Journal of Experimental and Theoretical Physics, Vol. 97, No. 1, 2003, pp. 154–161.
Translated from Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki, Vol. 124, No. 1, 2003, pp. 172–179.
Original Russian Text Copyright © 2003 by Marchenko, Podolyak.

SOLIDS
Electronic Properties

Phase Diagram of Surface Superconductivity

V. I. Marchenko* and E. R. Podolyak

Kapitza Institute of Physical Problems, Russian Academy of Sciences, Moscow, 119334 Russia

**e-mail: mar@kapitza.ras.ru*

Received January 31, 2003

Abstract—The Ginzburg–Landau theory is used to numerically analyze the stability of surface superconductivity. The singularities in the behavior of the solution on approaching the stability limit are described within the Landau theory of second-order phase transitions applied to a metastable state. It is found that the wetting must be observed upon transition from type I to type II superconductors: the thickness of surface superconductivity goes to infinity when the magnetic field tends to critical. *© 2003 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Saint-James and de Gennes [1] demonstrated the instability of the normal phase of a superconductor relative to the emergence of a layer of superconducting state in the vicinity of the sample boundary in fields below $H_{c3} = 2.3965\kappa H_c$. As was found by Feder [2], the critical value of the Ginzburg–Landau parameter $\kappa_F \approx 0.41$ exists, which separates superconductors by their behavior in fields below H_{c3}. For materials with $\kappa < \kappa_F$, no equilibrium solution of equations exists for the surface layer; i.e., the field H_{c3} is a field of supercooling of the normal state. In the case of materials with $\kappa > \kappa_F$, the surface superconductivity with a finite thickness on the order of the Ginzburg–Landau coherence length must be observed in a field below H_{c3}. The critical point found by Feder (we will refer to it as the Feder point) is in the region of metastability of the normal state $H < H_c$.

The supercooling of surface superconductivity was experimentally found as a result of measurements of the hysteresis of magnetization curves in tantalum and lead by McEvoy, Jones, and Park [3]. Khlyustikov and Berezin [4] have recently observed the effect of supercooling of surface superconductivity in lead when measuring the surface impedance.

Therefore, some region of metastability exists in the (κ, H) phase diagram of surface superconductivity. Park [5] determined the boundary $H_s(\kappa)$ of this region for the values of the Ginzburg–Landau parameter from the Feder point to $\kappa = 0.575$ where the limit approached the $H = H_c$ line. In this paper, we will clarify the further behavior of this boundary (see Fig. 1).

In order to determine the range of existence of surface superconductivity, we will perform a complete investigation of the stability (to small perturbations) of surface superconductivity. We will find that, for type I superconductors, the boundary is defined by the loss of stability of the surface solution relative to uniform (in the boundary plane) perturbations. It turns out that, at $\kappa > 0.575$, the field of supercooling continues to be pressed against the critical field H_c and becomes equal to H_c only at the point $\kappa = 1/\sqrt{2}$. For type II superconductors, the $H_{c2}(\kappa)$ serves as the stability boundary.

We will demonstrate that the singularities in the behavior of the solution on approaching the line of the loss of stability in type I superconductors may be understood from very general considerations within the Landau theory of second-order phase transitions applied to metastable states. In the neighborhood of the point $(1/\sqrt{2}, H_c)$, the thickness of the superconducting layer diverges; i.e., a wetting transition occurs. In this case, we suggest a macroscopic approach enabling one to explain the very unusual nonanalytical behavior of the surface solution.

2. THE STABILITY REGION OF SURFACE SUPERCONDUCTIVITY

In the units of $H_c = \delta = 1$, which are natural for the Ginzburg–Landau theory (see, for example, Paras. 45 and 46 in [6]), the free energy of a superconductor is

$$F = \frac{1}{8\pi} \times \int\left\{-2|\psi|^2 + |\psi|^4 + \left|\left(\frac{\sqrt{2}}{\kappa}\nabla - i\mathbf{A}\right)\psi\right|^2 + \mathbf{B}^2\right\}dV. \quad (1)$$

In the problem being treated, the external field **H** is directed along the sample boundary (z axis). For an equilibrium solution localized in the vicinity of the sur-

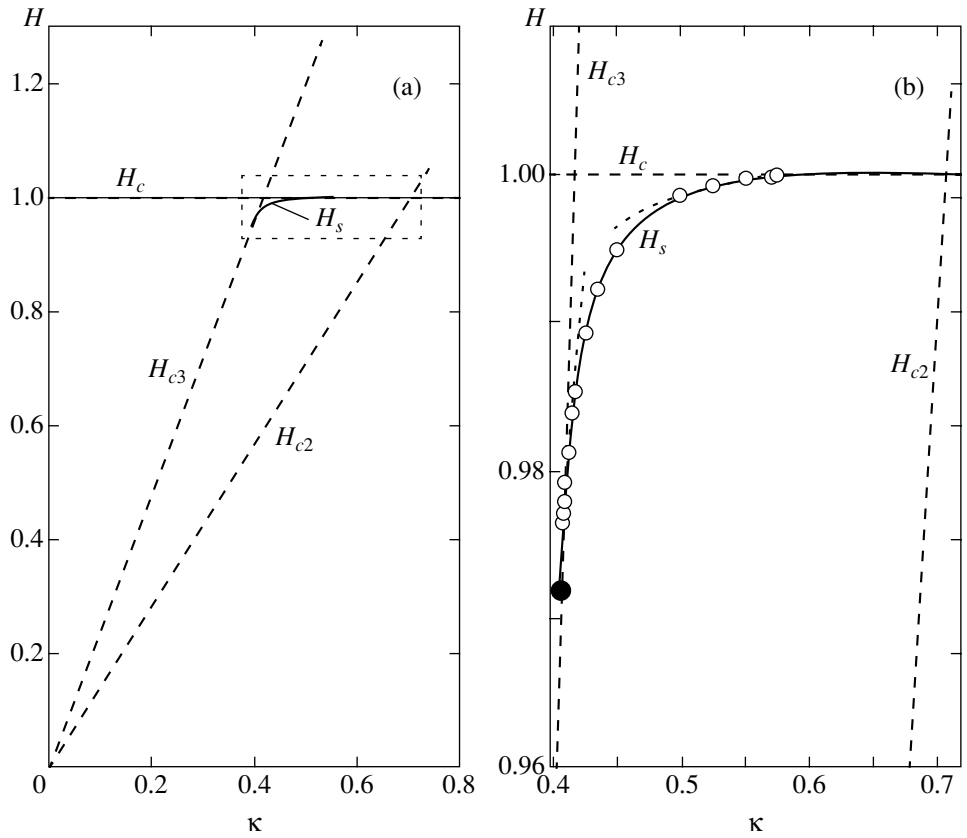

Fig. 1. (a) Phase diagram of surface superconductivity and (b) a part of the H_s curve indicated by dashed contour. The dark circle indicates the Feder point $\kappa_F = 0.4054$. The light circles indicate Park's results [5]. The dashed lines indicate the asymptotes in the vicinity of the Feder point: $H_s = 0.9623 + 0.211(\kappa - 0.4035)^{1/2}$ (see Section 2), and in the vicinity of the point $(1/\sqrt{2}, H_c)$: $H_s = 1 - 0.304\varepsilon e^{-0.793/\varepsilon}$ (see Section 4).

face, we select the gauge for the vector potential **A** such that the order parameter ψ should be a real function of distance x from the boundary,

$$A_y(\mathbf{r}) = A(x), \quad A_x(\mathbf{r}) = A_z(\mathbf{r}) = 0.$$

We will investigate the stability (to small perturbations) of the equilibrium solution $\{\psi(x), A(x)\}$ in the general case of nonuniform perturbations. For this purpose, it is necessary to check the positiveness of the variation of free energy in the case of arbitrary small fluctuations of the order parameter $\delta\psi(\mathbf{r})$ and of the vector potential $\delta\mathbf{A}(\mathbf{r})$. It is natural to expect that the most dangerous fluctuations will be those in which the magnetic field variation $\delta\mathbf{B}(\mathbf{r})$ will remain parallel to the external field **H** (i.e., the magnetic field lines will not bend). We use the gauge invariance to select $\delta\mathbf{A}(x, y) = (0, \delta A(x, y), 0)$. We expand the perturbation $\{\delta\psi(x, y), \delta A(x, y)\}$ into a Fourier series in $\exp(iqy)$ to represent the second variation of free energy as

$$\delta^2 F = \frac{1}{4\pi}\sum_q \int_0^\infty dx \left\{ \frac{1}{\kappa^2}|\partial_x \delta\psi_q|^1 + |\delta\psi_q|^2\left(\frac{A}{\sqrt{2}} - \frac{q}{\kappa}\right)^2 \right.$$
$$+ \psi\left(A - \frac{q}{\sqrt{2}\kappa}\right)(\delta A_q \delta\psi_q^* + \delta A_q^* \psi_q) + |\delta\psi_q|^2(\psi^2 - 1) \quad (2)$$
$$\left. + \psi^2|\delta\psi_q + \delta\psi_{-q}^*|^2 + |\partial_x A_q|^2 + \psi^2|A_q|^2 \right\}.$$

The quantity $\delta A(x, y)$ is a real function; therefore, $\delta A_{-q}(x) = \delta A_q^*(x)$. No such correlation exists for the components of $\delta\psi_q$, and expression (2) contains cross terms $\delta\psi_q$ and $\delta\psi_{-q}^*$. We introduce the Fourier components of the real, $\delta\psi'$, and imaginary, $\delta\psi''$, parts of $\delta\psi$,

$$\delta\psi_q' = \frac{1}{2}(\delta\psi_q + \delta\psi_{-q}^*), \quad \delta\psi_q'' = \frac{1}{2}(\delta\psi_q + \delta\psi_{-q}^*),$$

and proceed to perform the summation over positive values of q to reduce the second variation (2) to the sum of independent contributions $\delta^2 F_q\{\delta\psi_q', \delta\psi_q'', \delta A_q\}$. In order to investigate the stability, it is sufficient to find

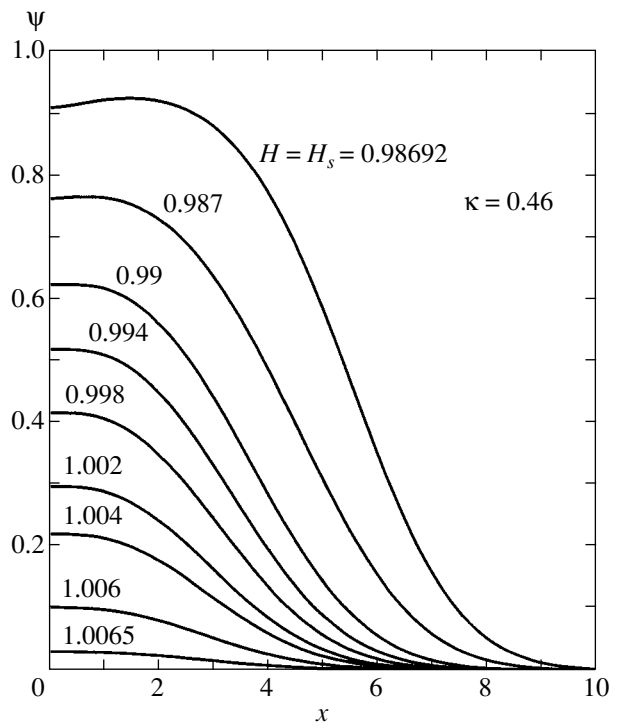

Fig. 2. The evolution of the Ginzburg–Landau ψ-function for surface superconductivity upon variation of the field from H_{c3} to H_s at $\kappa = 0.46$.

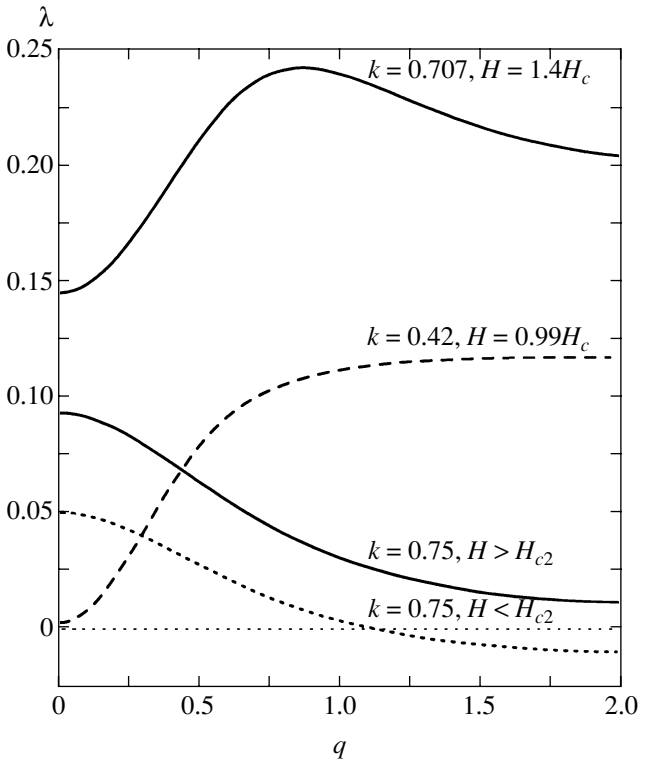

Fig. 3. Examples of spectra of eigenvalues $\lambda(q)$.

the minimum of quadratic functional $\delta^2 F_q$ with a fixed value of

$$\int_0^\infty |\delta\psi_q'|^2 dx. \qquad (3)$$

This formulation of the problem turns out to be convenient from the standpoint of numerical computation, where the asymptotic behavior of eigenfunctions at $x \longrightarrow \infty$ is of importance. Because of their awkwardness, we will not give here the appropriate Euler equations with natural (i.e., obtained as a result of variation) boundary conditions. They were numerically solved using the method of "shooting" from the point $x \longrightarrow \infty$ to the point $x = 0$. Three parameters were preassigned on the right-hand boundary, namely, the Lagrange multiplier λ_q corresponding to the constancy of integral (3) and the amplitudes of the asymptotics $\delta\psi_{-q}^*$ and δA_q. By virtue of the linearity of the problem, the amplitude of $\delta\psi_q$ may be arbitrary. On the left-hand boundary with $x = 0$, three conditions were to be met, namely, $\partial_x \delta\psi_q = \partial_x \delta\psi_{-q}^* = \partial_x \delta A_q = 0$. The latter of these conditions follows from the trivial solution $\delta\mathbf{B} = 0$ in the treated case of Maxwell equations ($\partial_x B_z = \partial_y B_z = 0$) outside the superconductor ($x < 0$).

The problem involves an infinite set of discrete levels λ (in the case of $\psi(x) = 0$, these are simply electron levels in a uniform magnetic field) for each value of the wave vector q. In order to analyze the stability, it is sufficient to find the ground level for which the eigenfunctions have no zeros. Figure 2 demonstrates the typical evolution of the order parameter of surface superconductivity upon variation of the field. Figure 3 gives the results of numerical counting for the spectrum of λ_q for different values of κ and H.

In type I superconductors in some field of supercooling H_s such that $H_{c2} < H_s < H_c$, the surface state loses stability at $q = 0$ and the unstable mode turns out to be localized in the region of surface superconductivity. This instability leads to the propagation of superconductivity from the surface into the bulk of the sample.

In type II superconductors at $q \longrightarrow \infty$, the function $\delta\psi_q(x)$ is localized at distances far away from the surface in the neighborhood of the point $x = x_0$, where $A(x_0) = \sqrt{2}\, q/\kappa$. Here, the function $\psi(x_0)$ is small, and the field $B(x_0)$ is almost equal to the external field. Therefore, the stability of the surface state deteriorates because of nucleation in the normal-phase volume; i.e., the stability limit of surface superconductivity for type II superconductors coincides with the stability limit of the normal state in the volume $H = H_{c2}$.

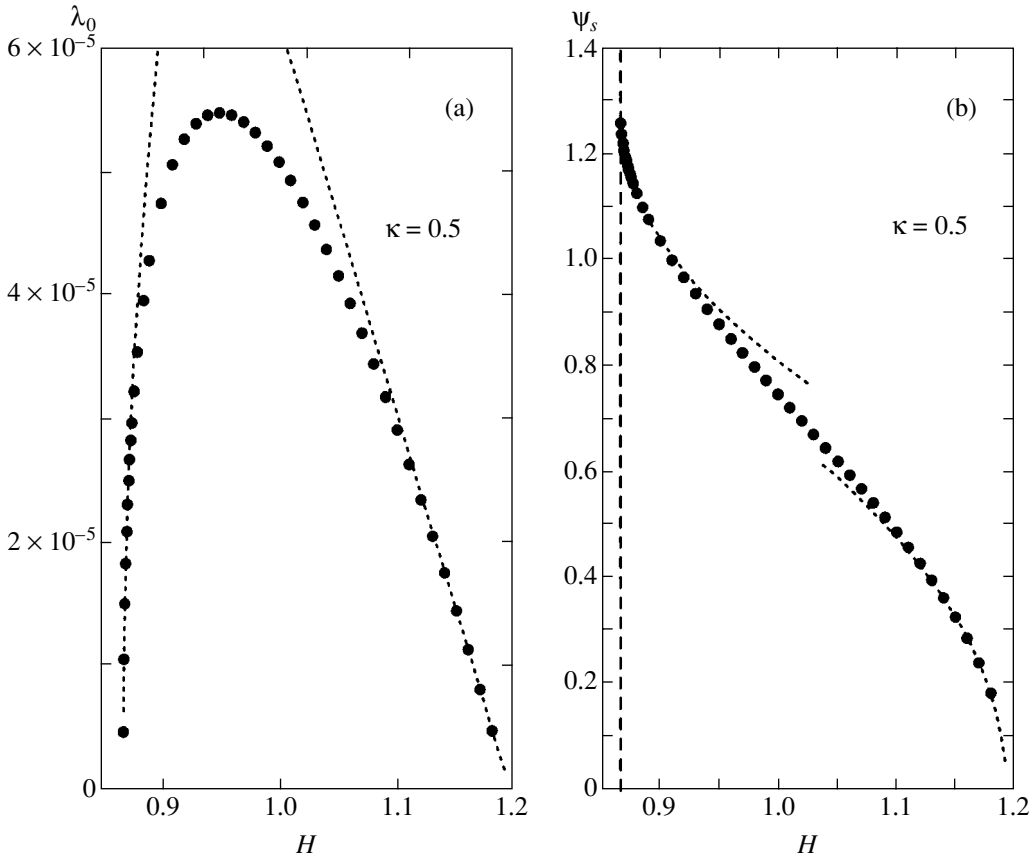

Fig. 4. The evolution of the "gap" in the excitation spectrum and of the integral order parameter ψ_s upon variation of the field from H_{c3} to H_s at $\kappa = 0.5$. The dotted line indicates the asymptotics in the vicinity of $H_{c3} = 1.19$: $\lambda_0 = 3.19 \times 10^{-4}(H_{c3} - H)$, $\psi_s = 1.56(H_{c3} - H)^{1/2}$ (see Section 2); and in the vicinity of $H_s = 0.866$: $\lambda_0 = 3.35 \times 10^{-4}(H - H_s)^{1/2}$, $\psi_s = 1.276 - 1.28(H - H_s)^{1/2}$ (see Section 3).

Figures 4–6 give the results of computation of the evolution of the quantity λ_0 ($q = 0$) and of the integral order parameter,

$$\psi_s = \int_0^\infty \psi dx, \qquad (4)$$

during motion over the field from H_{c3} to H_s at $\kappa = 0.5$ and $\kappa = 1/\sqrt{2}$, as well as during motion with respect to κ with the critical field H_c.

3. THE FEDER POINT IN THE LANDAU THEORY

The emergence of surface superconductivity in the vicinity of the field H_{c3} is an example of second-order phase transition in a two-dimensional system. The specific features in the behavior of the stability limit of metastable state in the vicinity of the Feder point may be clarified in the Landau theory of second-order phase transitions. The fact that the curve of the loss of stability of surface superconductivity turns out to be tangent to the straight line $H_{c3}(\kappa)$ at the Feder point is a property that is common to critical points of this type.

The Landau expansion for free energy of a metal surface has the standard form

$$A(\kappa, H)|\psi_s|^2 + B(\kappa, H)|\psi_s|^4 + C(\kappa, H)|\psi_s|^6 + \ldots. \qquad (5)$$

Note that the vector potential in the case of such (two-dimensional) description is of no significance if the field is parallel to the surface. For comparison with the results of numerical solution of Ginzburg–Landau equations, we will take the integral characteristic given by Eq. (4) as the order parameter of two-dimensional theory ψ_s. The range of validity of the two-dimensional approach away from the Feder point, when the effect of the sixth-order contribution in expansion (5) may be ignored, is seen in Figs. 4–6. Asymptotic curves are given in the vicinity of the field H_{c3}; these curves follow from expression (5) on the assumption (made in the Landau theory) that the coefficient A linearly goes to zero. It is clear that, in the vicinity of the field H_{c3}, the second derivative of free energy (5) with respect to the

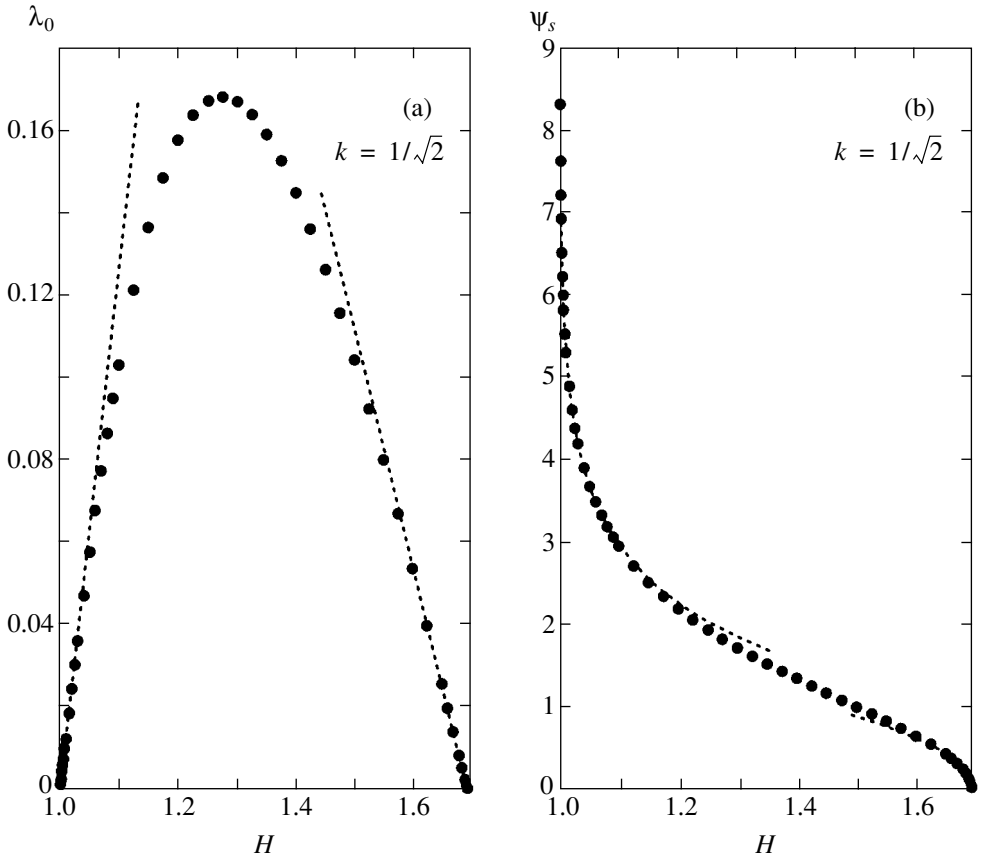

Fig. 5. The evolution of the "gap" in the excitation spectrum and of the integral order parameter ψ_s upon variation of the field from H_{c3} to H_s at $\kappa = 1/\sqrt{2}$. The dotted line indicates the asymptotics in the vicinity of $H_{c3} = 1.70$: $\lambda_0 = 0.576(H_{c3} - H)$, $\psi_s = 2.03(H_{c3} - H)^{1/2}$ (see Section 2); and in the vicinity of $H_c = 1$: $\lambda_0 = 1.27(H - 1)$, $\psi_s = -2.33\ln[0.52(H - 1)]$ (see Section 4).

two-dimensional order parameter ψ_s, which defines the stability of the solution, is linearly related to λ_0.

At the Feder point, the coefficient B obviously goes to zero (again by the linear law). In order to describe the behavior in the vicinity of this point, the sixth-order term must be taken into account. Here, however, in contrast to the critical point treated by Landau [7] (see also Para. 150 in [8]), the coefficient C must be taken to be negative, which corresponds to the metastability of surface superconductivity being investigated. With regard for the sixth-order term, we derive, in addition to the trivial $\psi_s = 0$, two possible extrema of functional (5):

$$|\psi_{s1}|^2 = \frac{-B - \sqrt{B^2 - 3AC}}{3C}, \qquad |\psi_{s2}|^2 = \frac{-B + \sqrt{B^2 - 3AC}}{3C}. \tag{6}$$

One solution ψ_{s1} exists at $A > 0$ and $B > 0$. This solution corresponds to a local maximum ensuring the metastability of normal state. With $B > 0$ and a change of sign for A, a new solution ψ_{s2} arises, which corresponds to a local minimum, i.e., to surface superconductivity. With further variation of A, when the quantity $B^2 - 3AC$ changes sign, both solutions coincide and the nontrivial extrema disappear. The equation

$$B^2 = 3AC \tag{7}$$

apparently corresponds to the critical curve of $H_s(\kappa)$. One can readily see that it is the quadratic dependence given by Eq. (7) between the small coefficients A and B that leads to the characteristic root approximation of curve $H_s(\kappa)$ to line $H_{c3}(\kappa)$ at the Feder point (see Fig. 1). One solution ψ_{s2}—a local maximum—exists in the region of $A > 0$ and $B > 0$. On the $A = 0$ line, this solution goes to zero and only one trivial extremum—a maximum—remains, $\psi_s = 0$.

4. SPECIAL FEATURES IN THE LOSS OF STABILITY IN METASTABLE STATE

A loss of stability of the surface solution relative to uniform perturbation ($q = 0$) occurs on the $H_s(\kappa)$ line. This means that two solutions merge on this line,

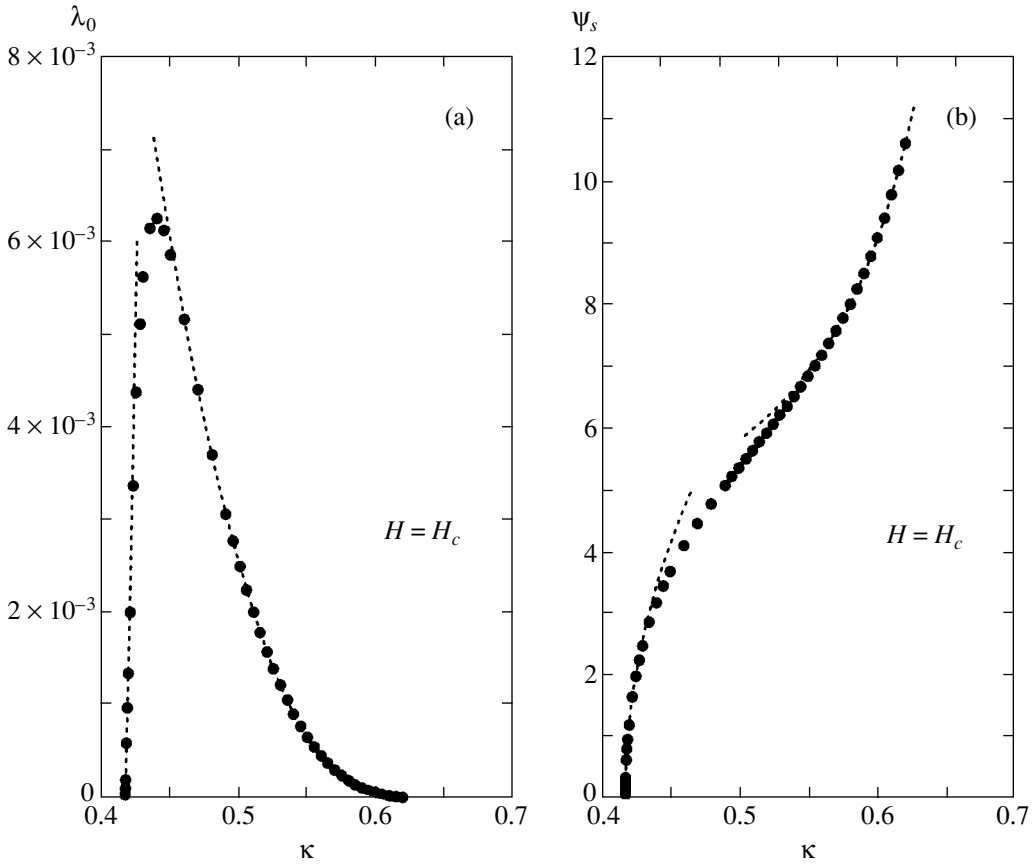

Fig. 6. The evolution of the "gap" in the excitation spectrum and of the integral order parameter ψ_s upon variation of κ from 0.417 to $1/\sqrt{2}$ in a field equal to the critical field. The dotted line indicates the asymptote in the vicinity of $\kappa = 0.417$: $\lambda_0 = 0.83(\kappa - 0.417)$, $\psi_s = 22.8(\kappa - 0.417)^{1/2}$ (see Section 2); and in the vicinity of $\kappa = 1/\sqrt{2}$: $\lambda_0 = 0.356\varepsilon e^{-0.701/\varepsilon}$), $\psi_s = 0.721\varepsilon^{-1} + 2.34$ (see Section 4).

namely, the local minimum (the surface solution being investigated) and maximum (the barrier providing for the metastability of the solution). It was such a merger of two solutions that was found by Park [5].

Let ψ_{s0} be the limiting solution on the line of the loss of stability. The Landau expansion with respect to the small parameter $\eta = \psi_s - \psi_{s0}$ in the vicinity of this line has the form

$$A(\kappa, H)\eta + B(\kappa, H)\eta^2 + C(\kappa, H)\eta^3 + \dots . \quad (8)$$

Because we treat the states with disturbed gage invariance ($\psi_{s0} \neq 0$), no symmetry exclusions exist in this case and odd-power terms are present in the expansion. The coefficient A goes to zero on the line being discussed simply by definition of the parameter η (equilibrium equations must have the solution of $\eta = 0$). The vanishing of the coefficient B corresponds to the merger of solutions. On approaching the critical line, we have two extrema of functional (8),

$$\eta_1 = \frac{-B + \sqrt{B^2 - 3AC}}{3C}, \quad \eta_2 = \frac{-B - \sqrt{B^2 - 3AC}}{3C}. \quad (9)$$

The stability of solutions will be defined by the positiveness of the second derivative,

$$F'' = 2B + 6C\eta > 0. \quad (10)$$

In the surface superconductivity problem under discussion, where the parameter ψ_s increases in the vicinity of the critical line, we must have $\eta < 0$ for a metastable solution. One can readily see that, for this purpose, it is necessary for the inequalities $A < 0$, $B > 0$, and $C < 0$ to be valid above the line of the loss of stability.

Given the linear vanishing of the coefficients A and B (which is standard for the Landau theory), on approaching the critical line ($\varepsilon \ll 1$), we obtain the following special features in the order parameter and in the "energy gap" (10):

$$\eta \propto -\sqrt{|\varepsilon|}, \quad F'' \propto \sqrt{|\varepsilon|}. \quad (11)$$

The resultant asymptotics in the vicinity of H_s are shown in Fig. 4.

5. WETTING TRANSITION

According to our numerical results, the integral order parameter (4) significantly increases on approaching the point $\kappa = 1/\sqrt{2}$. In this case, the Ginzburg–Landau ψ-function tends to unity almost everywhere within the layer; therefore, the parameter given by Eq. (4) defines the surface layer thickness in the limit being treated to an accuracy within the order of the width of the *ns*-boundary. The anomalous growth of this thickness makes possible a macroscopic description along the lines of the wetting theory (see Para. 160 in [8]). The specific features of superconductivity bring about the peculiarity of the thickness dependence of the free energy of the wetting layer.

In a homogeneous superconducting state, small perturbations of the order parameter and vector potential at distances far away from the plane source of perturbations decrease as $e^{-x/\xi}$ and $e^{-x/\delta}$, respectively, where $\xi = \delta/\sqrt{2}\kappa$ is the coherence length. Two sources of perturbations exist in the superconducting layer at the surface, namely, the sample surface and the boundary between the superconducting and normal phases. By complete analogy with, for example, the derivation of the law of interaction of electric charges in terms of the field of electric potential or elastic interaction of defects in crystals, one can state that the expression for the energy of interaction between the boundaries of the superconducting layer with its macroscopic thickness $L \gg \xi, \delta$ in the general case reduces to the sum

$$F_{int} = Ae^{-L/\xi} + Be^{-L/\delta}, \quad (12)$$

where A and B are some functions of parameter κ (the dependence on the magnetic field may be ignored, because the superconducting layer thickness may be significant only in the immediate neighborhood of $H = H_c$). Corresponding to the numerically established behavior of surface superconductivity in the neighborhood of the point $\kappa = 1/\sqrt{2}$ is the case of $A < 0$ (attraction), $B > 0$ (repulsion), with $B > |A|$. The free energy of superconducting layer, reckoned from the normal state, includes the energy of the superconductor boundary, the energy of the interface between superconducting and normal phases, the interaction energy given by Eq. (12), and the bulk contribution

$$\frac{1}{8\pi}(H^2 - H_c^2)L. \quad (13)$$

The equilibrium thickness of the superconducting layer is defined by the condition of the minimum of the sum of contributions (12) and (13),

$$F' = -\frac{A}{\xi}e^{-L/\xi} - \frac{B}{\delta}e^{-L/\delta} + \frac{1}{8\pi}(H^2 - H_c^2) = 0. \quad (14)$$

The solution will be stable in the case of the positive second derivative of energy with respect to L,

$$F'' = \frac{A}{\xi^2}e^{-L/\xi} + \frac{B}{\delta^2}e^{-L/\delta}. \quad (15)$$

On the $H_s(\kappa)$ curve, the stability of the solution is lost. From the condition $F'' = 0$, we find

$$L = \frac{\delta\xi}{\xi - \delta}\ln\left(\frac{B\xi^2}{|A|\delta^2}\right) \quad (16)$$

and substitute this value of L into Eq. (14) to derive

$$H_s^2 - H_c^2 = -8\pi\frac{|A|}{\xi^2}(\xi - \delta)\exp\left\{-\frac{\delta}{\xi - \delta}\ln\frac{B\xi^2}{|A|\delta^2}\right\}. \quad (17)$$

In view of the proximity to the critical point at which $\varepsilon = (\xi - \delta)/\delta \ll 1$, results (16) and (17) may be represented in the form of $L \propto \varepsilon^{-1}$ and

$$H_s - H_c \propto -\varepsilon e^{-a/\varepsilon}, \quad (18)$$

where $a = \ln(B/|A|)$ is a number on the order of unity. As we see in Fig. 1, the asymptotic form given by Eq. (18) is valid even at a considerable distance from the critical point being treated.

Following are the extreme expressions on approaching the critical point $(1/\sqrt{2}, H_c)$ along two preferred trajectories. For a superconductor with $\kappa = 1/\sqrt{2}$, the superconducting layer thickness logarithmically goes to infinity: $L \propto \ln\{1/(H - H_c)\}$, with $F'' \propto H - H_c$. In the case of motion along a straight line ($H = H_c$), the thickness increases by the law $L \propto \varepsilon^{-1}$ (as in the case of motion along a curve, $H = H_s$), and the "gap" in the excitation spectrum decreases by the law of $F'' \propto \varepsilon e^{-a/\varepsilon}$. The asymptotic laws obtained are given in Figs. 5 and 6. We used the above-identified relation between the integral parameter (4) and the superconducting layer thickness L, as well as the obvious linear dependence between the second derivative of energy F'' (15) and the quantity λ_0 in the vicinity of the critical lines.

ACKNOWLEDGMENTS

We are grateful to I.N. Khlyustikov for attention to our work and discussions and to I.A. Fomin for discussion of our work.

This study was supported by the Russian Foundation for Basic Research (project nos. 00-02-16250 and 03-02-16958).

REFERENCES

1. D. Saint-James and P. G. de Gennes, Phys. Lett. **7**, 306 (1963).
2. J. Feder, Solid State Commun. **5**, 299 (1967).
3. J. P. McEvoy, D. P. Jones, and J. G. Park, Solid State Commun. **5**, 641 (1967).
4. I. N. Khlyustikov and V. A. Berezin, Zh. Éksp. Teor. Fiz. **121**, 1370 (2002) [JETP **94**, 1176 (2002)].
5. J. G. Park, Solid State Commun. **5**, 645 (1967).
6. E. M. Lifshitz and L. P. Pitaevskiĭ, *Course of Theoretical Physics*, Vol. 5: *Statistical Physics* (Nauka, Moscow, 1978; Pergamon, New York, 1980), Part 2.
7. L. D. Landau, Phys. Z. Sowjetunion **8**, 113 (1935); *Collected Works* (Nauka, Moscow, 1969), p. 123.
8. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 4th ed. (Nauka, Moscow, 1995; Pergamon Press, Oxford, 1980), Part 1.

Translated by H. Bronstein