Discontinuity of capacitance at the onset of surface superconductivity

K Morawetz\textsuperscript{1,2,3}, P Lipavský\textsuperscript{4,5} and J J Mareš\textsuperscript{5}

\textsuperscript{1} Forschungszentrum Dresden-Rossendorf, PF 51 01 19, 01314 Dresden, Germany
\textsuperscript{2} International Center for Condensed Matter Physics, 70904-910 Brasília-DF, Brazil
\textsuperscript{3} Max-Planck-Institute for the Physics of Complex Systems, Noethnitzer Strasse 38, 01187 Dresden, Germany
\textsuperscript{4} Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 12116 Prague 2, Czech Republic
\textsuperscript{5} Institute of Physics, Academy of Sciences, Cukrovarnická 10, 16253 Prague 6, Czech Republic

E-mail: k.morawetz@fzd.de

Abstract. The effect of magnetic field on a capacitor with a superconducting electrode is studied with the Ginzburg–Landau approach. It is shown that the capacitance has a discontinuity at the onset of the surface superconductivity, which is expressed as a discontinuity in the depth of penetration of the electric field into metals. This new effect establishes a macroscopic signal of the onset of superconducting correlations. This discontinuity is observable with recent bridges for both conventional and high-$T_c$ superconductors.

Capacitors based on ferroelectric layers sandwiched between metallic electrodes are approaching the technical limits of their performance. Their capacitance is no longer exclusively given by the dielectric response of the isolating ferroelectric layer, but it is reduced due to the penetration of the electric field into the metallic electrodes. Concerning the large-scale integration of microscopic capacitors, the penetration of the electrostatic field into the electrodes is considered as a lumped series capacitance. From the viewpoint of fundamental research, however, this phenomenon offers an opportunity to study the interaction of metallic surfaces with an applied electric field.

Here, we discuss the possibility of observing the penetration of the electrostatic field into the metal in the vicinity of the transition from the normal to the superconducting state. We focus...
on the third critical magnetic field $B_{c3}$ at which field the superconducting state nucleates at the surface. We predict that at this field the capacitance or the penetration of the electrostatic field undergoes a jump.

The penetration of the electrostatic field into the normal metal is well understood. Ku and Ullman [1] have derived an analytic solution of the penetrating field for the jellium model within the Thomas–Fermi approximation. Their simple prediction is sufficient to explain the experimental data [2]. Much less is known about the penetration of the electrostatic field into superconductors. From the very beginning until now, the history of this problem has been full of contradictory concepts, yielding a wide scattering of predicted values.

The question of the penetration of the electrostatic field into superconductors was first addressed by the London brothers. In their early paper of 1935, they had expected that the penetration depths of the electrostatic and magnetic fields were identical [3]. One year later, H London measured the capacitance with superconducting electrodes controlled by the magnetic field and concluded that the penetration of the electrostatic field into the metal is not changed by the transition to the superconducting state [4]. While the former concept predicts thousands of ångströms for conventional superconductors, the latter concept suggests less than 1 Å.

In contrast, one encounters a move from small to large penetration depths in the papers by Anderson and co-workers. The Anderson theorem [5] states that the thermodynamic properties of the superconducting condensate do not depend on the electrostatic field. Accordingly, the condensate does not affect the penetration of the electrostatic field, which is thus the same as that in the normal metal. More recently, in the brief discussion of the effect observed by Tao et al [6], a large penetration depth of the electrostatic field using ideas of the Anderson model [7] of high-$T_c$ superconductivity was speculated on.

Apparently the problem of the electrostatic field penetrating the surface of a superconductor is far from being settled, and a clear experimental message is still missing. In this paper, we propose an experiment on a ferroelectric capacitor with one normal and one superconducting electrode. A magnetic field is applied to switch off the superconductivity, and we will explore the vicinity of the third critical field $B_{c3}$. Only this nucleation critical field is sensitive to the applied voltage bias, whereas $B_{c1}$ and $B_{c2}$ remain unchanged [8]. We restrict ourselves to surface superconductivity and do not consider the effects on vortex motion such as the change of the penetration barrier.

The sensitivity of ferroelectric devices to the screening in metals is striking. Indeed, the typical Thomas–Fermi screening length in metals is about 0.5 Å, whereas the width $L$ of the insulating layer has to be about 1000 Å to guarantee low leakage currents. The direct comparison of these scales is somewhat misleading, however. Taking into account the dielectric constants of the components involved, we immediately obtain

$$\frac{\delta C}{C} = \frac{\epsilon_d \delta L}{\epsilon_s L}. \quad (1)$$

The ceramic ferroelectric materials have $\epsilon_d \sim 10^3$ and metals have an ionic background permittivity $\epsilon_s \sim 4$, giving an enhancement factor $\epsilon_d/\epsilon_s \sim 250$. The capacitance can be measured with a sensitivity better than $\delta C/C \sim 10^{-6}$, which makes it possible to observe very subtle changes of the penetration depth $\delta L \sim 10^{-5}$ Å.

First, let us take a look at the interaction between the electrostatic field and superconductivity. The superconducting surface under the applied electrostatic field has been
theoretically studied at various levels by Nabutovsky and Shapiro [9]–[12]. They have shown that the phenomenological theory of Ginzburg and Landau (GL) yields basically the same result as the microscopic picture based on the Bogoliubov–de Gennes method. Their result was recovered in a simple form in [13], where it was shown that the effect of the applied electrostatic field $E$ merely modifies the extrapolation length $b$ in the de Gennes boundary condition for the GL function $\psi$,

$$\frac{\nabla \psi}{\psi} = \frac{1}{b} = \frac{1}{b_0} + \frac{E}{U_s}. \tag{2}$$

This field effect is measured on the voltage scale

$$\frac{1}{U_s} = \kappa^2 \frac{\partial \ln T_c}{\partial \ln n} \frac{e^* \epsilon_s}{m^* c^2}, \tag{3}$$

where $\kappa$ is the GL parameter. The logarithmic derivative of the critical temperature with respect to the electron density is of the order of unity. The need for strong applied fields follows from the ‘relativistic’ energy of an electron, which is rather large, $m^* c^2 \sim 1 \text{ MeV}$.

Below, we shall consider the second derivative of the surface energy. Therefore the absolute value is not as important as the shape. Though the usage of the GL theory is restricted to materials with large coherence length, we expect an correct estimate of the shape from the GL theory. Comparative studies between the GL and Bogoliubov De Gennes theories have been performed only for the infinite barrier situation, which prevents the effect of surface polarization that we claim to be an important one [14]. Therefore, we believe that a good estimate can be found from GL theory also for small coherence lengths.

The boundary condition (2) restricts the solution of the GL equation

$$\frac{1}{2m^*} \left(-i \hbar \nabla - e^* \mathbf{A}\right)^2 \psi + \alpha \psi + \beta |\psi|^2 \psi = 0 \tag{4}$$

at the surface [15]. Being nonlinear, the GL equation (4) has the ability to heal any perturbation of the GL function from its optimal value on the GL coherence length $\xi = \hbar / \sqrt{2|\alpha|m^*}$. The boundary condition thus affects the GL function only in the vicinity of the surface. As a consequence of this, the electric field has no remarkable effect on the bulk superconductivity.

Saint-James and de Gennes [16] have noticed that similarly to the condensation of vapor at surfaces, the boundary condition (2) implies a nucleation of the superconducting condensate at the surface. This becomes apparent at high magnetic fields, since the bulk superconductivity vanishes at the upper critical field $B_{c2}$, whereas a thin sheet of superconducting condensate survives near the surface up to the fields $B_{c3} \sim 1.69461 B_{c2}$. Their result applies to the infinite extrapolation length, $(1/b_0) + (E/U_s) = 0$.

Let us modify the method of Saint-James and de Gennes for a finite $b$ or nonzero $E$. For the third critical field, the GL function has an infinitesimally small amplitude so that one can neglect the cubic term in (4). As the diamagnetic current is also negligible, the vector potential reads $A = (0, B_{c3} x, 0)$. We have associated the surface with the plane $x = 0$. The GL equation (4) is then solved by the parabolic cylinder function of Whittaker [17]:

$$\psi(x, y, z) = N e^{i ky} D_{v-(1/2)} \left( \frac{2x}{l} - i l \right), \tag{5}$$

with $x$ scaled by the magnetic length $l^2 = \hbar / (e B_{c3})$ and

$$\nu = - \frac{\alpha m^*}{\hbar e^* B_{c3}} = \frac{l^2}{(2\xi)^2}. \tag{6}$$
Figure 1. The surface critical field $B_{c3}$ versus the applied electric field $E$ (solid line) in units of (2). The ratio of the third to the upper critical magnetic field relates to the argument of the parabolic cylinder function, $B_{c2}/B_{c3} = 2\nu$. The tangential line at zero bias is given as a dotted line. The inset shows the field dependence of the factor in (13).

So far, $\nu$ and $k$ are parameters of the nucleating GL function $\psi$. We are looking for the solution with the lowest $\nu = \nu_{\text{min}}$, because it corresponds to the highest magnetic field $B_{c3}$ for which the nucleation is possible at a fixed temperature [18]. This highest magnetic field $B_{c3}$ is the third critical field or nucleation field and its resulting value is shown in figure 1, which agrees with figure 1 of [18].

The dependence of the third critical field $B_{c3}$ on the applied electrostatic field $E$ indicates that the electrostatic field affects the surface superconductivity. The same interaction manifests itself in the effect of the magnetic field on the capacitance. The capacitance of the capacitor with one superconducting electrode reads

$$\frac{1}{C_s} = \frac{1}{C_n} - \frac{1}{\varepsilon_0^2 \varepsilon_s^2 S^2} \partial^2 F,$$

where $S$ is the area of the capacitor, $C_n$ is the capacitance when both electrodes are normal, and

$$F = S \int_0^\infty dx \left[ \frac{1}{2m^*} |(i\hbar \nabla + e^* A) \psi|^2 + \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 \right]$$

is the GL free energy describing the difference between the normal and the superconducting states in the superconducting electrode seen as surface energy density.

Near the transition line $B \sim B_{c3}$, the GL function has the shape of the nucleation function (5) with $\nu = \nu_{\text{min}}(E, B)$ and $k = k_{\text{min}}(E, B)$. If we keep the amplitude $N$ as a variational parameter, the free energy is its bi-quadratic function [8],

$$F_N = \frac{1}{2} S(\alpha - \alpha_E)I N^2 I_2 + \frac{1}{4\beta} S I N^4 I_4.$$
Here $\alpha_E = -(\hbar e^* B / m^*) v_{\text{min}}(E, B)$ stands for the kinetic energy obtained from the GL function (5), and $\alpha = \alpha'(T - T_c)$ is the temperature-dependent GL parameter. Integrals over powers of the parabolic cylinder functions are denoted by $I_n = \int_{\tau_k}^{\infty} d\tau D^n_{\nu e}(\tau)$. The condition of minimum, $\partial F_{\nu}/\partial N = 0$, is satisfied by $N_{\text{min}}^2 = (\alpha_E - \alpha) I_2 / (\beta I_4)$. From $F = F_{\nu_{\text{min}}}$ or directly from (8), one obtains the free energy

$$F = -S(\alpha_E - \alpha)^2 I_2^2 / (4 \beta I_4).$$

(10)

Now we can evaluate the jump of the capacitance, which appears as the magnetic field $B$ exceeds the critical value $B_{c3}$. Since $\alpha_E \to \alpha$ for $B \to B_{c3}$, the discontinuity of the inverse capacitance equals

$$\frac{1}{C_s} - \frac{1}{C_n} = \frac{\hbar^2 e^{*2} B_{c3}^2 I_2^2 / 2 \epsilon_0^2 \epsilon_s^2 m^2 \beta \bar{I}_4}{\partial \nu_{\text{min}} / \partial E},$$

(11)

where we have used

$$\frac{\partial \nu_{\text{min}}}{\partial E} = -\frac{\hbar e^* B}{m^*} \frac{\partial \nu_{\text{min}}}{\partial E}.$$  

(12)

The tangential line plotted in figure 1 yields $\partial \nu_{\text{min}} / \partial E = -0.82 \xi / U_s$, see [8] for details. The discontinuity in the capacitance is transparently expressed via the discontinuity in the penetration depth of the electric field

$$\delta L = \epsilon_0 \epsilon_s S \left( \frac{1}{C_s} - \frac{1}{C_n} \right) = \frac{0.397 \hbar^4 I_2^2}{\epsilon_0 e^* m^2 \beta U_s^2 I_4},$$

(13)

In the rearrangement, we have used $4 \xi^2 = I^2 / v$ and $e^* B_{c3} = 2 \hbar / I^2$. From $2 \nu = 1.694$ follows the numerical factor $0.82^2 / (2 \nu) = 0.397$. The field dependence of the factor $I_2^2 / I_4$ is plotted in the inset of figure 1.

To further simplify expression (13), we employ the parameter $\beta = 6 \pi^2 k_B T_c^2 / (7 \zeta(3) E_F n)$ derived from the BCS theory by Gor’kov [19], and rewrite it in terms of the BCS coherence length $\xi_{\text{BCS}} = \hbar v_F / (1.76 \pi k_B T_c)$. Moreover, we substitute $U_s$ from (3) so that we obtain finally

$$\delta L = 1.86 \times 10^{-8} \kappa^4 \epsilon_s \bar{a}_n^4 \left( \frac{\partial \ln T_c}{\partial \ln n} \right)^2 \frac{\xi_{\text{BCS}}^2}{T}.$$  

(14)

We have collected all universal physical constants into the Bohr radius $a_B = 4 \pi \hbar^2 \epsilon_0^2 / (m_0 e^2) = 0.53 \text{ Å}$ and the constant of fine structure $e^2 / (4 \pi \epsilon_0 \hbar c) = 1 / 137$. The latter appears in the fourth power giving the very small factors $1 / 137^4 = 2.8 \times 10^{-9}$. The mass of the Cooper pair is twice the effective mass of electrons in the metal $m^* = 2 m_0$ and $e^* = 2 e$. For $(1 / b_0) + (E / U_s) = 0$, the factor given by the profile of the GL function is $I_2^2 / I_4 = 2.42$; see figure 1.

Equation (14) is the main result of the paper. It expresses the jump in the capacitance (13) in terms of material parameters like the logarithmic density derivative of the critical temperature, the coherence length $\xi_{\text{BCS}}$ and the GL parameter $\kappa$. This result provides a convenient tool to access these parameters by measuring the jump in the capacitance at the third critical field $B_{c3}$. Indeed, the discontinuity is small but nevertheless observable.

For an estimate, we assume some typical numbers. The most sensitive measurements of capacitance performed in the $C \sim \mu F$ range are capable of monitoring the changes $\delta C / C \sim 10^{-6}$ with error bars of $\sim 10^{-7}$. From the capacitance $C = \epsilon_0 \epsilon_d S / L$, one sees that a 1000 Å-thick dielectric layer with $\epsilon_d = 40^3$ has an optimal area of $10 \text{ mm}^2$, which is approximately the usual.
size of such samples [20]. The penetration depth (13) yields the relative change of the capacitance according to (1). With $\epsilon_s = 4$ and the above assumed values for the capacitance, one finds that the changes $|\delta L| > 3 \times 10^{-6} \text{ Å}$ are conveniently detectable with error bars of $\delta L \sim 3 \times 10^{-7} \text{ Å}$.

It should be noted here that these estimates remain essentially valid even when the Wagner polarization diminishing the effective permittivity of thin dielectric layers is taken into account. The expected reduction of the numbers above corresponds only to a factor of $\sim 2$; see [21].

Now we will show that for niobium the discontinuity falls in the range of the error bars. For niobium at the temperature $T \sim 1 \text{ K}$, one can take $\kappa \sim 1.5$, see [22], and $m_s = 1.2$, giving $\kappa^4 \epsilon_s/m_s^2 = 11.7$. The logarithmic derivative is estimated in [23] as $\partial \ln T_c/\partial \ln n = 0.74$. The electron density $n = 2.2 \times 10^{28} \text{ m}^{-3}$ yields $a_{\text{B}}^2 n = 3.3 \times 10^{-3}$ and the Fermi velocity $v_F = \hbar (3\pi^2 n)^{1/3}/(m_0 m_s) = 7.2 \times 10^5 \text{ m s}^{-1}$. The critical temperature $T_c = 9.5 \text{ K}$ corresponds to the BCS coherence length of $\xi_{\text{BCS}} = 3120 \text{ Å}$. Finally, we need the third critical magnetic field $B_{c3}$ to estimate the magnetic length $l$. From $B_{c3} = 1.69 B_{c2}$ and the experimental value $B_{c2} = 0.35 \text{ T}$ [22], one finds that $B_{c3} = 0.59 \text{ T}$, which yields $l = 325 \text{ Å}$. With all these values, we obtain from equation (14) the discontinuity $\delta L \sim 1.2 \times 10^{-6} \text{ Å}$, which is comparable with the error bar.

There are a number of alloys [24] with the help of which one can easily reach a region of observable discontinuities. For example, an alloy of 50% niobium and 50% tantalum has the critical temperature $T_c = 6.25 \text{ K}$, while the GL parameter at $T_c$ is $\kappa = 3.9$ [25]. The upper critical magnetic field at $T \ll T_c$ is $0.7 \text{ T}$ [25], giving $B_{c2} = 1.2 \text{ T}$, which yields $l = 228 \text{ Å}$. We assume that the effective mass scales with the GL parameter so that $\kappa/m_s$ remains the same as in pure niobium along with the remaining parameters. In this case, the discontinuity increases to $\delta L = 1.1 \times 10^{-5} \text{ Å}$, which is still easily observable.

We note that among intermetallic alloys, there are even more promising candidates. The alloy of Nb–61% Ti has $T_c = 8.95 \text{ K}$ and $\kappa = 38.4$. The upper critical magnetic field $B_{c2} = 47 \text{ T}$ corresponds to $B_{c3} = 80 \text{ T}$, which is too high to be applied during slow measurements of the capacitance. One has to increase the temperature for the measurement so that the third critical field becomes comparable with a convenient field of 10 T, which corresponds to $l = 79 \text{ Å}$. This estimate suggests $\delta L = 1.5 \times 10^{-4} \text{ Å}$, which is 50 times larger than the experimental sensitivity.

Detectable amplitudes of the discontinuity also result for high-$T_c$ materials. Using the values of YBa$_2$Cu$_3$O$_{7-\delta}$, which are $T_c = 90 \text{ K}$, $\kappa = 55$, $m_s = 6.92$, $\epsilon_s = 4$, $n = 5 \times 10^{27} \text{ m}^{-3}$ [26] and $\partial \ln T_c/\partial \ln n = -2.4$, as well as $l = 79 \text{ Å}$ for 10 T of the applied magnetic field, one can expect a discontinuity $\delta L = 1.4 \times 10^{-5} \text{ Å}$.

It should be noted that the field effect on the high-$T_c$ materials has been extensively studied within the effort to develop superconducting devices analogous to the field-effect transistors [27, 29]. There were many measurements of the field effect directly detecting changes in $T_c$ with the applied electric field. These experiments employ the largest accessible fields because the changes in $T_c$ are very small. The discontinuity of the capacitance can supply the missing knowledge of the field effect for low applied fields. Since the mechanism of the field effect on the high-$T_c$ materials has not yet been fully clarified, the low-field effect is of interest.

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6 A depression of the transition temperature by the gate voltage in the superconductor–insulator–metal structures with a 4.5 nm layer of YBa$_2$Cu$_3$O$_{7-\delta}$ observed by Frey et al [27] yields $\partial \ln T_c/\partial \ln n = -2.4$. An alternative estimate made in [29] from chemical trends assumes only a charge density in planes giving $\partial \ln T_c/\partial \ln n_{pl} = -4.8$. Since the densities of states in planes and chains are comparable, only half of the induced charge enters CuO$_2$ planes so that both estimates agree.
In summary, we have shown that the capacitance of the planar capacitor with one normal electrode and one superconducting electrode possesses a discontinuity at the third critical field $B_{c3}$. This discontinuity is large enough to be observed in capacitors with ferroelectric dielectric layers having a width of 1000 Å. This effect is not expected to be distorted by the volume change due to superconducting transitions, since we restrict ourselves to nucleation fields where the bulk remains normal conducting. We would like to point out that compared with other regions of the magneto-capacitance, the discontinuity has the advantage of being a unique feature that is not obscured by other properties of the insulator. Indeed, exploring strong electric fields, one has to face the fact that the dielectric response of the ferroelectric material is nonlinear. Scanning through temperatures, one observes namely the Curie law of the ferroelectric transition. Moreover, the dielectric function of the ferroelectric isolator depends on the magnetic field. The measurement of the discontinuity circumvents all these problems, because all the troublesome dependencies are continuous at the onset of the surface superconductivity.

In conclusion, a new effect is presented that allows to measure the onset of surface superconductivity with the help of the interaction between electric fields and superconductivity. The effect is relevant to finite systems.

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