INVESTIGATION OF THE HEAT CONDUCTIVITY OF OXIDE CATHODE COATINGS

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Inzhenerno-Fizicheskii Zhurnal, Vol. 10, No. 1, pp. 106–114, 1966

UDC 536.212

A description is given of a proposed method of measuring the heat conductivity of oxide cathode coatings over a broad temperature interval (100°–1300° K).

Most research relating to oxide-coated cathodes is concerned with the study of their electrical properties.

However, as our investigations have shown [1–3], the question of the thermal regime of an oxide-coated cathode may play a large part in the elucidation of many important problems bearing on the physics and applications of such devices, notably those concerning the form of the pulsed current-voltage characteristics and sparking in the saturation regime.

So far, the literature lacks reliable data on a very important thermal parameter of oxides, namely, their heat conductivity, and the data reported by different authors differ by more than three orders [4–9].

On the one hand, this is due to the insufficient accuracy of the Pengelly method [7, 9] commonly used to measure the heat conductivity (see below), and, on the other, to an error of a more fundamental nature–failure to allow for the high degree of transparency of oxide materials with respect to the emission of the metal base. What usually happens is that the surface temperature of the layer is measured either by pyrometric methods [4, 5], which is impossible since such measurements give a temperature close to the core temperature [10, 3], or by means of a thermocouple embedded in the oxide [8], which is likewise impossible in view of the direct radiative transfer between the core and the thermocouple through the almost transparent oxide layer.

We have studied the heat conductivity of the oxide coating in experiments which form a continuation of a series of investigations [1–3] into the thermal regime of the oxide-coated cathode.

EXPERIMENTAL METHOD

There are two known methods of determining the heat conductivity of oxide coatings: the Pengelly method [7] and the Weston method [6].

Experience in measuring heat conductivities by the Pengelly method convinced us that this method is inaccurate and difficult to apply. The basic error here is connected with the fact that the heat flux passing through the oxide is determined as a small difference between two large quantities, the fluxes dissipated by the cathode assemblies.

The Weston method is much easier to apply. However, Weston's short note provides no theoretical basis for his method and gives a value of the heat conductivity at only one temperature 1000° K. As will be shown below, at this temperature the measured heat conductivity does not characterize the oxide material. Accordingly, in the course of our work we found it necessary to put Weston's method on a proper basis, expand the temperature interval of the measurements, and, finally, introduce some significant modifications.

Experimental specimens. Two types of vacuum specimens were investigated. In the first type the oxide layer was compressed between a nickel disc and a nickel cylinder (Fig. 1a). The oxide layer was deposited on the disc and on the core by spraying or cataphoresis [15]. The disc was pressed against the cylinder by a thin alundum needle, which could be separated from the disc during the measurements by means of a magnet. The needle ensured the rigidity of the system, and also the agglomeration of the oxide layers deposited on disc and core during activation of the specimen. The entire assembly was sealed into a vacuum tube. The temperatures of core and disc were registered by thin W-Ni thermocouples (W diam. 100 μ, Ni—70 μ), which were led out through tungsten pins in the tube.

The construction of specimens of type 2 is shown in Fig. 1b. In this case the oxide was deposited on both faces of the nickel disc and on the faces of two nickel cylinders, between which the disc was compressed. The pressure could be regulated by means of titanium springs—the basic advantage of the second variant. Moreover, it was also possible to investigate two layers of oxide at the same time. The other details of the construction are essentially the same as for the specimens of type 1. The tubes were evacuated by means of a vacuum pump with simultaneous heating of the cylinders. Activation was considered complete when the vacuum in the tube was steady at not worse than 10^{-6}–10^{-7} mm Hg and the resistance of the oxide reached a minimum stable value.

Method of measuring the heat conductivity. The method of measuring the heat conductivity on specimens of both types is essentially a variant of the comparative steady-state method.

Let us consider first a specimen of type 1 (Fig. 1a). The heat flux through the oxide from the heated lower cylinder can escape from the disc by radiation from its surface and by leakage through the thermocouple.

The power radiated from the surface of the disc is easily calculated from the Stefan-Boltzmann law:

$$Q_1 = \varepsilon_{\mathrm{Ni}}(T)\,\sigma_0\,(T_{\mathrm{d}}^4 - T_0^4)\,S_{\mathrm{d}}\,, \tag{1}$$

where $\varepsilon_{\mathrm{Ni}}(T)$ is the emissivity of nickel at the given temperature, σ_0 is the Stefan-Boltzmann constant, T_{d}

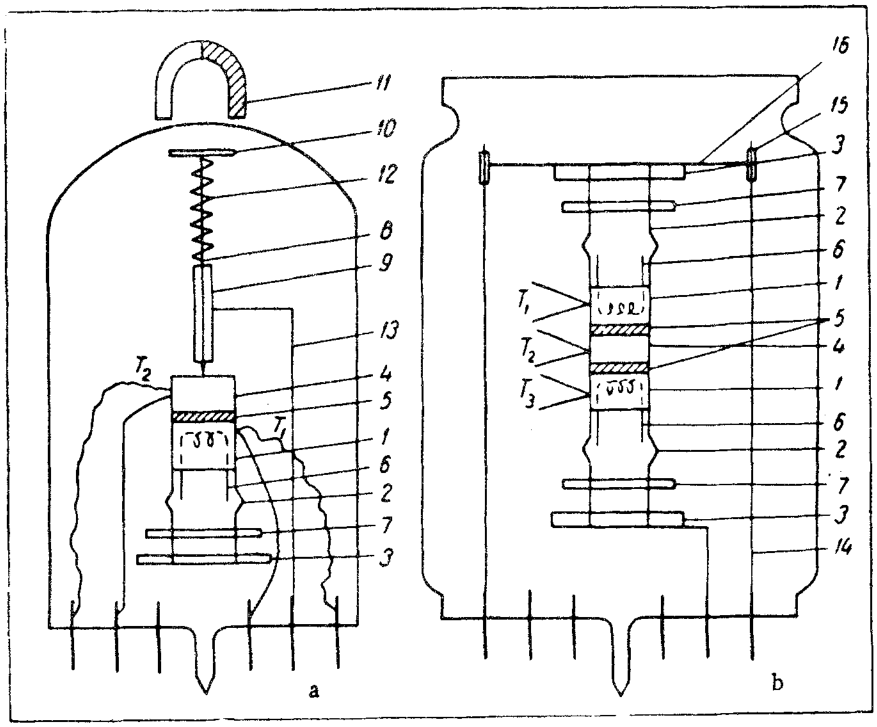

Fig. 1. Construction of experimental specimens of type 1 (a) and type 2 (b): 1) nickel cylinder-core (diam. 8 mm, height 6 mm), 2) core holder, 3) ceramin mounting plate, 4) nickel disc (diam. 8 mm, height 3 mm), 5) oxide layer, 6) alundumized heaters, 7) screens, 8, 9, 10, 11, 12) alundum needle, needle guide, weight attracted to magnet, magnet, and spring, respectively, 13) holder, 14, 15, 16) spring guide, cap, and titanium spring, T_1, T_2, T_3—thermocouples.

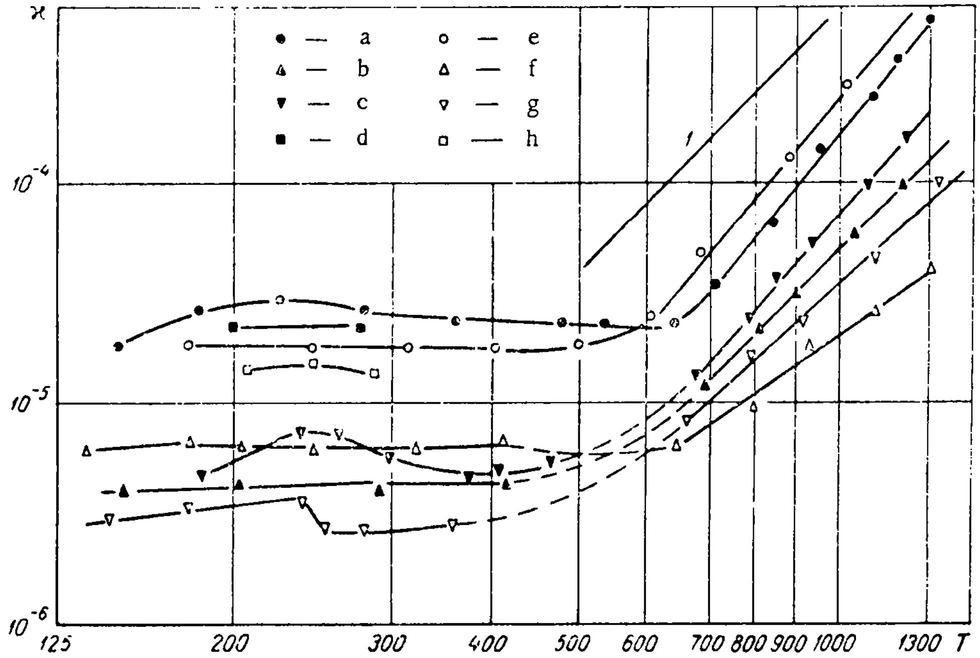

Fig. 2. Heat conductivity ϰ, W/cm · deg, of oxide as a function of temperature T, °K, for specimens of type 2: a, b, c, d) respectively, for specimens nos. 20, 25, 26, and 27, lower layer; e, f, g, h) for the same specimens, upper layer; 1—for $\varkappa_{\text{eff}} \sim T^4$.

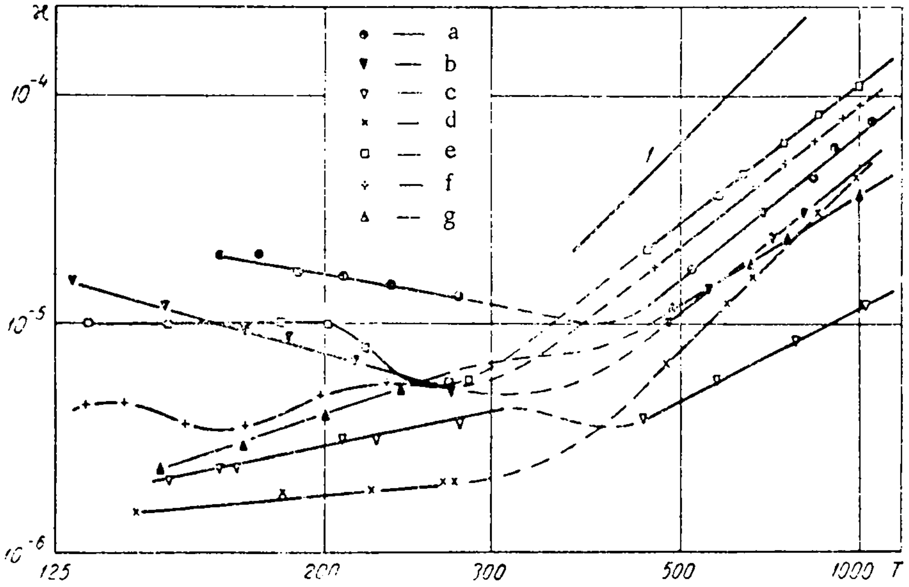

Fig. 3. Heat conductivity ϰ, W/cm · deg, of oxide as a function of temperature T, °K, for specimens of type 1: a) for no. 15, b) 18, c) 14, d) 4, e) 1, f) 2, g) 11; 1—for $\varkappa_{\text{eff}} \sim T^4$.

is the temperature of the disc, T_0 is the ambient temperature, and S_d is the emitting surface of the disc. The leakage through the thermocouple is more difficult to compute, since together with the conductive component it is necessary to allow for radiation from the lateral surface.

We shall consider a thermocouple wire of radius r and length l, one end of which is heated to a temperature T_h and the other to a temperature T_c. The temperature distribution equation [11] is

$$\pi r^2 \varkappa \frac{\partial^2 T}{\partial x^2} = \sigma_0 2\pi r \varepsilon(T)(T^4 - T_0^4). \qquad (2)$$

Here ϰ is the heat conductivity of the thermocouple wire, ε(T) is the emissivity of the material of which the thermocouple is made, and T is the temperature of an element of volume.

The boundary conditions are

$$T|_{x=0} = T_h;\ T|_{x=l} = T_c.$$

Integrating a first time and setting

$$\left.\frac{dT}{dx}\right|_{x=0} = A,$$

we get

$$\left(\frac{dT}{dx}\right)^2 + \frac{4\sigma_0}{r\varkappa}\int_T^{T_h} \varepsilon(T)(T^4 - T_0^4)\,dT - A = 0.$$

Integrating a second time and satisfying the second boundary condition, we get an equation for A:

$$l = \int_{T_c}^{T_h}\left(A^2 - \frac{4\sigma_0}{r\varkappa}\int_T^{T_h} \varepsilon(T)(T^4 - T_0^4)\,dT\right)^{-1/2} dT. \qquad (3)$$

Evaluation of the integral (3) presents no difficulties and enables us to obtain the quantity A, which gives the exact value of the heat flux escaping through the thermocouple.

The measurements were made in two temperature intervals: 293–1273°and 293–77° K. The measurements at low temperatures were made in order to avoid the effect of radiation and to isolate the conductive component of the oxide heat conductivity. For this purpose the specimen was placed in a Dewar vessel with liquid nitrogen, and the ends of the thermocouples, welded to the pins of the envelope, were always at a temperature of 77° K. Calculation of the heat fluxes from (1) and (3) using literature data on the heat conductivity and emissivity of tungsten and nickel [12–14] showed that at 650° K and above the heat flux through the oxide escapes mainly due to radiation from the disc and in calculating the oxide heat conductivity it is possible to use the flux given by Eq. (1). At 250° K and below the heat escapes mainly as a result of conduction through the thermocouple, and to compute the heat conductivity of the oxide at these temperatures it is possible to use, as in [1], the simple formula

$$S_W \varkappa_W \Delta T/l + S_{Ni} \varkappa_{Ni} \Delta T/l = \varkappa_0 S_0 \Delta T_0/d. \qquad (4)$$

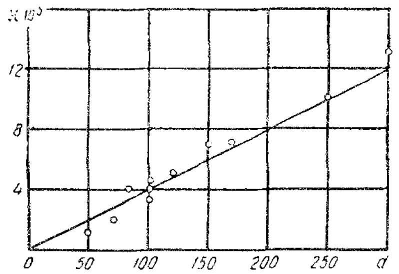

Fig. 4. "Apparent" heat conductivity ϰ, W/cm · deg, at 1000° K as a function of the layer thickness d, microns.

Here $\varkappa_W$ and $\varkappa_{Ni}$, $\varkappa_0$ are the heat conductivities of tungsten and nickel and the oxide, respectively, l_W and l_{Ni} are the lengths of the thermocouple leads, ΔT is the temperature drop along the thermocouple, S_W and S_{Ni} are the cross-sectional areas of the thermocouple wires, ΔT_0 is the temperature drop at the oxide, d is the thickness of the layer, and S_0 is the cross-sectional area of the oxide layer. In the region from 250° to 650° K it is possible to use formulas (1) and (3) together.

We note that for oxides the intermediate region 250°–650° K (as will follow from the subsequent discussion) is of no special interest. Therefore most of the data on the heat conductivity of oxides obtained in this research relate to temperatures in the intervals 100°–300° and 650°–1300° K, the intermediate region being obtained by interpolation.

In measuring the heat conductivity on specimens of the second type, the temperature of one of the nickel cylinders and the disc is kept the same with the aid of filaments and the resulting temperature drop between the second cylinder and the disc is measured. In this case the heat flux passes only through one layer and is radiated from the lateral surface of the disc. Similarly, the heat flux can be made to pass through the other layer of oxide only. Then the calculation of the power radiated from the disc is exactly the same as in the method described above.

EXPERIMENTAL RESULTS AND DISCUSSION

High-temperature component of heat conductivity. At high temperatures the heat can be transported through the oxide layer in several ways: by electromagnetic radiation, by conduction through the oxide grains (photons), by molecules of residual gas, and by conduction electrons.

During the measurements the vacuum in the tubes was not worse than $5 \cdot 10^{-7}$ mm Hg. At such pressures the values obtained for the heat conductivity are not greater than 10^{-11} W/cm · deg, i.e., there is practically no heat transfer by residual gas.

The heat conduction due to the electron gas in the pores can be estimated using the Wiedemann-Franz

Investigated Specimens

No. of specimen	Oxide and method of deposition	Thickness of layer, μ	Specimen type	Value of $\varkappa$, W/cm · deg at ~ 300° K	Density of layer g/cm^3	Exponent in $\varkappa \sim T^m$	Apparent heat conductivity W/cm · deg, at 1000° K
1	$(BaSrCa)CO_3$, spraying	310	1	$5.3 \cdot 10^{-6}$	1.1	3.0	$1.12 \cdot 10^{-4}$
2	$(BaSrCa)CO_3$, spraying	250	1	$2 \cdot 10^{-6}$	1.3	3.2	10^{-4}
4	$(BaSr)CO_3$, spraying	100	1	$2.5 \cdot 10^{-6}$	—	4.0	$4.2 \cdot 10^{-5}$
21	$(BaSrCa)CO_3$ + 7 % Ni formate, cataphoresis	200	1	$2.5 \cdot 10^{-5}$	2.5—3	—	—
14	$(BaSrCa)CO_3$, spraying	50	1	$4 \cdot 10^{-6}$	1.7	2.2	$1.17 \cdot 10^{-5}$
15	$(BaSrCa)CO_3$, cataphoresis	150	1	$1.5 \cdot 10^{-5}$	2.5—3.0	3.4	$7.2 \cdot 10^{-5}$
18	$(BaSrCa)CO_3$ + 7% Ni formate, cataphoresis	80	1	$7 \cdot 10^{-6}$	2.5—3.0	3.6	$4.2 \cdot 10^{-5}$
11	$(BaSr)CO_3$ spraying	100	1	$7 \cdot 10^{-6}$	—	2.7	$4 \cdot 10^{-5}$
20	$(BaSrCa)CO_3$, cataphoresis	upper 300 lower 250	2	$2.5 \cdot 10^{-5}$ $2 \cdot 10^{-5}$	2.0—2.5	4.8 4.8	$2.5 \cdot 10^{-4}$ $1.7 \cdot 10^{-4}$
25	$(BaSrCa)CO_3$, spraying	upper 70 lower 120	2	$6.3 \cdot 10^{-6}$ $4.4 \cdot 10^{-6}$	1.4	3.0 4.0	$2 \cdot 10^{-5}$ $5 \cdot 10^{-5}$
26	$(BaSrCa)CO_3$, spraying	upper 100 lower 170	2	$3 \cdot 10^{-6}$ $5 \cdot 10^{-6}$	1.3	3.6 4.4	$3.3 \cdot 10^{-5}$ $7.2 \cdot 10^{-5}$
27	$(BaSrCa)CO_3$, spraying, intense baking	upper 150 lower 100	2	$2 \cdot 10^{-5}$ $1.2 \cdot 10^{-5}$	2.0—3.0	—	—

law. The electrical conductivity at 1273° K is 2–3 × $\times 10^{-2}$ ohm^{-1} · cm^{-1}, which corresponds to a heat conductivity of about $6 \cdot 10^{-7}$ W/cm · deg, i.e., not more than one order below the heat conductivities obtained in our experiments at 1273° K. We shall show that at high temperatures of 650°–1300° K the main role in heat transfer through the oxide is played by electromagnetic radiation (photons) passing through the almost nonabsorbing layer of oxide from the heated nickel electrodes.

We shall consider the extreme case when between the heated electrodes at temperatures T_1 and T_2 there is no oxide at all. In this system the radiative transfer is actually determined by the reduced emission coefficient [16]

$$\varepsilon_{\mathrm{red}} = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2 - \varepsilon_1 \varepsilon_2},$$

where ε_1 and ε_2 are the emission coefficients of the electrodes. It is usual in such cases to introduce a quantity $\varkappa_{\mathrm{eff}}$ the so-called "effective" or "apparent" heat conductivity, by writing formally the equation

$$\varepsilon_{\mathrm{red}} = \sigma_0 (T_1^4 - T_2^4) S = \varkappa_{\mathrm{eff}} \frac{\Delta T}{d} S. \qquad (5)$$

Assuming that $\Delta T = T_1 - T_2$ is small as compared with T_1 and T_2, from (5) we get the following equation for the effective heat conductivity:

$$\varkappa_{\mathrm{eff}} = 4 \sigma_0 \varepsilon_{\mathrm{red}} T^3 d. \qquad (6)$$

The formula gives the correct order of magnitude of the effective heat conductivity, close to that obtained in our experiments (Figs. 2, 3), and also the dependence of the conductivity observed at high temperatures on the thickness of the layer (Fig. 4). Moreover, formula (6) explains (Figs. 2, 3) the observed exponential character of the temperature relation $\varkappa_{\mathrm{eff}}(T)$. Indeed, $\varkappa_{\mathrm{eff}} \sim T^3 \varepsilon_{\mathrm{red}}$, and since $\varepsilon_{\mathrm{red}} \sim T$, $\varkappa_{\mathrm{eff}} \sim T^4$; however, in our experiments the exponent is close to 4 only on average (see table). A simple study of this kind is inadequate to account for this deviation. Qualitatively, however, it shows that at high temperatures we have to deal mainly with heat transfer due to electromagnetic radiation through a weakly absorbing layer of oxide. The low absorption in the oxide layer was to be anticipated from general considerations, since the oxide is a semiconductor with a broad forbidden band of about 4 eV [17]. Although absorption in the oxide is low, scattering of radiation in such a highly dispersed layer plays an important part. Analogous behavior is characteristic of visible light in a layer of snow or powdered glass: it is strongly scattered, but only weakly absorbed.

In [1–3] we succeeded in estimating the coefficients of absorption and scattering of radiation in a layer of oxide. It was found that at cathode working temperatures the absorption coefficient is close to 1 cm^{-1}, i.e., really small, while the scattering coefficient is 200–300 cm^{-1}.

A more precise examination of the problem of the passage of radiation through an oxide layer compressed between two heated electrodes can be made on the basis of a solution of Schuster's equation [18, 1]. However, it turns out that such an examination does not lead to qualitatively new conclusions. Therefore, a more detailed study of the high-temperature component of heat conduction does not make much physical sense. This is not always clearly understood, and frequently the apparent component of conductivity is taken as the true heat conductivity of the material and used unjustifiably in thermal calculations.

Low-temperature component of heat conductivity of oxides. Measurements at 100°–350° K excluded the possible influence of radiation from the nickel electrodes on the low-temperature component of the heat conductivity. Therefore, this component was conditioned by the vibrations of the oxide crystal lattice, and it may be called the "true" value in the sense that it characterizes the oxide and at the same time is not a characteristic of the system used for measuring the heat conductivity. Precisely for this reason, the low-temperature component, as distinct from the high-temperature component, does not depend on the thickness of the oxide layer. On the other hand, a surprising feature is the extremely small magnitude of the low-temperature component and the spread, over an order, of its absolute values. Since the oxide usually has a porosity of about 70–90%, we can attempt, using data on the heat conductivity of such single crystals as CaO and MgO [19], to take into account the high porosity according to known formulas for the heat conductivity of two-phase systems [22–24]. Not one of these formulas gives values of the heat conductivity approaching the measured value of $\varkappa$. The discrepancy is 2–3 orders. This discrepancy may be understood if we assume that the contacts between grains play a dominant role in the thermal resistance of the oxide layer. It then also becomes possible to understand the observed spread of the data with respect to absolute magnitude of the heat conductivity, since this depends not only on the total porosity but also on the size of the grains, their shape, the contact area between grains, and so on. It is clear that with increase in the density of the oxide its heat conductivity must increase. This dependence was observed in our experiments, particularly with specimens of type 2—layers deposited by cataphoresis or specially baked on (specimen no. 27) have the greatest heat conductivity as compared with the other layers (see table).

The values obtained for the low-temperature component enabled us to estimate the ratio of contact dimension and grain size. Shlykov [20] examined the problem of the passage of heat through a system consisting of a set of cylinders of height h and radius r_0 in contact with each other at a point of the base. The contact is a spot of radius a ($a < r_0$). The heat conductivity of such a system is expressed by the formula

$$\varkappa_{\mathrm{s}} = \frac{\varkappa_{\mathrm{m}}(1-p)}{1 + \psi(r_0/a)\, \pi r_0^2 / 4ha}.$$

Here $\varkappa_s$ and $\varkappa_m$ are the heat conductivities of the system and the material, p is the porosity, $\psi(r_0/a)$ is some function whose graph is given in Shlykov's paper and which, for $r_0/a \geq 50$, is very close to 1. Assuming $\varkappa_m = 1.5 \cdot 10^{-1}$ W/cm · deg, p = 0.8, and r_0 not very different from h, we get $r_0/a = 10^2$–10^3.

The data obtained for the low-temperature heat conductivity make it possible to estimate the true heat conductivity at working temperatures, the quantity usually of chief interest in the analysis of cathode thermal regimes.

The heat conductivity at cathode working temperatures of 1073°–1173° K is not very different from the value at low temperatures (300° K). It is known that the heat conductivity of solid solutions, such as cathode oxides, varies only slightly at temperatures above the Debye temperature. Moreover, recent direct measurements carried out by another method [21] have shown that the true heat conductivity of the oxide varies by not more than a factor of 2 for a change in temperature from 300° to 900° K. It may be assumed that the measured values of the heat conductivity at 300° K presented in the table correspond to the true values at cathode working temperatures correct to a factor 2.

In conclusion, I consider it my duty to express my thanks to B. Ya. Moizhes for his guidance and also to V. Ya. Frenkel and B. M. Mogilevskii for valuable advice.

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28 June 1965

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