the researches enumerated in the text were employed.

of a dependence of Δ on T/Θ as well as the dependence of Δ on T/T_k considered in the theory.

Thermal Conductivity

In the normal state, the thermal conductivity K_n of the metals under consideration is linearly proportional to the temperature in all intervals of measurement:

$$K_n = K_0 T.$$

The quantity K_0 is connected with the chemical and physical impurities of the specimen, just as is the residual resistance. The values obtained for K_0 (see Table I) confirm the relatively high purity of the samples under investigation.

It is known that for sufficiently low temperatures, transfer of heat to the superconductor is entirely governed by the lattice. In our measurements this temperature region is achieved for aluminum only below 0.2°K, where a sharp change is observed in the thermal conductivity in both samples. At the higher temperatures for Al, and over the whole range of measurements for Zn, the transfer of heat is essentially related to the thermal conductivity of the electrons, K_{es}. The dependence of K_{es} on T_k/T is shown in Fig. 10; it can be represented by

$$K_{es} = k_{0s} \exp(-\beta T_k / T),$$

where the values of β are 1.5 ± 0.1 for Al and 1.30 ± 0.1 for Zn; k_{0s} is a constant, related to the quantity K_0 of the given sample. This is the same law (but with other values of β) established previously for tin.

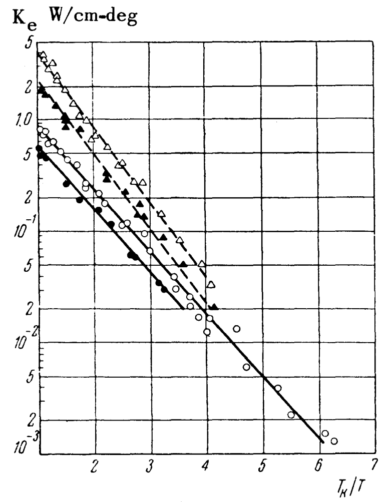

FIG. 10. Thermal conductivity of electrons: ○ – Zn-1; ● – Zn-2; △ – Al-1; ▲ – Al-2.

The characters of the temperature variations of thermal conductivity and specific heat of electrons of the superconductor are interrelated. This is shown by a detailed measurement of the exponents α and β in the exponential laws for c_{es} and K_{es}, although this means of comparing K and c does not appear to be very trustworthy. More accurate evidence on the relation of the specific heat and the thermal conductivity is given by the results of measurement of the thermometric conductivity $a^2 = K/c\rho$; this permits us to establish even a very small difference in the temperature dependence of these quantities. Since the thermal characteristics of Al and Zn are chiefly determined by the electrons in this case,* we have for these metals, with accuracy to within several percent: $a^2 = K_{es}/c_{es}\rho$. For convenience, the value of the temperature conductivity was taken in the normal state at T_k, and the dependence of $\xi = a_s^2/a_n^2$ on T/T_k was considered. It turned out that Al and Zn have the same type of dependence of ξ on T/T_k, although the possibility is not excluded that, the absolute magnitude of ξ contains the value of α or β, since ξ_{Al}/ξ_{Zn} is approximately inversely proportional to α_{Al}/α_{Zn}.

All these quantities can be considered from the point of view of the new theory of superconductivity. If, within the framework of this theory, we compute the thermal conductivity of the electrons in the temperature range where the path length is determined by scattering from impurities,† then

$$\frac{K_{es}}{K_{es}(T_k)} = \frac{12}{\pi^2}\frac{T}{T_k}\int_{\Delta(T)/2T}^{\infty}\frac{x^2\,dx}{\mathrm{ch}^2 x},$$

where $\Delta(T)$ is the width of the energy gap in the superconductor, or

$$K_{es}(T)/K_{es}(T_k) \approx 5.75 \exp(-\beta T_k/T),$$

where $\beta = 1.75$. Although this law agrees qualitatively with the experimentally established dependence of K_{es} on T_k/T, the quantity β, as also α in the specific heat, is not a universal constant, changing from one metal to another. In the same way, starting out from the model developed recently, it is not possible quantitatively to determine the thermal conductivity of the electrons of the superconductor in a sufficiently wide temperature range.

It is natural to expect that the change in α and β from one metal to another is determined either by the appearance of anisotropy in the metal or by

*For aluminum, measurements of the temperature conductivity are considered only above 0.3°K where, in accord with the data of Fig. 1, the thermal conductivity of the lattice of specimen Al-2 contributes less than 10% of the total thermal conductivity.

†The author acknowledges his deep gratitude to B. T. Geilikman who kindly reported the results of this computation prior to publication.[22]

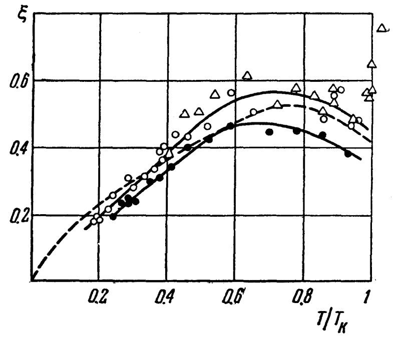

FIG. 11. Dependence of $\xi = a_s^2/a_n^2$ on T/T_k: ● – Al-1; ○ – Zn-1; △ – Zn-2. Dashed line – theoretical curve.

a different dependence of Δ on the temperature. From this point of view, we may assume that the ratio K_{es}/c_{es} can be theoretically determined more accurately than K_{es} or c_{es} alone. Evidently this is so. Thus, for example, while the deviation between the experimental and theoretical values of K_{es} and c_{es} for Zn at 0.2°K amounted to a factor of six, the quantity ξ, computed on the basis of the theoretical dependence of K_{es} and c_{es}, differs from the experimental value by not more than 10%. However, even in this case, it is still possible that in detail the theory does not accurately determine the dependence of ξ on T/T_k (see Fig. 1).

In conclusion, I take this opportunity to express my deep gratitude to P. L. Kapitza, A. I. Shal' nikov, Iu. B. Sharvin, and P. G. Strekov for valuable remarks in the course of completion of the research, and to V. I. Shishkin for help in the measurements.

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