

## Quantum Size Effect in Superconducting Aluminum Films

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Received April 15, 2019; revised April 22, 2019; accepted April 24, 2019

**Abstract**—High-quality aluminum films on GaAs substrates are studied experimentally. The critical temperature of superconductivity is found to increase markedly with decreasing the film thickness. The observed phenomenon is considered as a manifestation of the quantum confinement effect, which affects both the density of states and the electron–phonon interaction.

**Keywords:** superconductivity, critical temperature, thin films, quantum size effect

**DOI:** 10.1134/S1063783419090038

### 1. INTRODUCTION

In the very early works on superconductivity, it was discovered that for thin films the critical temperature of transition  $T_c$  to the superconducting state can be considerably different from its value for corresponding bulk material [1]. Remarkably, as the film thickness diminishes,  $T_c$  becomes lower in some (e.g., niobium [2]) and higher in other materials (e.g., aluminum [3, 4]). Despite a fairly large body of experimental data on the subject and abundance of theoretical models, to date there is no consensus in the scientific community regarding the nature of this phenomenon. One explanation is by Ginsburg [5], and it states that a complex system of poorly interacting grains may form in a real thin film, which leads to considerable deviations of  $T_c$  from its value anticipated for a single-crystal quasi-two-dimensional system of the same thickness. The aim of this work was to investigate experimentally the critical temperature of superconductivity for high-quality thin aluminum films.

### 2. THEORY

The contribution of quantum size effect (QSE) to the superconducting properties of a material can be easily understood on a qualitative level. Consider a simple metal with a parabolic dispersion  $E(\mathbf{p})$  (dashed curve in Fig. 1). If the system is so small in one dimension (e.g.,  $Z$ ) that the QSE cannot be neglected, then

the dependence  $E(\mathbf{p}_{\{X, Y\}})$  degenerates into a system of quantum-size levels  $E_n$  (solid curves in Fig. 1) for any direction in the  $\{X, Y\}$  plane of the film. With each of these levels within the energy window  $\mu \pm \nabla\omega_D$ , where  $\mu$  is the chemical potential and  $\omega_D$  is the Debye frequency, the resonance condition is fulfilled, which leads to singularity of the density of states and, accordingly, to the increase of critical temperature  $T_c$ .

To obtain a quantitative estimation of the contribution of QSE to superconducting order parameter  $\Delta(r)$ , one can make use of the Bogoliubov–de Gennes equations [6, 7]:

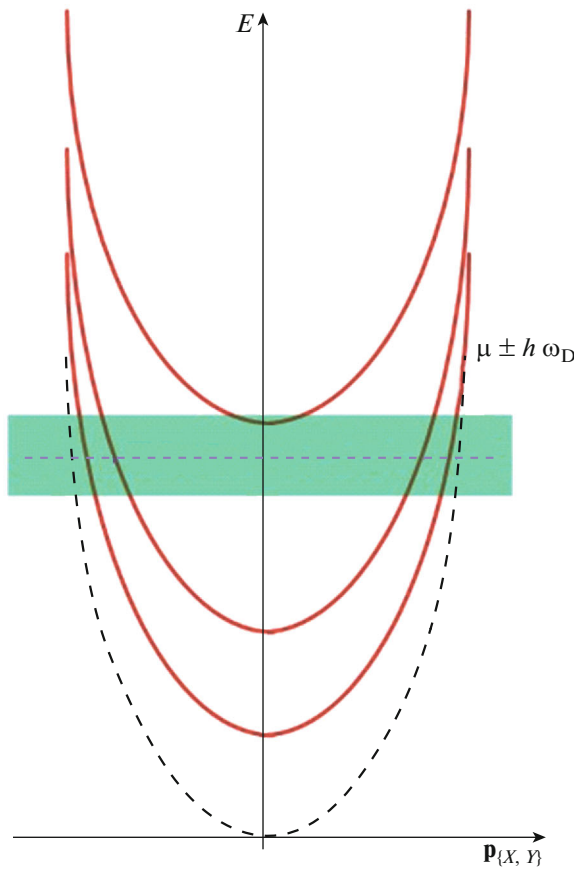
$$\begin{pmatrix} H_e & \Delta(r) \\ \Delta^*(r) & -H_e^* \end{pmatrix} \begin{pmatrix} u_n(r) \\ v_n(r) \end{pmatrix} = E_n \begin{pmatrix} u_n(r) \\ v_n(r) \end{pmatrix}, \quad (1)$$

in which single-electron Hamiltonian in zero magnetic field is

$$H_e = -\frac{\hbar^2}{2m^*} \nabla^2 + U(r) - \mu; \quad (2)$$

and the interaction potential is determined by  $u_n(r)$  and  $v_n(r)$  eigenvalues, the chemical potential  $\mu$ , and the electron–phonon coupling constant  $g$ :

$$U(r) = g \sum_n \{|u_n(r)|^2 f_n + |v_n(r)|^2 (1 - f_n)\}, \quad (3)$$



**Fig. 1.** Energy–momentum diagram showing a typical parabolic dispersion for a bulk metal (dashed line) and dispersions in the presence of quantum confinement along the  $Z$  direction, perpendicularly to the film's  $\{X, Y\}$  plane (solid lines). With each  $n$ -th quantum confinement energy level  $E_n$  within the range  $\mu \pm \nabla\omega_D$ , the condition for resonance is fulfilled, which leads to singularity of the density of states and, accordingly, an increase in critical temperature  $T_c$ .

where  $f_n(E)$  is the Fermi–Dirac distribution function for the  $n$ -th quantum-size energy level. The order parameter is defined as

$$\Delta(r) = g \sum_n \{u_n(r)v_n^*(r)(1 - 2f_n)\}. \quad (4)$$

Here, the summation is over all energy levels for which  $E_n < 0$  and with the additional condition  $|\xi_n| < \nabla\omega_D$ , in which the zero of energy scale coincides with chemical potential  $\mu$  and one-electron energy of the  $n$ -th level is given by the expression

$$\xi_n = \int d^3r \{u_n^*(r)\hat{H}_e u_n(r) + v_n^*(r)\hat{H}_e v_n(r)\}. \quad (5)$$

Density of states  $N(0)$  and chemical potential  $\mu$  are found from the normalization condition

$$n_e = \frac{2}{V} \int d^3r \sum_n \{|u_n(r)|^2 f_n + |v_n(r)|^2 (1 - f_n)\}. \quad (6)$$

For a thin film with dimensions  $L_z \ll L_x, L_y$ , the boundary conditions are  $\Delta(r) = \Delta(z)$  and  $U(r) = U(z)$ , which leads to a peculiar expression for the eigenfunctions:

$$u_l(r) = \frac{e^{ik_x x} e^{ik_y y}}{\sqrt{L_x} \sqrt{L_y}} \tilde{u}_l(z), \quad v_l(r) = \frac{e^{ik_x x} e^{ik_y y}}{\sqrt{L_x} \sqrt{L_y}} \tilde{v}_l(z), \quad (7)$$

where set of quantum numbers is  $l = \{k_x, k_y, j\}$ , and quantum number  $j$  is related to spectrum quantization in the  $Z$  direction.

Considering the boundary conditions  $\tilde{u}_l(0) = \tilde{u}_l(L_z) = 0$  and  $\tilde{v}_l(0) = \tilde{v}_l(L_z) = 0$ , the eigenfunctions can be expanded in a harmonic series:

$$\phi_{l'} = \sqrt{\frac{2}{L_z}} \sin\left(\frac{\pi(l'+1)z}{L_z}\right), \quad l' = 0, 1, 2, \dots \quad (8)$$

Clearly, the electron–phonon coupling in thin films depends on proximity to the boundary. It has been noted [8] that deviation of electron–phonon coupling constant  $g$  from its bulk value  $g_{\text{bulk}}$  is proportional to  $1/M$ , where  $M$  is the number of atomic monolayers in a thin film sample, since  $1/M$  is actually the fraction of atoms located near the boundary. In calculations performed in works [6, 7], the effect of finite film thickness on the electron–phonon coupling constant was taken into account using this basic approximation:

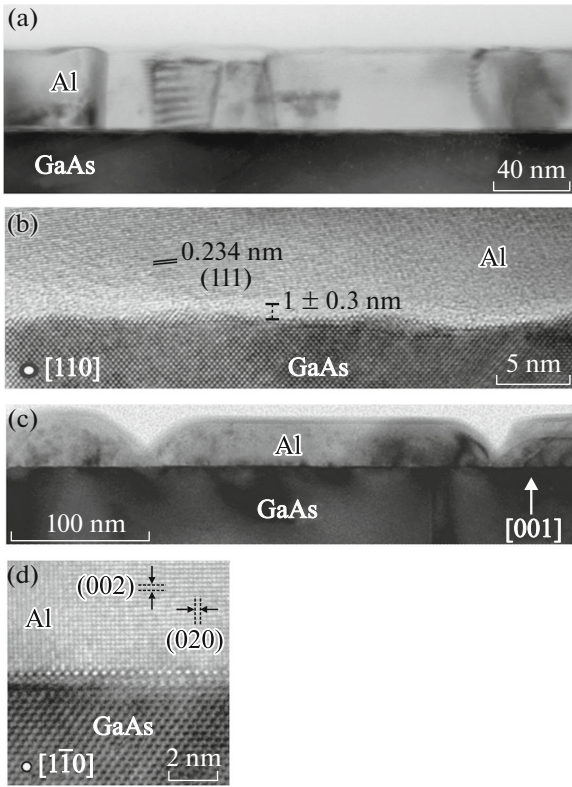
$$g = g_0 - \frac{g_1(4\pi a M/\lambda_F)}{M} = g_0 - \frac{g_1(2k_F a M)}{M}, \quad (9)$$

where  $a$  is the interatomic distance;  $\lambda_F$  and  $k_F$  are the Fermi wavelength and wave vector, respectively; and  $[g_0 N(0)]_{\text{bulk}} = 0.18$  is the reference value for bulk aluminum. Periodic function  $g_1(0) = g_1(2\pi)$  was the fitting parameter.

With the self-consistent solution of Eqs. (1)–(9), we were able to calculate a numerical value for order parameter  $\Delta(z)$ . Critical temperature  $T_c$  is defined as the point at which  $\Delta(z) = 0$  and it is the only solution of these system of equations. An example of calculations of the dependence of critical temperature  $T_c$  on the aluminum film thickness  $d$  is given in Fig. 4.

### 3. SAMPLE PREPARATION AND MEASUREMENT TECHNIQUE

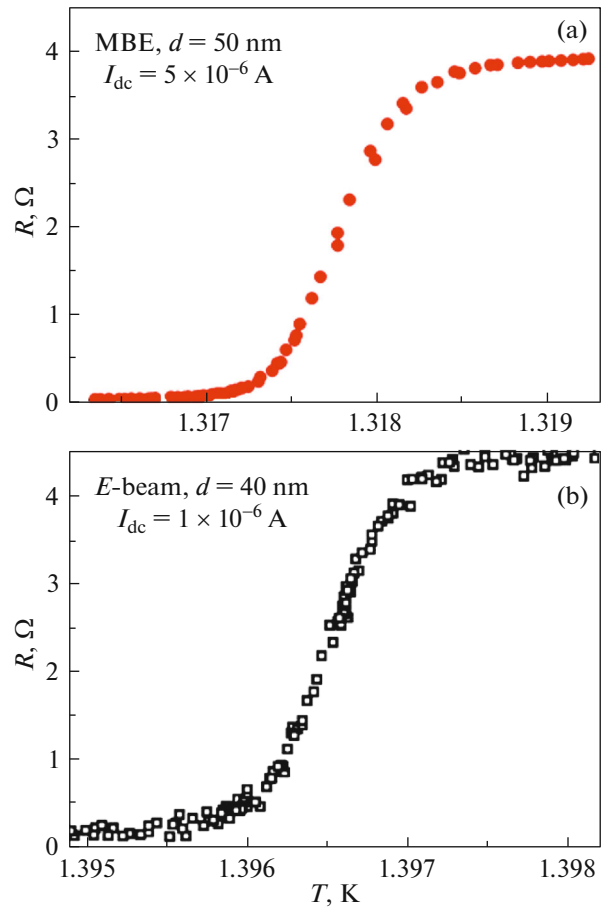
Aluminum films were deposited on GaAs substrates using electron beam evaporation (vacuum  $\sim 10^{-9}$  mbar) and molecular beam epitaxy. The film thickness was varied from 5 to 100 nm, the width was 500  $\mu\text{m}$ , and the length was 10 mm. The quality of prepared film samples was evaluated using transmission electron microscopy. All film samples were polycrystalline, and the characteristic size of crystallites in the film's plane was comparable to, or larger than, the film thickness (Fig. 2). Crystal lattice mismatch defects were seen at grain boundaries. Impurities,



**Fig. 2.** High-resolution transmission electron microscopy images of aluminum films deposited onto GaAs substrates: (a, b) a polycrystalline aluminum film, thickness 50 nm, fabricated by electron beam evaporation; (c, d) 35 nm film fabricated by molecular beam epitaxy. (b–d) Ultra-high-resolution images in which the metal–substrate interface is seen distinctly.

however, were not detected at all. Microscopic analyses of film samples showed that the size of crystallites in the film’s plane was considerably larger for films prepared by molecular beam epitaxy than for films prepared by electron beam evaporation. We, however, were not able to prepare a quasi-two-dimensional single-crystal sample, the desired technological product.

Experimental measurements of  $R(T)$  dependences were carried out using both dc and ac four-probe technique. The current range (typically, 1–10  $\mu\text{A}$  for dc measurements and 0.1–1  $\mu\text{A}$  for phase-sensitive measurements at a frequency of 17 Hz) was chosen so that no marked effect on the phase transition temperature was observed if current increased by an order of magnitude. Measurements at temperatures higher than  $T = 1.3$  K were performed in a continuous-flow  $^4\text{He}$  cryostat. For measurements at lower temperature, we used a sorption pumped  $^3\text{He}$  cryostat. Thermometers used in these two systems were calibrated using  $^4\text{He}$  vapor pressure scale and reference points for superconductivity transitions in pure bulk superconductors (Ti, Al, Sn, and In). The resulting absolute error in temperature was  $\sim 10$  mK, and the relative error was

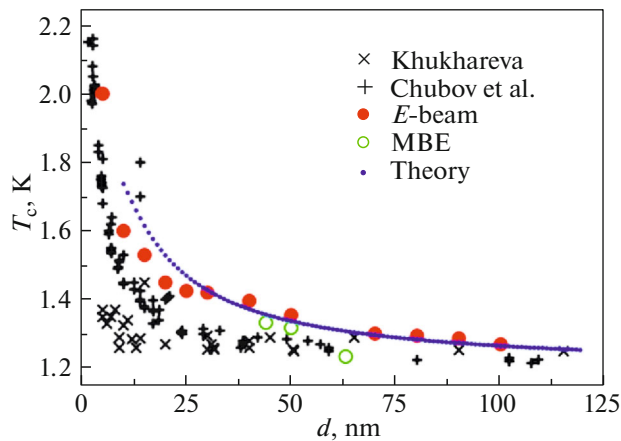


**Fig. 3.** Variation of the resistance with temperature,  $R(T)$ , for aluminum films with a thickness of (a)  $d = 50$  nm (fabricated using molecular beam epitaxy) and (b)  $d = 40$  nm (fabricated using electron beam evaporation).

less than 1 mK. Parallel measurements of  $T_c$  for the same sample performed using two different  $T_c$  units differed by no more than a few microkelvins. Running ahead, we note that the error in temperature measurements was considerably smaller than size-dependent variations of  $T_c$ .

#### 4. RESULTS AND DISCUSSION

A representative dependence of the resistance of aluminum films on temperature,  $R(T)$ , is shown in Fig. 3. If to define the critical temperature as a point at which the resistance falls by half relative to the normal state value, one can obtain the dependence of  $T_c$  on film thickness  $d$  (Fig. 4). There is a clear trend: the critical temperature increases, as the film becomes thinner. For the thinnest sample, i.e., with a film thickness of 5 nm, the critical temperature doubles relative to its value for bulk aluminum, for which  $T_c(\text{bulk}) = 1.19$  K. Our results are in good agreement with previous studies [3, 4]. It is reasonable to assume



**Fig. 4.** Variation of the critical temperature  $T_c$  for aluminum films with their thickness  $d$ : the data for samples prepared using electron beam evaporation are shown with filled circles (●); data for molecular beam epitaxy samples, open circles (○); samples on glass substrates, crosses (×) [3]; samples on glass and/or quartz, pluses (+) [4]; theoretical calculations, dots (•). For bulk aluminum, the critical temperature  $T_c(\text{bulk}) = 1.19$  K.

that the structure of weakly interacting grains [5], which hypothetically may have formed, must be decisively different for films of different quality. Therefore, additionally there must be a general mechanism that underlies the variation of critical temperature in thin films of superconducting materials.

Strictly speaking, we did not observe oscillations of the critical temperature with the film thickness,  $T_c(d)$ , because with the methods used here it was impossible to fabricate films with uniform thickness with precision equal to one atomic layer. Observation of such oscillations would have been a strong argument in favor of the presence of QSE. However, a recent study showed that the increase in  $T_c$  in superconducting aluminum films can be described well at the expense of averaging oscillating dependence  $T_c(d)$  by taking into consideration the QSE, which leads to renormalization of the density of states and the electron–phonon coupling constant [9]. That said, we can conclude that the experimental data reported herein can support applicability of the model that is based on the Bogoliubov–de Gennes equations and takes into account the QSE [6, 7].

## 5. CONCLUSIONS

High quality superconducting aluminum films deposited on GaAs substrates were studied experi-

mentally. We found that the critical temperature of superconducting transition increased markedly with decreasing the film thickness. These results are in line with earlier observations for similar samples fabricated by different techniques and on different substrates, which attests to the general character of this phenomenon. The observed phenomenon is considered as a manifestation of the quantum confinement effect, which affects both the density of states and the electron–phonon interaction. The proposed theoretical model based on Bogoliubov–de Gennes equations showed satisfactory quantitative agreement with the experimental data. We believe that the results of our work will instigate further research in this area.

## FUNDING

This work was conducted within Russian–Greek collaboration project RFMEFI61717X0001 and T4ΔPΩ-00031. The results were analyzed and the paper was prepared by K. Yu.A. The work was also supported within project no. 19-01-050 under the Program “Research Fund of the National Research University “Higher School of Economics” in 2019–2020” and within state support program “5-100” for leading Russian universities.

## CONFLICT OF INTEREST

We have no conflicts of interest to declare.

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*Translated by A. Kukharuk*