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DEPENDENCE OF THE CRITICAL TEMPERATURE AND ENERGY GAP ON THE THICKNESS OF SUPERCONDUCTING ALUMINUM FILMS[1)]

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The dependences of the critical temperature T_c and the energy gap limit $2\Delta_0$ on film thickness d are found to be the same for aluminum films deposited on glass or quartz in a vacuum at 293°K. For thicknesses between 2000 and 40 Å the relative increase of the critical temperature, $\Delta T/T_{c\infty}$ is proportional to 1/d. The deformational increase of the critical temperature ($\Delta T_c < 0.1$°K) due to the difference between the thermal expansion coefficients of aluminum and the substrates is independent of the thickness. The much greater increase of T_c observed for the thin films is attributed to size limitations of one or more kinds.

The critical temperature T_c of thin superconducting films depends on many parameters that are governed by the preparation of the films.[1-8] For example, in the case of aluminum films T_c can be several times greater than for the bulk metal. Since several theoretical studies in recent years[9-15] have obtained different relationships between T_c and film thickness, an experimental determination is obviously necessary. The experimental values obtained hitherto for the critical temperatures of aluminum films having different thicknesses conflict considerably.[2-4] The spread of the experimental points is also very large. The BCS theory[16] indicates that the variation of T_c should be accompanied by a corresponding variation of the maximum (limiting) energy gap $2\Delta_0$ (at T = 0°K). In[3] $2\Delta_0$ was measured as a function of aluminum film thickness in the range 9850—420 Å; however, the large spread of the experimental results revealed only that the gap tends to increase. The possible causes of the increase that were suggested by the investigators included stresses, impurities, a mean free path effect etc.

In the present work we have aimed to determine how such factors as sample size and structural deformation affect T_c for aluminum films prepared at room temperature. The critical temperature and energy gap were measured for aluminum films having thicknesses ranging from about 2000 Å to 16 Å. We were especially interested in enhancing the accuracy of thickness measurements and to achieve constant thickness in each entire metallic layer. We also investigated the effect of annealing at 400°C, and the stresses generated while cooling because of the difference between the thermal expansion coefficients of aluminum and the substrate. The resistivity of the aluminum films was measured as a function of their thickness.

SAMPLES AND EXPERIMENT

T_c was measured as a function of thickness in film strips about 11 mm long and 0.5—1.5 mm wide. Four-contact resistance measurements were obtained by means of taps at the ends of the strips. Aluminum of 99.9995% initial purity was evaporated onto glass and quartz substrates at room temperature, in a vacuum chamber that was evacuated to $(2-3)\times 10^{-7}$ Torr. During the deposition of the aluminum the pressure rose to $5\times 10^{-6}-5\times 10^{-5}$ Torr depending on the evaporation rate. It must be noted that the vacuum was not affected in this way by heating of the chamber parts; heating the evaporator without aluminum to a considerably higher temperature produced little change in the vacuum. The evaporators were made of twisted triple wire (three strands of 0.5—0.6-mm-diameter tungsten wire) or a 0.8—1-mm single strand. Following preliminary heating of the evaporator to a white heat in a high vacuum, pieces of aluminum that were hung on the downward-bent middle portion became nearly spherical as they melted in the vacuum. The substrate at 40 cm distance thus faced practically a point source. The thickness "from weight" (d_w) of the films was computed from the change in weight of the aluminum source, which was taken to have a density of 2.7 g/cm³. The deposition rate of the metal on the substrate was 1—2 Å/sec, as a rule. Although in individual instances the rate was several times greater or less, no appreciable effect was produced thereby on the results.

Since the preparation of aluminum-based tunneling samples involves oxidation,[17] all of our films were oxidized to minimize any nonuniformity that might result from the presence or absence of the oxide. The aluminum films intended for the measurement of T_c from the temperature dependence of their resistivity were oxidized first in a technically pure oxygen atmosphere (at 760 Torr) and then in air. Resistance measurements of the films beginning at their formation in the vacuum and continuing during the oxidation process showed a jump of the oxidation rate, followed by its decrease, at the transitions from the vacuum to oxygen and from oxygen to air. Most of the resistance change and thus of the oxide thickness occurred during the period of oxidation in oxygen. Oxidation was practically complete after the films had been kept in air 2—3 hours; identical oxide layers could therefore be assumed.

[1)] This work was reported at the 14th All-Union Conference on Low Temperature Physics at Kharkov, June, 1967.

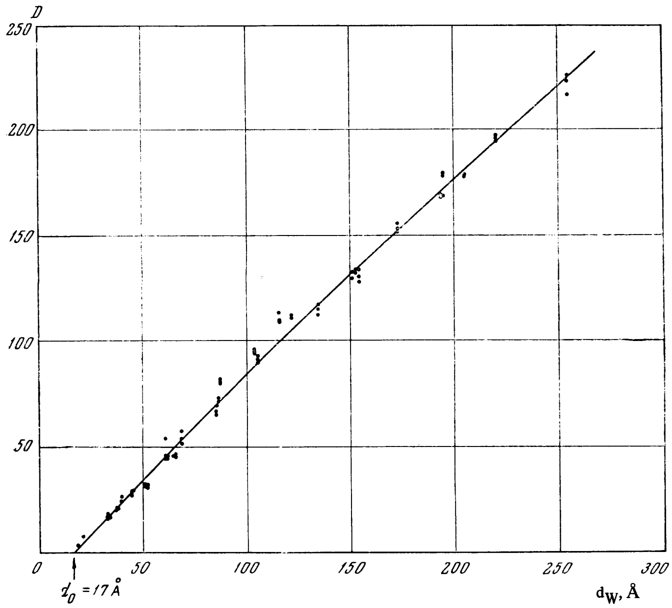

FIG. 1. Optical density of aluminum films having oxidized surfaces versus thickness from weight.

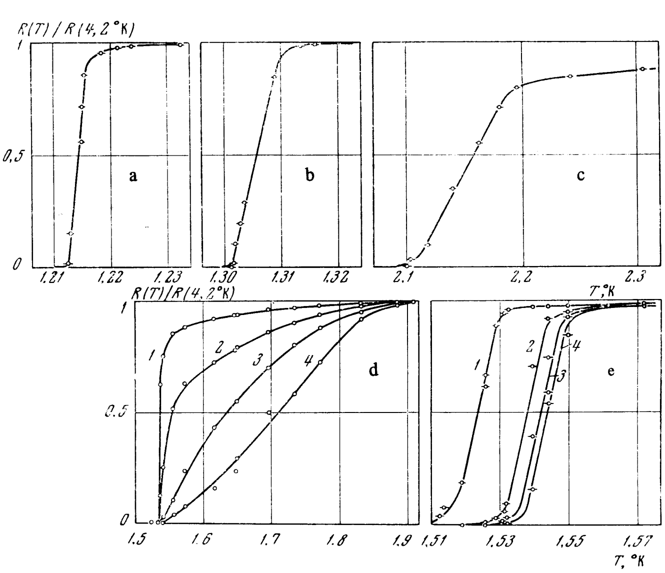

FIG. 2. Temperature dependences of the resistance ratio R(T)/R(4.2°K), illustrating the superconducting transitions of films. (a - c) film thicknesses d = 1073, 237, and 16 Å; edges trimmed; measuring current 1 – 7.5 μA. (d) d = 71 Å; edges untrimmed; measuring current: 1 – 300, 2 – 75, 3 – 30, and 4 – 7.5 μA. (e) same as (d) with edges of film trimmed.

An MF-2 microphotometer was used to measure the optical density D of the metal films together with their oxidized surfaces; the degree of uniformity of film thickness was indicated by values obtained at different points. Figure 1 shows the average value of D for each film as a function of thickness from weight; the continuous line represents averaging over all experimental points. This relationship is required as a secondary control of film thickness in case the evaporator did not function as a point source. Thickness from weight here pertains to unoxidized layers. For film thicknesses under 300 Å a considerable fraction of the total thickness of metal goes into the oxide. The thickness d_0 of this metal fraction is obtained from Fig. 1 by extrapolating to D = 0 while neglecting the optical density of the oxide layer; $d_0 = 17$ Å was obtained. The thickness of the oxide is then obtained through multiplication of d_0 by the factor a, which exceeds unity but evidently does not exceed the value 2. Subsequent oxidation of the films for an entire day increased the oxide thickness by only 2–4 Å.

Good reproducibility and accuracy of the thickness measurements was achieved by putting the substrates at a considerable distance from the evaporator and imposing only very moderate requirements on the accuracy of measuring the required geometrical factors and the weights of the aluminum sources. The average deviation of the experimental thicknesses from the line in Fig. 1 is ± 5 Å; we shall hereinafter assume no greater inaccuracy for each particular film than the deviation from this line, but that ± 5 Å is the minimum error. The possibly greater deviations for thicknesses lying beyond the line are not important, because the effects investigated here are appreciable only for thicknesses below 300 Å. The thicknesses from weight of thicker films agree, within accuracy limits, with measurements obtained using a Linnik MII-4 microinterferometer.

Edge effects were eliminated by removing the edges of the films before they were mounted in the cryostat.[19] The superconducting transition temperature was obtained from the ratio R(T)/R(4.2°K) = 0.5 [where R(T) and R(4.2°K) are the film resistances at the temperatures T and 4.2°K] using a measuring current that approached zero. For the thinnest films the last condition was fulfilled in practice with currents of 1–7.5 μA. To ignore the edge effect in these measurements could lead to large errors (Fig. 2). For each film thickness the critical temperature was measured simultaneously for two "twin" samples deposited simultaneously. In the cases of films above 70 Å the two values of T_c did not differ by more than a few thousandths of a degree, as a rule. The width δT_c of the transition, obtained from the shortest linear segment of the transition curve, increases for thinner films; this occurs most rapidly for the very thinnest films. When d ≥ 400 Å, δT_c does not usually exceed $(4-6) \times 10^{-3}$ deg, but for the minimal thicknesses a value ~ 0.1° is reached.

$Al-Al_2O_3-Pb$ tunneling samples were prepared under conditions similar to those already described. However, the distance between evaporators and substrates was 20 cm; also, the aluminum layer was oxidized during 10–20 min in oxygen at 0.3 mm Torr prior to deposition of the lead. In this way we obtained the thinner layer of oxide that is required for a tunnel junction. For our measurements we used samples in which at voltages several times greater than the half-sum of the aluminum and lead gaps, the tunneling resistance was 0.2–5 ohm-mm^2.

All measurements were performed using a conventional potentiometer circuit. For each sample, at temperatures up to T_c for the aluminum film, we obtained a series of current-voltage (I–V) curves. Each of these curves was an averaged-data line for a large series of points. From the well-known[17] properties of the I–V characteristic curves we determined the energy gaps

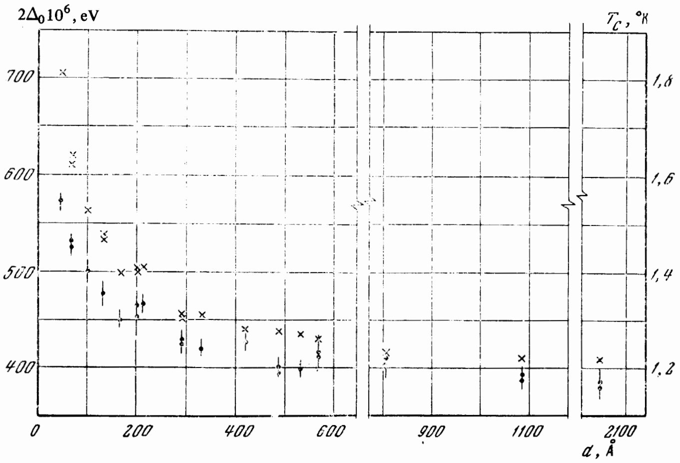

FIG. 3. Dependences of the maximum energy gap (dots) and critical temperature T_c (crosses), measured with tunneling technique, on film thickness.

2Δ of the metals at given temperatures T. To the half-sum of the gaps for aluminum and lead we assigned the voltage pertaining to the point of the I–V characteristic where dI/dV is maximal immediately after the region corresponding to the gap for aluminum; the derivative was determined graphically. From the experimental dependence of Δ on T and from the theoretical dependence of Δ/Δ_0 on T/T_c (where Δ_0 is the gap at 0°K) we derived the maximum energy gaps $2\Delta_0$ for the aluminum films (Fig. 3). The vertical bars in Fig. 3, representing the uncertainty of $2\Delta_0$, are deviations from the mean values and were determined both from measurement errors and from possible discrepancies between the experimental and theoretical dependences $\Delta(T)$.

A tunneling technique was used to investigate aluminum films from 46 to 2073 Å. Thicknesses in the range 400–800 Å were computed for the lead films. The cryostat used in the low-temperature measurements was capable of reaching and maintaining temperatures from 4.2 to 0.88°K within ±0.001°K. The samples were in direct contact with liquid helium. The temperature was measured and monitored with a McLeod gauge and a carbon thermometer and was determined on the T_{58} scale.[20]

RESULTS AND DISCUSSION

Figure 4 shows the thickness dependence of T_c for the aluminum films used in the present work. On the basis of a comparison with similar data in[2-4] we make the following comments. The measurements were extended to films of the smallest thicknesses that are feasible with the film preparation technique which was used. The experimental points are close to the averaged-data curve. The region in which the critical temperature increased appreciably is shifted toward thinner films than in earlier results. It can be stated that a well reproducible thickness dependence of T_c was observed for the aluminum films.

We know from the BCS theory[16] that the maximum energy gap and the critical temperature are related by $2\Delta_0 = 3.52\ kT_c$. It could therefore be expected that $2\Delta_0$ would depend on thickness in the same way as T_c. Figure 3 demonstrates this behavior for the maximum energy gap, from tunneling measurements. For the aluminum films the average value of the maximum energy gap is 3.7 ± 0.1 in units of kT_c and is independent of the thickness. The spread of the points shown in Fig. 3 somewhat exceeds that in Fig. 4, although the gap and critical temperature are here again dependent principally on film thickness.

The average value $(1360 \pm 10) \times 10^{-6}$ eV was obtained (incidentally) for the half-width of the energy gap in the case of the lead films. This can be assumed in practice as the maximum value because of the low reduced temperature at which measurements were performed, and agrees with the measurements in[21].

Some idea of the aluminum film properties is obtained from room-temperature measurements of their resistivity ρ as a function of thickness. The observed increase of ρ as d was reduced, except for thicknesses under ~ 45 Å, agrees well with a theoretical curve for the size effect in thin plates[22] (Fig. 5). We compared theory and experiment using the resistivity of bulk aluminum at room temperature, $\rho_\infty = 2.65$

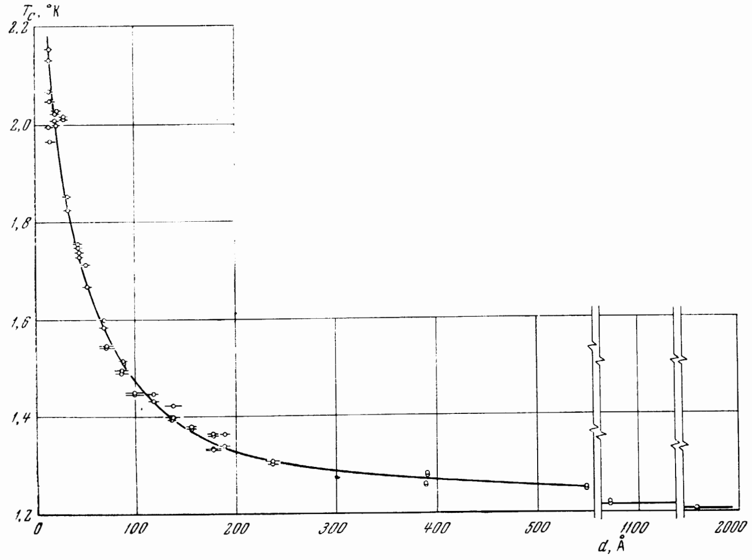

FIG. 4. T_c of oxidized aluminum films versus thickness of metal layer, $d = d_w - d_o$. The horizontal bars represent the deviations of thicknesses from the curve in Fig. 1.

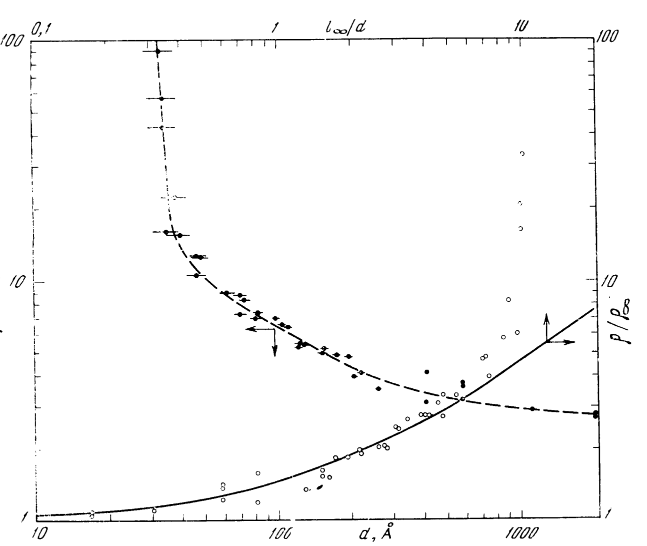

FIG. 5. Dependence of electrical resistivity ρ (at 293°K) on d for unoxidized aluminum films. Filled circles - experimental data of the present work, accompanied by the corresponding averaged-data curve. Plot of ρ/ρ_∞ versus l_∞/d for the same films: solid curve – theoretical dependence from [22]; open circles – present experimental data (l_∞ is the mean free electron path for an infinite sample).

$\times 10^{-6}$ ohm-cm.[23] From the best theoretical-curve fit of the experimental data we obtained $\rho l = 0.8 \pm 0.1 \times 10^{-11}$ ohm-cm^2 (where l is the mean free electron path in the film); this does not conflict with values given in the literature (among which large discrepancies are found[2,6]).

As the film thickness is reduced below $\lesssim 45$ Å, discontinuities undoubtedly develop rapidly in the films.

The properties of a film formed by vacuum evaporation of a metal depend on the temperature of the substrate. This temperature influences the grain size and mechanical stresses in the film. It was previously observed[2,8] that for aluminum films deposited at helium temperature T_c is strongly affected by annealing. It can reasonably be assumed that films produced at room temperature will be less sensitive to annealing. We performed experiments required to determine more definitely the role played by structural imperfections and stresses in our aluminum films.

The critical temperature was first measured, as previously, for "twin" samples on glass substrates. The measurements were repeated after one of the samples had been annealed, while the second sample served as a control. The anneal was concluded with heating of the first sample up to 400–420°C during 1½ hours, followed by maintenance of the same temperature during about 30 additional minutes. The reduction to room temperature required 3 hours. During the anneal the vacuum was maintained within the limits 2–8 $\times 10^{-6}$ Torr, and was thus as good as during the aluminum evaporation process. We obtained somewhat unexpected results.

Each annealed film exhibited a higher value of T_c instead of the anticipated lower value. At the same time, the conductivities and the resistance ratios, $\delta_{77} = R(293°K)/R(77°K)$ and $\delta_{4.2} = R(293°K)/R(4.2°K)$, increased; this is evidence of an improvement in the structure. Annealing of a 406-Å film raised the room-temperature conductivity about 6%, and raised $\delta_{4.2}$ about 22%. With decreasing thickness the influence of annealing on these properties diminishes steadily. In the cases of films having the thickness (from weight) 406, 206, 86, 195, 46, and 40 Å on cover glasses (All-union Standard 6672-59) the increase of T_c is 0.04 ± 0.01°K and is independent of the temperature. This result proves that the change of T_c is not caused by decreased thickness of the metal layer resulting from possible further oxidation of the films; otherwise the effect would be more pronounced for the thinnest films.

Similar measurements were obtained for films on fused quartz substrates. In this case the rise of T_c was 0.09 ± 0.01°K. Unannealed films of identical thickness on the different substrates yield a value of T_c that is 0.025°K higher on quartz than on glass. It should be noted that measurements of the critical temperature in the control films were nonreproducible by at most a few thousandths of a degree.

The foregoing experiments indicate that annealing up to 400°C has only a small effect on T_c for thin aluminum films prepared at room temperature, and that this effect results mainly from mechanical stresses arising when the samples are cooled from 400°C to room temperature, because the films and their substrates have different thermal expansion coefficients. This conclusion is supported both by the qualitative agreement of experiment with the anticipated greater increase of T_c for an aluminum film on quartz than on glass, and by computations.

Notarys[24] investigated the increase of T_c for an ~400-Å aluminum film (on a Mylar substrate) that was stretched. Anhysteretic linear variation of T_c was observed when the tensile strain was varied from 0 to 0.04. The ratio between any increment of T_c and the corresponding strain was 7°K. Calculations based on our data, neglecting dimensional changes of the quartz substrate compared with such changes of the Al film,[25,26] show that for a film cooled from 400° to 20°C the additional tensile strain was 0.011. The ratio between the anneal-associated change of T_c and this strain is 8°K, in full agreement with Notarys' result. A similar calculation yielded at most a few hundredths of a degree as the increase of T_c due to tensile strain when samples were cooled from room temperature to helium temperature. The thickness dependence of T_c (Fig. 4) can therefore not be accounted for quantitatively by mechanical stresses in the case of aluminum films prepared at room temperature.

For aluminum films prepared at liquid helium temperature Rühl[15] observed that following their oxidation T_c rises from 2.6–2.7° to 3.0–3.1°K. We shall now discuss two of Rühl's conclusions: a) The thinner the metal film, the greater the influence of the oxide layer becomes, and b) the strength of the electric field generated when the oxide is formed, and the change of the critical temperature, do not depend on the thickness of the oxide film. There appears to be insufficient justification for the second conclusion, which was based on an experiment using a 30-Å aluminum film. Following the first oxidation process the aforementioned increase of T_c was observed. Further oxidation induced only a slight reduction (by about 0.05) of T_c. On the basis of the change in residual resistance it was assumed that the oxide had doubled in thickness. However, increase of the oxide must be associated with a diminution of the metal layer and thus, according to conclusion a), T_c should increase. The failure to observe this increase can be attributed to weakening of the electric field due to increase of the oxide thickness. This suggests that the Rühl effect is small in our films with their definitely thicker oxide layers and that it cannot account for the results shown in Fig. 4.

It has been shown theoretically[9,13,14] that within the framework of the conventional phonon mechanism of electron pairing an increase of T_c in very thin superconducting films can be associated with quantization of electron energy due to one-dimensional finiteness of the film. When comparing the experimental curve in Fig. 4 with the theoretical curve one must take into account the unavoidable microscopic roughness of real films, although the optical density (D) measurements may still indicate a constant mean film thickness. Evidence for this is found in the aforementioned progressive broadening of the superconducting transition. From such film inhomogeneity taken alone we would expect smoothed thickness dependences of T_c and 2Δ, rather than oscillating dependences (with a period of a few angstroms). The experimental results obtained in the present work may therefore be considered consistent with the theoretical calculations for aluminum.

Among the aforementioned theoretical investigations we may include the theory of Shapoval,[15] who derived an equation, valid for $\Delta T \ll T_{c\infty}$, that can be compared conveniently with experiment:

$$\frac{\Delta T}{T_{c\infty}} = \alpha \frac{S}{2p_\infty V} \ln \frac{2\gamma\omega_D}{\pi T_{c\infty}}.$$

Here $\Delta T = T_c - T_{c\infty}$, where T_c is the critical temperature of the superconducting transition in a film; α is a coefficient that equals $\pi/4$ for a plane surface; V and S are the volume and surface of the sample; p_∞ and $T_{c\infty}$ are the Fermi momentum and the superconducting transition temperature in an infinite volume; $\gamma \approx 1.78$; ω_D is the Debye frequency. For films having thicknesses of the order of 10^{-6} cm this equation predicts that the critical temperature would rise 10–15% above $T_{c\infty}$. We observed experimentally that for a 100-Å film the increase of the critical temperature was ~20%, which is very close to the theoretical result.

The same equation predicts that $\Delta T/T_{c\infty}$ would be inversely proportional to the thickness. Figure 6 shows the experimental values obtained for $\Delta T/T_{c\infty}$ plotted logarithmically as a function of d. Except for the smallest thicknesses ($d \lesssim 45$ Å) the results are well fitted by a straight line. This indicates that the dependence can be represented by $\Delta T/T_{c\infty} = A(1/d)^\beta$, where A and B are constants. With $T_{c\infty} = 1.194$°K, which is quite reasonable for aluminum, we have $\beta = 1$. Determining A from the graph and using Shapoval's equation, we can obtain α. When we use a value of p_∞ that is calculated on the free electron model and assume $S/V = 2/d$, as for a plane-parallel plate, we obtain a value of α that is almost one order of magnitude greater than the theoretical value. However, we can always be doubtful concerning this result, since we lack the necessary information regarding p_∞ and S/V for real aluminum films. In any event, for films deposited by evaporation S/V could be several times larger than for a film having geometrically plane surfaces.[27]

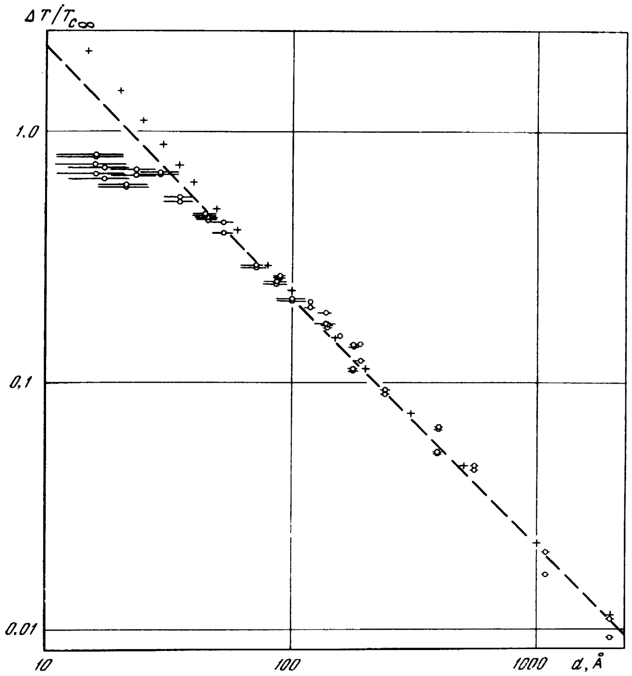

FIG. 6. $\Delta T/T_{c\infty}$ versus film thickness. ○ – experimental results obtained in the present work; dashed line – averaged data line; the horizontal bars represent deviations of the thicknesses from the curve of Fig. 1 ; + denotes calculations based on the equation of de Gennes.[11]

In Fig. 6 the experimental data are compared with de Gennes' theoretical dependence, in the same way as this was done by Strongin et al.,[4] who assumed that the increase of T_c as the thickness of oxidized aluminum films diminished is associated with Ginzburg's surface superconductivity.[10] When we insert into de Gennes' equation the same parameters that were used in[4], along with $T_{c\infty} = 1.194$°K, we find that our results indicate a thickness of about 5 Å for Ginzburg's layer. This comparison is of interest since we cannot exclude the possibility that T_c increases because of inhomogeneous thickness properties of aluminum films,[12] although the oxide may not be a necessary concomitant of the inhomogeneity.[7]

Figure 6 shows that experimental values for very thin films lie considerably below the 1/d dependence of $\Delta T/T_{c\infty}$ that is predicted by the aforementioned theories. We can account for the discrepancy, if, as a result of the aforementioned roughness, the variations of film thickness near its average value are comparable with the actual thicknesses of very thin films. We know that when the thickness of a film is close to a certain critical value the film consists of more or less connected metal islands.[18,28] The thickness of some of these islands considerably exceeds that of a hypothetical uniform atomic distribution upon the substrate surface. Since every macroscopic area of the film includes empty regions, the mean thickness of the film islands exceeds the difference $d_W - d_0$. Consequently the critical temperature must be considerably below that corresponding to $d = d_W - d_0$. As the amount of deposited metal is increased d becomes an increasingly better determinant of T_c.

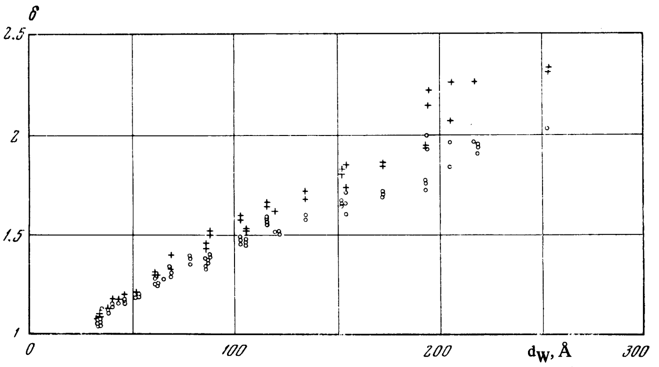

FIG. 7. $\delta_{4.2} = R(293°K)/R(4.2°K)$ (crosses) and $\delta_{77} = R(293°K)/R(7.7°K)$ (circles) versus thickness from weight.

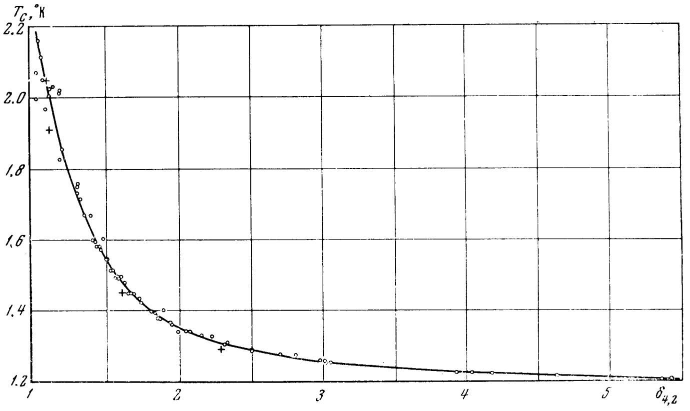

FIG. 8. Dependence of the critical temperature on $\delta_{4.2}$: O present work; + from [4].

It is observed experimentally that the increase of T_c in aluminum films is affected critically by the finiteness of one or more kinds of measurements. The discrepancies between the experimental T_c (d) curves obtained in the present work and in similar investigations can be attributed to the fact that the film thickness may not be the only dimension responsible for the variation of the critical temperature. When we consider that real films are polycrystalline and that the grain size varies, it becomes clear that the effective size limitation of a sample depends on competition between the film thickness d and the average grain size r. If $r \ll d$, then T_c will be practically independent of d; this condition appears to occur in the case of films deposited at helium temperature.[2] If the film is monocrystalline or consists of grains such that $d \ll r$, then T_c will depend on the film thickness. A complication arises when the average grain size depends on the thickness of very thin films. This occurs in a broader range of film thicknesses for aluminum deposited at room temperature than at low temperatures. At helium temperature this kind of dependence is practically absent down to $\sim 10^{-7}$ cm thickness.

We consider a sponge to be the most suitable model of a polycrystalline film. Aluminum is one of the metals in which the separations of the crystallites are much smaller than the dimensions of the latter. Therefore most of the volume of the sponge structure is occupied by the metal; the "intercrystallite surface," which is more or less highly developed depending on the size of the crystallites, acts as a barrier to conduction electrons. The barrier varies at different points, from very high transparency down to the value for an open surface. Surfaces having low transparency are most effective in the sense that their average separation must determine the effective size limitation of the sample and therefore of T_c for the film. Any physical property of the film that is associated with this size will, of course, be correlated with the critical temperature.

The quantity $\delta_{4.2}$, which is associated with film resistivity, provides a factor that is very sensitive to film thickness and grain size. The resistivity is dependent on the aforementioned effective size limitation of the sample. If the resistance of a film depends mainly on the barriers between crystallites (with tunneling of electrons through the barriers), the relation of $\delta_{4.2}$ to the effective size limitation is considerably weakened. In this limiting case a sample consisting of practically isolated grains may be a good model. The grain size affects T_c for this model (measured magnetically, for example), but does not significantly influence $\delta_{4.2}$, which can even be smaller than unity.[2)]

The foregoing argument has been confirmed experimentally. Values of $\delta_{4.2}$ and δ_{77} obtained in the present work are shown in Fig. 7 as functions of film thickness from weight. The electrical resistance of aluminum films is seen to be of metallic character down to the smallest thicknesses. The small spread of the points in the dependence of T_c on $\delta_{4.2}$ (Fig. 8) is evidence that these quantities are well correlated except in the region where discontinuity of the metallic layer plays an important role. It is interesting that our data and similar data from[4] fit on practically the same curve.[3)] In virtue of the discussed ideas regarding the structure of aluminum films, the difference between T_c(d) in our work and in[4] results from the difference between the effective size limitations of the respective samples. In our work the film thickness is dominant, whereas in[4] film grain size also appears to play a very important role. This contrast may be associated technologically either with considerable difference in metal deposition rates, or with qualitative and quantitative differences of the residual gases during evaporation.[6] Residual gas contamination of the deposited metal is more likely to influence grain size and the electronic transparency of the intercrystallite barriers than to have any other effect. The annealing experiments show that not all distortions are important with regard to increase of the critical temperature. It appears that distortions associated with point defects do not contribute significantly to large changes of T_c for aluminum films, although they can have an appreciable effect on $\delta_{4.2}$, for example.

It must be admitted that the experiments described in the present work do not indicate unambiguously the principal mechanism responsible for the increase of T_c in thin aluminum films. The effect could possible result

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[2)] Semiconductor character of electrical resistance in aluminum films has been observed in [4,6].

[3)] The congruence of the results occurs, in actuality, for δ_{77} (since [4] does not give data for $\delta_{4.2}$), although it will also occur for $\delta_{4.2}$ if we assume that for films used in the compared investigations the difference $\delta_{4.2} - \delta_{77}$ exhibits identical dependence on T_c.

from other mechanisms that have not been mentioned in our discussion. For example, Cohen and Douglass[29,4] have presented the very attractive idea of a possibly more efficient pairing of electrons separated by a barrier. Also, there may be several mechanisms capable of inducing the experimentally observed increase of T_C. Further investigations should determine whether the available diverse experimental results reflect different dominant mechanisms, or differences in the actual experimental conditions have dissimilar effects on a single mechanism.

In conclusion, we wish to thank B. I. Verkin for his constant interest and for his support, and also N. V. Zavaritskiĭ, I. O. Kulik, and Yu. F. Komnik for useful discussions.

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