SUPERCONDUCTING PROPERTIES OF PURE NIOBIUM

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An induction method has been used to measure the temperature dependence of the fields H_{c1}, H_{c2}, and H_{c3} in niobium samples with resistance ratios R(300°K)/R(4.2°K) ~ 10^4 and ~ 3×10^2. It has been established that the experimental value of $H_{c2}(0)$ is five times that calculated from the microscopic theory, and that the behavior of $H_{c3}(T)$ depends on the purity of the sample. The magnetic properties of niobium have been studied in an inclined magnetic field. The applicability of the isotropic theory of superconductivity to niobium, which has a complicated Fermi surface, is discussed.

INTRODUCTION

At the present time niobium is the only superconductor of the second kind[1] in which it is possible to obtain the "pure" limit, i.e., to achieve a mean free path l many times greater than the coherence length ξ_0.[1] As the result of the calculations of Mattheiss[2] and of recent measurements of the optical constants,[3] magnetoresistance, Hall effect[4], and de Haas–van Alphen effect,[5] the Fermi surface of niobium has been plotted, its total area and extremal section areas measured, and the electron concentration, effective electron mass, and average electron velocity at the Fermi surface determined.

At the same time the formulas of the microscopic theory of superconductivity[6,7] connect the experimentally measured superconducting parameters with the electronic constants of the material. By comparing data on electron energy spectra obtained from measurements of the superconducting properties with values determined by more direct methods,[3-5] we can assess the applicability of the isotropic theory of superconductivity to description of the properties of niobium. Previously the theory of V. L. Ginzburg, L. D. Landau, A. A. Abrikosov, and L. P. Gor'kov (GLAG) had been repeatedly verified in the "dirty" limit, when $l \ll \xi_0$. Here, as a rule, the experiments brilliantly confirmed the main results of the theory. In the present article we evaluate the possibility of applying the isotropic theory to a superconductor of the second kind in the case where $l \gg \xi_0$, and the Fermi surface has a complicated topology.

Our second goal is to study the effect of the demagnetization coefficient n on the superconducting properties of niobium. Since niobium lies almost at the limit separating superconductors of the first and second kinds,[1)] it is not excluded that for $n \neq 0$ the vortex and intermediate states can coexist in it. It is of interest to study also the temperature behavior of the upper critical field H_{c3}, particularly near T_c where anomalies arise which are associated with thermodynamic fluctuations of the order parameter.[8]

[1)] The parameter κ of the GLAG theory corresponding to the limit is 0.71; $\kappa_{Nb}(T_c) = 0.83$.

1. SAMPLES AND METHOD OF MEASUREMENT

Samples. The investigations were made in samples of diameter 0.4 mm and length 10–30 mm, prepared from niobium wires recrystallized and outgassed in a vacuum of 10^{-8}–5×10^{-11} torr. The method of preparation of the samples and their impurity concent have been described in detail in previous articles.[9-11]

In samples of the batch Nb-1 the resistance ratio Γ = R(300°K)/R(4.2°K) ~ 10^4, and for the batch Nb-2 about 3×10^2. For magnetization measurements (see Sec. 2) an additional sample having the shape of an ellipsoid was prepared.

Method of measurement. The method of measurement and the arrangement of the apparatus have been described previously.[9] Values of the critical magnetic fields H_{c1}, H_{c2}, and H_{c3} were determined by recording on a strip chart the real part of the magnetic permeability μ' as a function of the external magnetic field. The measurements were made at a frequency of 370 Hz with a modulation amplitude of ~0.01 G. Examples of the recordings of μ'(H) are shown in Fig. 1, where the critical-field values are indicated by arrows. The magnetization curves were obtained by a ballistic method.[10] The H_{c1} and H_{c2} values obtained by recording μ'(H) agree with the ballistic measurement data with an accuracy of ~3%.

2. MAGNETIC PROPERTIES OF NIOBIUM IN AN INCLINED MAGNETIC FIELD

A. The dependence of the critical field H_{c1} on the angle α between the sample axis and the external magnetic field. The demagnetization coefficients of an ellipsoid of rotation, of which a particular case is an infinitely long cylinder, obey the relation

$$2n_x + n_z = 1, \tag{1}$$

where z is the rotation axis. If the angle α is not equal to 0 or $\pi/2$, the direction of the magnetic induction **B** does not coincide with the direction of the external field H_0 and is determined by the expressions

$$H_x^0 = H_x + n_x(B_x - H_x),$$
$$H_z^0 = H_z + n_z(B_z - H_z). \tag{2}$$

Here **B** = **H** + 4π**M**, and **M** = M_0(H) is the magnetization

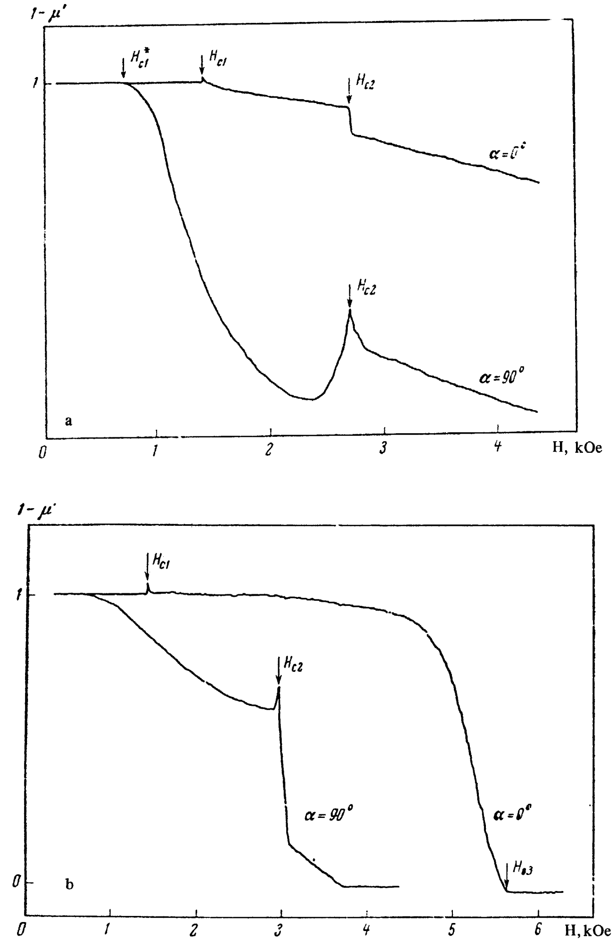

FIG. 1. Plot of $1-\mu'$ as a function of external magnetic field intensity: a–Nb-1, sample; b–Nb-2, sample; T = 4.2°K.

curve. The vectors **M**, **H**, and **B** are collinear.[11-14]

In order to find $H_{c1}^*(\alpha)$, we set $B_x = B_z = 0$ in Eq. (2). Then

$$H_x = \frac{H_x^0}{1-n_x} = \frac{H_0 \sin\alpha}{1-n_x}, \quad H_z = \frac{H_z^0}{1-n_z} = \frac{H_0\cos\alpha}{1-n_z}. \qquad (3)$$

Taking into account that by definition

$$H_x^2 + H_z^2 = H_{c1}^2 \qquad (4)$$

and that $H_0 = H_{c1}^*(\alpha)$, we have

$$H_{c1}^*(\alpha) = H_{c1}(0)\left[\frac{\sin^2\alpha}{(1-n_x)^2} + \frac{\cos^2\alpha}{(1-n_z)^2}\right]^{-1/2}. \qquad (5)$$

In the case of an infinite cylinder $n_z = 0$, $n_x = 1/2$, and

$$H_{c1}^*(\alpha) = H_c(0)/\sqrt{1+3\sin^2\alpha}. \qquad (6)$$

We have made an experimental check of Eq. (6). For this purpose a sample of Nb-1 with measuring and modulating windings[9] was placed at a fixed angle to the external magnetic field vector. Then the fields were turned on. The value of $H_{c1}^*(\alpha)$ was determined from the break in the transition curve (see Fig. 1a). Measurements were made at two different temperatures, in the angular range $0 \le \alpha \le \pi/2$. The results obtained are shown in Fig. 2. The agreement between the calculated and experimental values shows that edge effects are absent and that the sample behaves as an infinitely long cylinder.

B. Shape of the magnetization curve of an ellipsoid of revolution. According to the definition given by Abrikosov,[15] the area under the reversible magnetization curve of a superconductor of the second kind

$$S = \int_0^{H_{c2}} M\, dH_0 = -\frac{H_c^2}{8\pi} = (F_s - F_n)_{B=0} \qquad (7)$$

characterizes the difference in the free energies between the superconducting and normal states. Since Eq. (7) is a thermodynamic identity, it is natural to assume that S does not depend²⁾ on n and the angle α. We made an experimental verification of the constancy of S by comparing the magnetization curves of two specimens—a long cylinder in a longitudinal field (Nb-1) and a sample of nearly ellipsoidal shape. The results obtained are shown in Fig. 3. Measurement of the areas under the magnetization curves with a planimeter showed that they agree with an accuracy of ±3%.

We will show that the maximum value of the magnetic moment also does not depend on n and α. According to Eq. (3),

$$|M| = \frac{H_0}{4\pi}\left[\frac{\sin^2\alpha}{(1-n_x)^2} + \frac{\cos^2\alpha}{(1-n_z)^2}\right]^{1/2}. \qquad (8)$$

The magnetic moment reaches a maximum value when the magnetizing field is

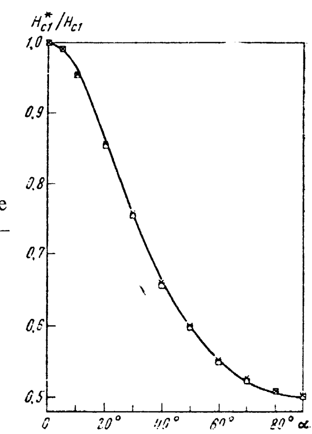

FIG. 2. Angular dependence of the first critical field H_{c_1}. Batch Nb-1: □–T = 4.2°K, ×–6.5°K. Solid curve–theory.

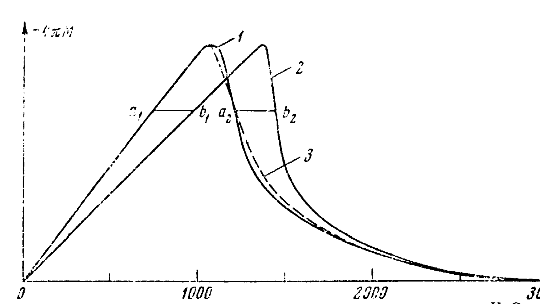

FIG. 3. Magnetization curves for different values of the demagnetization coefficient: curve 1–n_z = 0, curve 2–n_z = 0.2, curve 3–theoretical curve for n_z = 0.2. The Meissner part is plotted from formula (8), and the region $H_{c_1} < H < H_{c_2}$ by means of the segments $a_1b_1 = a_2b_2$, . . . , $a_nb_n = a_{2n}b_{2n}$.

²⁾The invariance of S for the case in which the external field is parallel to one of the principal axes of the ellipsoid is proved analytically by Kulik. [12].

$$H_0 = H_{c1}^*(\alpha). \tag{9}$$

Taking into account Eqs. (5), (8), and (9), we find that

$$|M|_{max} = H_{c1}^0(0)/4\pi \tag{10}$$

(Here $H_{c1}^0(0)$ is the first critical field of the long cylinder.) The fact that $|M|_{max}$ is independent of n gives us the right in comparison of magnetization curves with different n to plot them on the same scale. In Fig. 3 we show three M(H) curves: one for the case $n_z = 0$, $\alpha = 0$ and two for ellipsoids—experimental and theoretical. The closeness of the latter two curves, shown to the same scale, indicates the correctness of Eq. (10) and the absence of an intermediate state in niobium. Consequently, both for n = 0 and for n ≠ 0 a phase transition of the second kind occurs at the field H_{c1} from the Meissner state to the vortex state.[12]

3. TEMPERATURE DEPENDENCE OF THE CRITICAL MAGNETIC FIELDS H_{c2} AND H_{c1}

A. The critical field H_{c2}. Near $T = T_c$ the field H_{c2} is related to the thermodynamic field H_c by the well known relation[15]

$$H_{c2} = \sqrt{2}\varkappa_0 H_c. \tag{11}$$

For T = 0, according to Gor'kov,[7]

$$H_{c2}(0) = 1.77\varkappa_0(T_c)H_c(0). \tag{12}$$

Absolute values of $H_c(0)$ and $\kappa_0(T_c)$ for "pure" superconductors ($l \gg \xi_0$) with a spherical Fermi surface have been calculated by Gor'kov.[7] The equations derived in refs. 6 and 7 have been used by Eilenberger[16] to calculate the ratio $\kappa_0(T)/\kappa_0(T_c)$ for different mean free paths.

The results of our measurements of $H_{c2}(T)$ are shown in Fig. 4, together with the data of other authors.[17,18] The values of $H_{c2}(0)$ were obtained by extrapolation of a curve of $H_{c2}(t^2)$ to $t = T/T_c = 0$. Our specimens differ from those investigated by Finnemore et al.[17] and French[18] in a lower content of tantalum (2×10^{-5}% compared to 2×10^{-2}%), and batch Nb-1 further in that its outgassing was carried out at a higher vacuum than in refs. 18 and 19, (5×10^{-11} Torr compared to 10^{-9} Torr).

It follows from Fig. 4 that the value of H_{c2} and its dependence on temperature are not affected in an important way by the quantity of tantalum, but by the residual gas content. Thus, the value of $H_{c2}(T)$ in a sample of Nb-2, whose preparation differed only in the degree of vacuum during outgassing, lies noticeably above the corresponding values for Nb-1. The increase of H_{c2} in the Nb-2 sample can be explained as follows. According to Gor'kov,[6] in the "pure" limit ($l \to \infty$)

$$\varkappa_0 \approx 0.96\lambda_0/\xi_0, \tag{13}$$

where λ_0 is the London penetration depth. In the "dirty" limit ($l \ll \xi_0$) the role of ξ_0 in this formula is played by the mean free path. In the intermediate case κ depends both on ξ_0 and on l (see ref. 19):

$$\varkappa = \varkappa_0 + 7.53 \cdot 10^3 \rho_0(l)\gamma^{1/2}, \tag{14}$$

where γ [erg/cm^3-deg] is the coefficient of the linear term in the specific heat, and ρ_0[ohm-cm] is the residual resistivity. Taking into account that the thermodynamic field H_c is only a weak function of the impurity content and that for niobium $\gamma = 7.8$ mJ/mole-deg,[20] we obtain

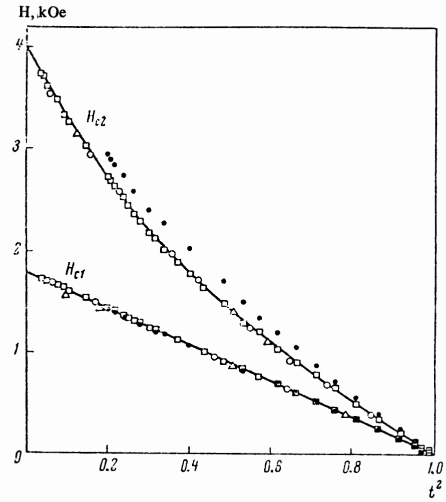

FIG. 4. H_{c1} and H_{c2} as a function of the square of the reduced temperature: □—batch Nb-1, ○—Nb-2, △—from ref. 17, ○—from ref. 18.

$$H_{c2}(0) = H_{c2}^0(0) + 1.46\rho_0 \text{ [kOe]} \tag{15}$$

(here $H_{c2}^0(0)$ is the critical field for $l \to \infty$ in kG, and ρ_0 is expressed in micro-ohm-cm). Knowing from our measurements the values of Γ and H_{c2} for the Nb-1 sample, we find $H_{c2}^0(0) = 3.998$ kG ≈ 4 kG.

Equation (15) makes possible calculation of the residual resistivity ρ_0 in batch Nb-2 and comparison of it with the data of direct measurements. The calculated value Γ ~ 110 agrees in order of magnitude with the measured value ~300. It is interesting that for a resistance ratio of ~10^4, the difference between $H_{c2}(0)$ and $H_{c2}^0(0)$ is only ~2 G.

Let us turn now to the formulas given by Gor'kov[7]:

$$H_c(0) = 2.48\hbar^{-1} m^{*1/2} n_0^{1/6} kT_c, \tag{16}$$

$$\varkappa_0 = 0.485 kT_c c m^{*3/2}/e\hbar^2 n_0^{5/6}, \tag{17}$$

where m* is the electron effective mass and n_0 is the number of charge carriers per unit volume.

Knowing $H_{c2}(0)$ and $H_c(0)$ from the experimental data and using Eqs. (12), (16), and (17), we can calculate values of m* and n_0 and compare them with the data in the literature.[3-5] This comparison is not completely proper, since niobium is a transition metal and its Fermi surface has a complicated topology.[2] However, our problem is also to show the urgent need of constructing a microscopic theory of superconductivity, taking into account the specific structure of the electron energy spectrum. The results of the comparison are shown in the table, together with values of $H_{c2}(0)$, $H_c(0)$, and $\kappa_0(T_c)$ calculated by substitution into Eqs. (16) and (17) of the value $m^*/m_0 = 3.2$, taken from experiments on the de Haas—van Alphen effect,[6] and the value $n_0/n_A = 0.84$ obtained from Hall effect measurements[4] (a similar value $n_0/n_A = 0.82$ is found by Golovashkin et al.[3]: n_A is the number of atoms per unit volume). It is evident that the discrepancy between

Table. Superconducting properties of pure niobium

	Measured values*						Values calculated from formulas (16) and (17)	
	[*]	[17]	[18]	[5]	[4]	[9]	[17, 18, *]	[3-5]
n_0/n_A	—	—	—	—	0.84	0.82	3	—
m^*/m_0	—	—	—	3.2	—	—	7, 15	—
$H_{c2}(0)$, э	4060	3978 **, 4010 ***	3909	—	—	—	—	770
$H_c(0)$, э	—	1993	1950	—	—	—	—	750
$\varkappa(T_c)$	—	0.78	0.83	—	—	—	—	0.53

*[*] — our measurements.
**From the formula $H_{c2} = \sqrt{2}\,\kappa(0)H_c(0)$, where $H_c(0) = 1993$ G, $\kappa(0) = 1.43$.
***From an experimental plot of $H_{c2}(t^2)$.

the calculated and measured values³⁾ of H_{c2}, H_c, m^*/m_0, and n_0/n_A lie in the range from 200 to 500%. The difference in κ_0 is ~30%.

If we take for comparison with Gor'kov's theory[7] the lighter masses observed by Scott et al.[5] and the smallest value $n_0/n_A = 0.56$ found by Reed and Soden,[4] the discrepancy increases. The same effect is obtained if we assume that niobium is an intermediate-coupling superconductor.[17] According to McMillan,[21] in the case of intermediate or strong coupling the electron-phonon interaction modifies the experimentally measurable cyclotron mass. Therefore we must substitute in Eqs. (16) and (17) not $m^*/m_0 = 3.2$, but $(m^*/m_0)/(1 + \lambda)$, where λ is the electron-phonon interaction parameter, which for niobium is equal to 0.82.[21] In regard to Eilenberger's theory,[16] comparison of his theory with the experimental $H_{c2}(t)$ curve gives nothing new, since according to ref. 16 for $l \to \infty$ the field H_{c2} increases monotonically from the value of Eq. (11) to the value of Eq. (12) with reduction of temperature.

Thus, the experimental data do not fit into the framework of an isotropic theory of superconductivity.

In existing anisotropic theories[22,23] only the crystallographic anisotropy is taken into account; this anisotropy is absent in niobium, which has a body-centered cubic lattice. In connection with the small anisotropy of H_{c2} observed in a number of experiments, Hohenberg and Werthamer[24] have taken into account nonlocal corrections to the Gor'kov theory[6,7] for a Fermi surface of arbitrary shape. However, these small corrections (< 5%) also cannot explain the substantial discrepancy of Gor'kov's results[7] with experiment. In addition to refs. 6, 7, 16, and 24, there is the work of Moskalenko[25] in which a two-band theory of superconductivity is constructed especially for the transition metals. However, it is impossible to compare Moskalenko's theory[25] with the experimental data, since his theory contains five arbitrary parameters.

We note in conclusion that the results presented above also cannot be explained by anisotropy of the gap in niobium, which according to the data of tunnel measurements made on samples with a resistance ratio of 250–700, does not exceed 12%.[26]

B. The critical field H_{c1}. It is evident from Fig. 4 that over the entire temperature range studied the behavior of $H_{c1}(t)$ is described by the simple relation $H_{c1}(t) = H_{c1}(0)(1 - t^2)$, where t is the reduced temperature. The departure from a quadratic law of the empirical formula $H_{c1}(t) = H_{c1}(0)(1 - t^{2.13})$ obtained by Finnemore et al.[17] is evidently due to the difficulty of exact determination of H_{c1} in ballistic measurements. In view of the fact that in the GLAG theory the behavior of H_{c1} has been investigated only for $T \to T_c$, there is nothing with which to compare the experimental data on the temperature dependence of H_{c1}.

4. THE SURFACE SUPERCONDUCTIVITY CRITICAL FIELD H_{c3} AND ITS TEMPERATURE DEPENDENCE

Theoretical calculations of the ratio H_{c3}/H_{c2} have been carried out both in terms of the extended Ginzburg-Landau theory[27,28] and with the microscopic theory.[29] In the first case[27] the authors obtain the formula

$$H_{c3}(t) / 1.695 H_{c2}(t) = 1 + 0.214p(1-t)^{1/2} + (0.614 - 0.458p + 0.069p^2)(1-t), \qquad (18)$$

where p is the degree of diffuseness in reflection of electrons from the surface (p = 0 for a mirror and p = 1 for diffuse reflection). In the second case[29] it is found that

$$H_{c3}(0) / H_{c2}(0)\,|_{p=0} = 1.99, \quad H_{c3}(0) / H_{c2}(0)\,|_{p=1} = 2.09. \qquad (19)$$

Experimental studies of the behavior of $H_{c3}(t)$ in niobium[9,18,30] have been made on samples of different purities, and the results obtained are contradictory. Webb[30], in the temperature range $0.25 \le t \le 0.7$ obtained $A(t) = H_{c3}(t)/H_{c2}(t) \approx 1.9$, and in the region $0.85 \le t \le 1$, A(t) falls linearly to 1.65. French[18], at T = 4.2°K, found $A \approx 3.3$. The most interesting data are given by Akhmedov et al.[9]: with a change of temperature t from 0.9 to 1 the function A(t) falls from 1.65 to 1. The approach of A(t) to unity as $T \to T_c$ completely contradicts the conclusions of the Ginzburg-Landau theory (formula (18)), whose accuracy, it would seem, should increase as T_c is approached.

The results of our measurements of $H_{c3}(t)$ and A(t) in samples of Nb-1 and Nb-2 are shown in Figs. 5 and 6. Since H_{c3} is the field at which the surface superconductivity completely disappears, we determined it as the point at which μ' approaches unity—Fig. 7 (more accurately, as μ' approaches the constant characterizing the

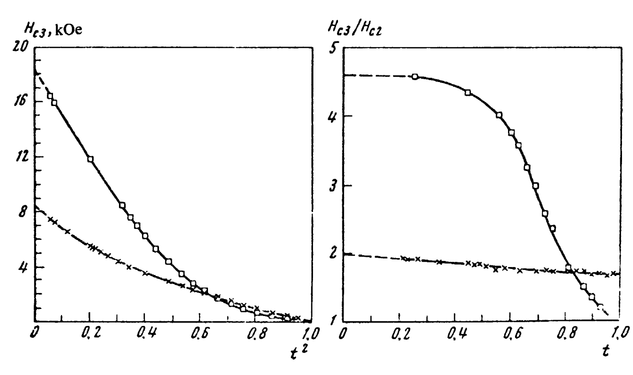

FIG. 5. FIG. 6.

FIG. 5. H_{c3} as a function of the square of the reduced temperature: □—batch Nb-1, X—Nb-2.

FIG. 6. The ratio H_{c3}/H_{c2} as a function of reduced temperature: □—batch Nb-1, X—batch Nb-2.

³⁾At the same time the value of $H_c(0)$ calculated from the well known BCS formula $H_c^2(0) = \gamma T_c^2/0.17$ agrees astonishingly well with experiment if we take for γ and T_c in niobium the generally accepted values γ = 7.8 mJ/mole-deg and T_c = 9.25°K. [17,18]

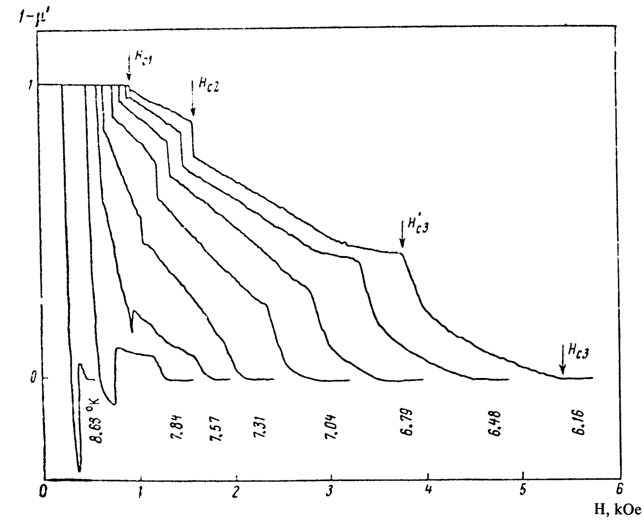

FIG. 7. Plot of $1-\mu'$ as a function of longitudinal magnetic field near T_c. Batch Nb-1, $\alpha = 0°$.

magnetic permeability of the normal metal). In batch Nb-1 the field H_{c3} was also determined by another method—from plots of μ' as a function of the angle α, obtained for fixed values of the external magnetic field (Fig. 8). In this case a sharp peak in $\mu'(\alpha)$ was observed near $\alpha = 0$,[9] whose amplitude decreased with increasing field and approached zero at $H = H_{c3}$. The values of H_{c3} determined by the two methods described agreed within $\pm 3\%$. Control measurements made up to T_c showed that the peak in $\mu'(\alpha)$ disappears at $T = T_c$. Consequently, it is associated with surface superconductivity, and not with galvanomagnetic effects, for which T_c is not a special point.

The difference in the shape of the $\mu'(H)$ curves in batches Nb-1 and Nb-2 will be discussed in Sec. 5. We note only that in the $\mu'(H)$ curves of the Nb-1 sample in the region $H_{c2} < H < H_{c3}$ an anomaly is observed. The field at which it occurs we have designated H'_{c3} (Fig. 7).

Let us compare the experimental results with the theory. It follows from Fig. 6 that the dependence of A(t) for the Nb-2 sample agrees qualitatively with Eqs. (18) and (19). For $t \to 1$ the function $A(t) \to 1.675$, which is close to the theoretical value of 1.695. According to Eq. (18), the increase in the ratio H_{c3}/H_{c2} as the temperature is lowered to t = 0.5 is 26% for p = 1 and 30.5% for p = 0. The experimental value for Nb-2 is 18%; on extrapolation of the experimental A(t) curve to t = 0, the value 1.98 is obtained (the theoretical value is 2.09—1.99).

In order to check the validity of comparing the behavior of Nb-2 with theories constructed for $l \to \infty$, let us calculate the ratio $l/\xi(0)$. According to Lifshitz and Kaganov[31],

$$\bar{l} = 6\cdot 10^{-23}\sigma / S_F \ [\mathrm{cm}] \tag{20}$$

where σ[CGSE] is the conductivity, and S_F[Å^{-2}] is the area of the Fermi surface.

In order to calculate $\bar{l}$ we will take the value of S_F from ref. 3. Taking into account that in niobium $\sigma(300°K) = 6 \times 10^{16}$ and $\Gamma(\text{Nb-2}) \approx 300$, we obtain $\bar{l} \approx 5 \times 10^{-4}$ cm. Determining $\xi(0)$ from the formula[1]

$$\xi^2(t) = \varphi_0 / \pi H_{c2}(t)\,|_{t\to 0}, \tag{21}$$

where φ_0 is the magnetic flux quantum, we find $\bar{l}/\xi(0) \sim 10$.

Although the calculations which we have made are approximate and are in the nature of estimates, they show that batch Nb-2 occupies an intermediate position between the "dirty" and "pure" limits. Therefore, the accuracy with which its behavior is described by the theories of Usadel and Schmidt[27] and Kulik[29] must be considered satisfactory.

The same estimates, when made for batch Nb-1, give $\bar{l}/\xi(0) \sim 300$. If we arbitrarily take the value designated in Fig. 7 as H'_{c3} as the upper critical field of this sample, then its temperature dependence agrees qualitatively with theory.[27,29] However, it follows from Figs. 7 and 8 that the transition of the surface superconducting layer of Nb-1 is completed at a field H_{c3}, which is appreciably greater than H'_{c3}.

Let us consider the possible causes of this phenomenon. Rothwarf[32] suggested that, if on the surface there exist nonuniformities with linear dimensions R comparable with $\xi(t)$, then nucleation of superconductivity will occur at a field

$$H(R,t) \geqslant 2\xi(t) H_{c2}(t) / R \tag{22}$$

and near T_c A(t) will be given by

$$A(t) = H(R,t)/H_{c2}(t) \sim \xi(t) = \xi(0)(1-t)^{-1/2},$$

i.e., A(t) will rise rapidly as $T \to T_c$. However, experiment gives the reverse result. A(t) does not rise, but falls, approaching unity as $T \to T_c$ (Fig. 6). Our experimental results are also in disagreement with the

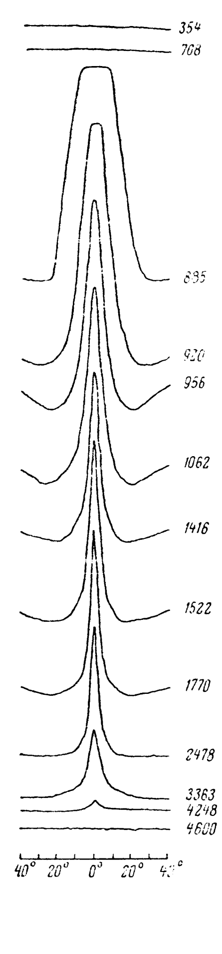

FIG. 8. Plot of $1-\mu'$ as a function of the angle between the sample axis and the external magnetic field direction. Batch Nb-1, T = 6.48°K. The values of the field in Gausses are shown on the curves.

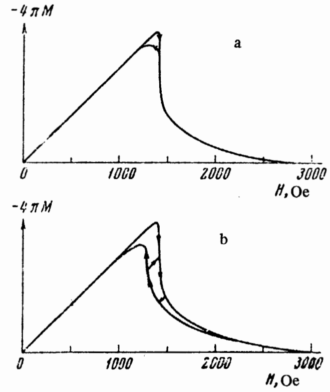

FIG. 9. Magnetization curves obtained with the ballistic method at T = 4.2°K: a—batch Nb-1, b—batch Nb-2.

calculations of Houghton and McLean,[33] who considered nucleation of surface superconductivity in wedge-shaped points. According to them H_{c3}/H_{c2} does not depend on temperature.

Lowell[34] suggests that the anomalously large value of H_{c3} may be associated with a decrease in the mean free path in the near-surface layer as the result of defects. However, then the value of H_{c3}/H_{c2} should not depend on temperature.

MacVicar and Rose[26] established in that in air at room temperature, a thin oxide film (< 100 Å) is formed on the surface of niobium. According to Ginzburg[35] a dielectric covering can affect the superconducting properties of the layer next to it, and in turn T_c.[4)] However, the value of T_c obtained by us agrees with the data of Webb,[30] who took special measures to avoid the presence of an oxide film, and in agreement with other investigators[15,16] is 9.20 ± 0.03°K. We note also that samples of Nb-1 and Nb-2 should have the same oxide film, but their properties are different.

Thus, the existing ideas as to the causes of anomalously high values of H_{c3} cannot explain the temperature behavior of A(t) in batch Nb-1. A qualitative explanation of this effect can be given if we assume that it is associated with thermodynamic fluctuations of the order parameter.[8] Evidently the surface superconductivity of batch Nb-1 in the region $H'_{c3} < H < H_{c3}$ is a fluctuation "tail" existing over the entire temperature region investigated by us, 2.4–9.2°K. In the samples studied by Ostenson and Finnemore,[8] which have a purity intermediate between Nb-1 and Nb-2 ($\Gamma \sim 500-700$), fluctuations appear in a narrower temperature region (8–9.2°K). Finally, in Nb-2 they are practically absent. This means that, the purer the sample, the wider the temperature interval in which fluctuations appear.

5. THE SHAPE OF MAGNETIZATION CURVES AND THE RESISTIVE STATE

Let us consider some additional results obtained in study of Nb-1 and Nb-2 samples.

A. Shape of the magnetization curves. Magnetization curves taken at T = 4.2°K are shown in Fig. 9. It is evident that in batch Nb-1 hysteresis is observed only near the field H_{c1}, while in Nb-2 it occupies the region $H_{c1} \le H \le H_{c2}$. The difference in the shape of the M(H) curves in samples of Nb-1 and Nb-2 is explained as follows.

According to Fink and Kessinger,[36] who used a computer to obtain an exact solution of the nonlinear Ginzburg-Landau equation for the near-surface layer, the surface superconducting layer exists up to the field H_{c1}. However, Akhmedov et al.[9] have shown that finite critical currents exist in the surface layer only in the presence of impurities, defects, and other current-stabilizing factors. If the sample is sufficiently pure, the critical currents approach zero.[5)] Therefore hysteresis is absent in the Nb-1 samples. In the Nb-2 sample the near-surface layer forms in effect a doubly connected region capable of reversing its magnetization in a magnetic field. The shape of the magnetization reversal curve can be seen in Fig. 9, where a minor hysteresis loop is shown. The straight lines bounding the loop on the right and on the left have a slope $-1/4\pi$ corresponding to ideal diamagnetism, which also proves the surface nature of the currents responsible for the hysteresis.

Measurements of $\mu'(H)$ showed that both in Nb-1 and in Nb-2 the value of H_{c1} obtained by increasing the external field is almost identical with the value obtained by decreasing the field. This result is consistent with the data of Fink and Kessinger[36] on the disappearance of the surface superconducting layer at the point $H = H_{c1}$.

B. The resistive state. The reversability of the magnetization curve of batch Nb-1 and the inability of its surface layer to screen even extremely small alternating magnetic fields (~0.01 G) for $H > H_{c1}$ indicates that in the region $H_{c1} \le H \le H_{c3}$ an induced alternating current of low frequency transforms it to the resistive state.[38]

Strictly speaking, the resistive state in the presence of alternating magnetic and electric fields should be described by the time-dependent GLAG equations. The corresponding theories are still in the developmental stage.[39,40] Taking into account this fact and also the fact that in the low-frequency region the process is apparently quasistationary, we will use for discussion of the shape of the transition curves the reasoning given by Kim.[38] According to Kim, if $j \perp H$, the array of vortices moves uniformly with the velocity

$$\mathbf{v} = [\mathbf{j}\varphi_0]/c\eta, \qquad (23)^*$$

where η is the viscosity coefficient of the medium. On movement of the vortices an electric field $\mathbf{E} \parallel \mathbf{j}$ arises, which is equivalen to a "flow" resistance

$$\rho_F = dE/dj, \qquad (24)$$

where

$$\rho_F/\rho_N = H/H_{c2}(0), \qquad (25)$$

and ρ_N is the resistance in the normal state.

The process described is equivalent to a situation in which the vortex array is at rest and the current flows uniformly through the superconductor, dissipating inside

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4) T_c was determined as the temperature at which $H_{c1} = H_{c2} = H_{c3}' = H_{c3} = 0$, and also by an induction method in an external field equal to zero.

5) The cause of the approach of the critical currents to zero is the nonideal surface, the nonuniformity of the magnetic field, and other factors which always are present in a real experiment and which lead to appearance of vortex structure [9] in the surface superconducting layer.

*$[\mathbf{j}\varphi_0] = \mathbf{j} \times \varphi_0$.

the cores of the vortices, whose total area increases in proportion to H. From the macroscopic point of view there exists in the superconductor an effective electrical resistance which depends on the magnetic field strength according to Eq. (25) and is related to the real part of the magnetic permeability measured in our experiments by the equation[41]

$$\mu' = \mathrm{Re}\left(\frac{2J_1(ka)}{kaJ_0(ka)}\right), \quad k = \frac{1+i}{c}\left(\frac{2\pi\omega}{\rho_f}\right)^{1/2}, \qquad (26)$$

where J_0 and J_1 are Bessel functions, and a is the radius of the sample.

In the superconducting state $\rho_F = 0$, and in the normal state $\rho_F = \rho_N$. In view of the complex nature of the functional relation between μ' and ρ_F, we will make no quantitative calculations of the behavior of $\rho_F(H)$ and will limit ourselves to a qualitative discussion.

Figure 7 shows a set of $\mu'(H)$ curves taken on batch Nb-1 at different temperatures. It is evident that for $H < H_{c1}$ the alternating magnetic field does not penetrate into the sample, $\mu'(H) = 0$, and $\rho_F = 0$. For $H = H_{c1}$ the sample transfers to the resistive state. The jump in the curve is due to the fact that in materials with $\kappa_0 \sim 1$ the number of vortices arising at the field H_{c1} is very large. Therefore ρ_F changes sharply from zero to a finite value. In the region $H_{c1} < H < H_{c2}$ the resistivity ρ_F increases monotonically. At the point $H = H_{c2}$ the transition occurs from the volume resistive state to the surface resistive state, the nature of which has been explained in ref. 9. At $H = H_{c3}$ the surface layer completely transforms to the normal state. If the angle α between the sample axis and the magnetic field is different from zero, the $\mu'(H)$ curve has another form (Fig. 1): near H_{c2} a maximum appears whose nature is not yet clear.

The shape of the transition curves of batch Nb-2 in a longitudinal field ($\alpha = 0$) is due to the finite value of the critical current of the surface layer.[9,42] For $\alpha = 90°$ the current j_c drops sharply,[9] and the $\mu'(H)$ curve of batch Nb-2 approaches in shape the corresponding curve for Nb-1.

We note an interesting feature of the behavior of the $\mu'(H)$ curves for Nb-1 at temperatures close to the critical temperature. It is evident in Fig. 7 that for $T \sim 7.5°$K the $\mu'(H)$ curve passes through a minimum near H_{c2}, whose depth increases rapidly as $T \to T_c$. The explanation of this phenomenon will present interest. It is possible that the appearance of the minimum is associated with fluctuations of the magnetic moment or of the resistivity. However, then it is necessary to explain why the temperature interval in which the fluctuations exist is anomalously large.

CONCLUSION

Thus, development of the microscopic theory with inclusion of the structure of the electron energy spectrum is necessary for an adequate description of the superconducting properties of niobium. It is also necessary to carry out a theoretical calculation of the effect of fluctuations on the resistivity and magnetic permeability and to evaluate the relation between the fluctuations and the electron mean free path.

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