that the energy gap E_g and the cyclotron mass m_b at the bottom of the band are the same as those in pure bismuth, a Fermi energy in $Bi_{95}Sb_5$ is calculated to be $E_e = 0.007$ eV. The values for the Fermi energy and E_g in pure bismuth are taken to be those measured by Brown, Mavroides, and Lax in magnetoreflection measurements.[9] They are $E_e = 0.025$ eV and $E_g = 0.015$ eV. The number of electrons per ellipsoid is derived from Eq. (2) to be

$$N_e = (8\pi/3h^3)[2E_e(1+E_e/E_g)m_0(\det\alpha_b)^{-1/3}]^{3/2},$$

where $m_0(\det\alpha_b)^{-1/3}$ is the density-of-states effective mass at the bottom of the band. In pure bismuth, N_e is calculated to be $N_e = 0.8\times10^{17}/\mathrm{cm}^3$ and in $Bi_{95}Sb_5$, $N_e = 0.05\times10^{17}/\mathrm{cm}^3$. A three-ellipsoid model for the electrons in $Bi_{95}Sb_5$ gives the total number of electrons $N = 0.15\times10^{17}/\mathrm{cm}^3$ quoted earlier.

The occurrence of a long relaxation time in such a nondilute alloy is somewhat surprising. This is plausible, however, since the electron wavelengths are of the order of 1000 Å and will not be strongly scattered by individual solute atoms.

The author is grateful to B. Bingham for technical assistance and to J. J. Schott for growing the crystal.

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HIGH-FIELD SUPERCONDUCTIVITY IN NIOBIUM

S. H. Autler and E. S. Rosenblum
Lincoln Laboratory,* Massachusetts Institute of Technology, Lexington, Massachusetts

and

K. H. Gooen
National Magnet Laboratory,† Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received September 13, 1962)

Many superconductors, including niobium, maintain zero resistance when exposed to magnetic fields substantially higher than their thermodynamic or bulk critical fields, H_{cb}. In this sense niobium is a high-field superconductor, and explanations of its behavior may be applicable to more complex materials such as alloys or compounds. Present explanations of high-field superconductivity invoke, directly or indirectly, the thermodynamic argument[1] that if a superconducting region is thin enough to permit substantial field penetration, it will remain superconducting for $H > H_{cb}$. These theories fall into two classes:

(A) Inhomogeneities such as fine filaments exist which have a higher H_{cb} than the surrounding material. In a strong field the current flows along these filaments, which may be dislocations.[2] As the applied field is increased these filaments shrink in size, raising their critical fields. A model of this type has been used[3] to explain the observed dependence of current-carrying capacity on the direction of the applied field.

(B) In the presence of a magnetic field the sample can lower its free energy by breaking up into normal and superconducting regions thin enough to allow field penetration into the superconducting regions. This increases the normal-superconducting surface area, and may be thought of as resulting from a negative surface energy. Abrikosov[4] and more recently Goodman[5,6] and Yntema[7] have proposed theories of this type.

This Letter describes and interprets a number of experiments on Nb wires in magnetic fields. The main points may be enumerated as follows:

(1) The resistance of current-carrying Nb wires behaves in a very unusual manner in some regions;

with the current I and the temperature T held constant, the resistance may decrease by orders of magnitude as the applied field is increased by a few hundred gauss. In some cases the resistance becomes undetectably small, and one can regard this as a restoration of superconductivity by an increase of field.

(2) When I and H are constant and T is varied, there are regions where the sample goes from a resistive to a superconducting state as the temperature is increased.

(3) I vs H measurements at constant voltage, across a number of Nb samples which have undergone different heat treatments, indicate two different mechanisms governing high-field superconductivity in Nb; sometimes evidences of both are seen in the same sample.

(4) There is strong evidence, based on interpretation of the resistance measurements mentioned above, that one of these mechanisms is of the Abrikosov type.

(5) Preliminary magnetization measurements on some of the samples confirm this.

(6) Pure niobium is probably a superconductor of the second group in the Ginsburg-Landau sense, with $\kappa = 1.3$ at 4.2°K.

Figure 1 shows R/R_n vs H for one sample at 4.2°K, with I as a parameter. The following observations apply to this figure:

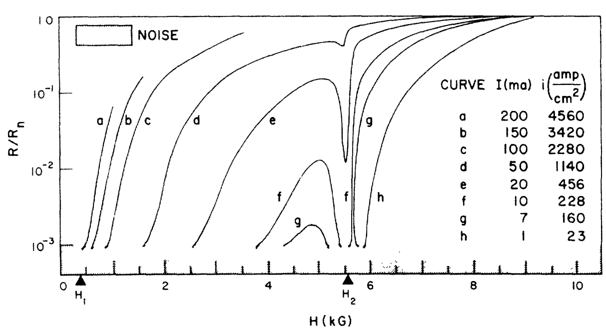

FIG. 1. R/R_n vs H for sample Nb-H-6 (Table I) at 4.2°K. This, and Fig. 2, are tracings of an x-y recorder plot. The voltage across the sample, after preamplification, was fed into a logarithmic converter, whose output was adjusted at each current to the same ordinate on the y axis of the recorder at a field high enough to make the sample entirely normal. Thus, ordinates are proportional to $\log(R/R_n)$. H_2 was determined from plots such as this one, while H_1 was obtained from a series of runs at high currents in which the preamplifier gain was greatly increased to allow sample voltages smaller than 0.1 μV to be observed. The samples were perpendicular to the field in all experiments illustrated by Figs. 1 and 2.

(a) The resistive behavior may be divided into three regions.

(b) For $H < H_1$, the sample remains superconducting up to quite high current densities.

(c) For $H_1 < H < H_2$, resistance is restored by moderate currents. If the current is fixed and the field is raised, resistance is first observed at some field $H' > H_1$. As the current is increased, H' appears to approach a limit. H_1 is defined as that limit. In determining H', it is necessary to include the magnetic field generated by current in the wire as well as the externally applied field. Thus, even in the absence of external field, resistance will be observed if the field generated by the current exceeds H_1.

(d) In this region, R/R_n is a maximum at a field which is relatively insensitive to the value of I and the angle between H and I.

(e) As H_2 is approached, the resistance suddenly drops to a minimum which defines H_2. The position of H_2 is almost independent of the current or the angle between H and I, although the detailed dependence of R/R_n on I is quite sensitive to this angle.

(f) For $H > H_2$, the currents required to restore resistance are distinctly smaller and decrease as H increases.

The values of H_1 and H_2, measured as described above, are listed for a number of samples in Table I, along with other pertinent data.

In Fig. 2 measurements of R/R_n vs T are shown for a different sample. The temperature at which the resistance minimum occurs is seen to depend strongly on H. H_2 as a function of T can be obtained from these data, or from a series of R vs H curves at various temperatures. Preliminary measurements indicate a considerable departure from a quadratic dependence of H_1 and H_2 on T.

Figure 3 shows measurements of current density, i, vs H for constant voltage (10^{-7} V) across a series of samples at 4.2°K. The field was transverse to the samples, which were prepared for us in the laboratory of Professor John Wulff of the MIT Department of Metallurgy. The unannealed sample and those annealed below 2000°C show the typical characteristic for hard superconductors with a fairly sharp "knee" after which i decreases approximately exponentially with H.[8] The current-carrying capacity at low fields is greatly reduced by annealing. The 2000°C curve shows a distinctly different behavior than the others. The current peak at about 2.9 kG is the manifestation on a i-H curve of the type of behavior near H_2 illustrated in Fig. 1, and confirms the value obtained by R

Table I. Summary of properties of samples tested.

Sample[a]	Source[b]	Diam (cm)	Normal Resistivity (μohm-cm) 300°K	4.2°K	$\rho_n(300)/\rho_n(4.2)$	Field at 4.2°K (kG) H_2	H_1	H_m[c]
7*N*	MIT	0.025	16.7	0.167	100	2.9	1.1	1.0 ± 0.1
Nb-H-2	Armetco	0.0075	22.8	0.93	24.5	4.0	0.6	
Nb-H-3	MRC	0.024	20.3	0.84	25	3.5	0.6	
Nb-H-6	Fansteel	0.0075	19.6	3.6	6.0	5.6	0.4	0.37 ± 0.10

[a]All samples were vacuum annealed at ~2000°C for ~15 min.
[b]MIT: Department of Metallurgy, Massachusetts Institute of Technology; Armetco: Armetco, Inc.; MRC: Materials Research Corp.; Fansteel: Fansteel Metallurgical Corp.
[c]Field at which maximum magnetization occurs—from preliminary data by S. Kern, MIT Lincoln Laboratory, and S. Foner, National Magnet Laboratory, MIT.

vs *H* curves for the same sample, 7*N*. At higher fields, the *i*-*H* characteristic looks similar to that of the less-annealed samples.

It will be shown below that the above data are consistent in many respects with the theories of Abrikosov[4] and Goodman,[6] and with the work of Berlincourt and Hake.[9] Abrikosov, following Ginsburg and Landau,[10] divides the magnetic properties of superconductors into two groups, according to whether the parameter κ of the Ginsburg-Landau theory is less than (group 1) or greater than (group 2) $1/\sqrt{2}$. For group 2 superconductors in a longitudinal field, he finds that there should be two critical fields, H_{c1} and H_{c2}, which divide the magnetic behavior into three ranges.[11] For $H < H_{c1}$ there should be no field penetration; for $H_{c1} < H < H_{c2}$ there is partial penetration in the form of flux filaments, having a square symmetry and maintained by a vortex-like distribution of internal currents. Above H_{c2} the material is completely normal. A second-order phase transition is predicted at H_{c2}, but the phase transition at H_{c1} may be either first or second order, depending on κ. Goodman[6] calculates a somewhat similar behavior, using a lamellar model, and compares his and Abrikosov's predictions with experimental magnetization data for a number of

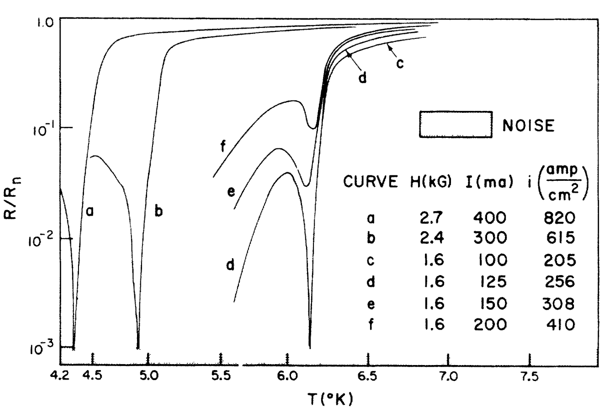

FIG. 2. R/R_n vs T for sample 7*N* (Table I) at several values of H, with the current in each case adjusted for a maximum "dip" in $\log(R/R_n)$. Also shown is a series of curves at 1.6 kG and various currents.

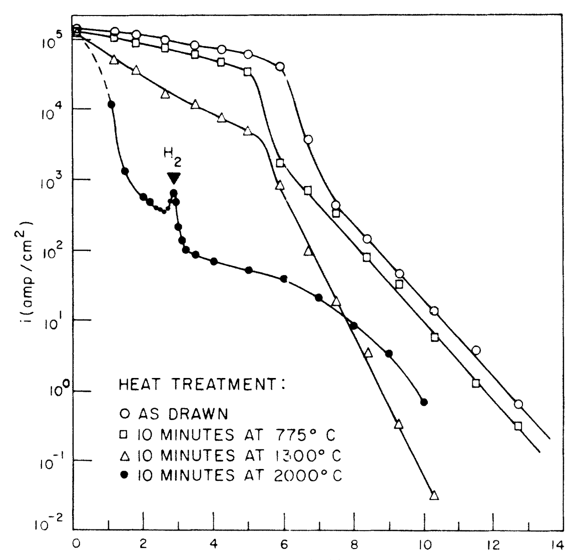

FIG. 3. *i*-*H* curves at constant voltage (0.1 μV) for several samples of Nb, all from the same batch of wire but with different heat treatments as shown. The 2000°C curve is for sample 7*N*.

alloys. Neither paper discusses the behavior of the resistivity or considers the effects of transport current. It seems reasonable, however, that in the absence of a transport current the resistivity should be zero for $H < H_{c2}$, and that the presence of a transport current should modify this behavior.

It is tempting to identify our three regions of different resistivity dependence on H and I with Abrikosov's regions and thus our H_1 and H_2 with H_{c1} and H_{c2}. Recently, Berlincourt and Hake[9] have reported a current peak at 60 kG on an I-H curve for a Ti-Mo alloy and have observed that the low-current critical field H_γ of a number of alloys is insensitive to geometry and degree of cold work. He suggests the identity of H_γ and H_{c2} and shows that they agree within a factor of two for various Ti-V alloys. We believe this viewpoint is correct and that H_2, H_γ, and H_{c2} are basically the same quantity. According to Abrikosov, $H_{c2} = \sqrt{2}\kappa H_{cb}$, where H_{cb} is the bulk critical field. Gor'kov[12] has derived κ from the BCS theory in the local limit where the electronic mean free path is small compared to the BCS coherence length, ξ_0. Goodman generalizes this to

$$\kappa = \kappa_0 + 7.5\times10^3\gamma^{1/2}\rho_n, \quad (1)$$

which should also be valid in the nonlocal case. κ_0 is characteristic of the pure metal, γ is the electronic specific heat coefficient in ergs/cm^3-deg^2, and ρ_n is the normal resistivity of the metal in ohm-cm. Then,

$$H_{c2} = \sqrt{2}H_{cb}(\kappa_0 + 7.5\times10^3\gamma^{1/2}\rho_n). \quad (2)$$

Gor'kov's expression for κ_0 is

$$\kappa_0 = 0.96\lambda_L(0)/\xi_0, \quad (3)$$

where $\lambda_L(0)$ = the London penetration depth at $T = 0$.

Our measurements of ρ_n, H_1, and H_2 at 4.2°K on "niobium" from four different sources are listed in Table I. These wires were all vacuum annealed at 2000°C, so the variation in ρ_n may be attributed to differences in nonvolatile impurities. We may regard these samples as dilute alloys, although the nature of the impurities is not known at present. In Fig. 4, H_1 and H_2 are plotted against ρ_n. We see that H_2 is linear in ρ_n, as we expect H_{c2} to be. If we assume that this linearity extends to $\rho_n = 0$, then H_{c2} for pure Nb is about 2.8 kG.

Values of H_1 are also plotted in Fig. 4. Because

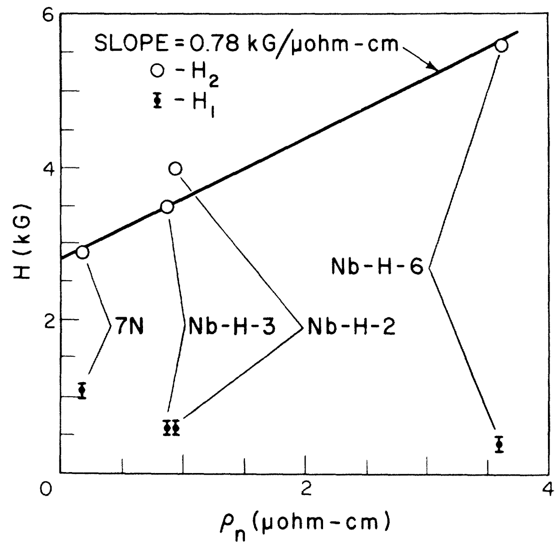

FIG. 4. H_1 and H_2 vs normal resistivity at 4.2°K, for the samples listed in Table I.

Abrikosov explicitly calculates H_{c1} only for the range $\kappa \gg 1$, and because our measurements of H_1 were made in a transverse magnetic field, no precise comparison can be made at this time. However, H_1 does have the properties expected of H_{c1}; in all cases H_1 is less than H_{cb}, increases as H_2 decreases, and agrees numerically to within a factor of two with Abrikosov's interpolated curve (see reference 6, Fig. 2). It therefore seems quite plausible on this evidence to associate H_1 with H_{c1}.

Magnetization measurements, however, should provide the best tests of this connection. Our colleagues, S. Foner and S. Kern, have carried out preliminary measurements on two of our Nb samples. Using vibrating sample magnetometers[13] to observe $\vec{M}$ vs $\vec{H}$ in a uniform applied field, they obtain curves of the form expected for group 2 superconductors; also the maximum magnetization occurs within 100 gauss of our values of H_1 (Table I) which were obtained from resistance measurements. They observed some hysteresis (~10%) which made it difficult to measure precisely the field (H_{c2}) at which magnetization disappeared. Their estimates, however, were in agreement with our H_2.

The handbook[14] values for H_0 (H_{cb} at $T = 0$) and γ are $H_0 = 1.96$ kG and $\gamma \approx 19\times10^{-4}$ cal/(mol deg^2) $= 6.9\times10^3$ erg/(cm^3 deg^2). Assuming a quadratic temperature dependence for H_{cb}, H_{cb}(4.2°K) $= 1.5$ kG and $H_{c2}(\rho_n = 0)/(\sqrt{2}H_{cb}) = 2.8/1.5\sqrt{2} = \kappa_0 = 1.3$, which implies that pure niobium is intrinsically a superconductor of the second group.

From Eq. (2), assuming the above values for H_{cb} and γ, the slope of H_{c2} vs ρ_n equals $\sqrt{2}H_{cb}\times 7.5\times 10^3\gamma^{1/2} = 1.3$ kG/μohm-cm, as compared with our measured value in Fig. 4 of 0.78 kG/μohm-cm. The agreement is close enough to support this picture of niobium as a superconductor of the second group. In our present sample, the mean free path of the electrons is roughly comparable to ξ_0. One cannot be certain, however, of the validity of our extrapolation to $\rho_n = 0$ until similar measurements have been made on samples with considerably lower values of ρ_n.

Measurements of H_2 from $T = 9°K$ to $T = 1.5°K$ have been made on several samples and will be reported in detail elsewhere. The functional relationship is more nearly linear than quadratic, but there is no indication of the concave-upwards behavior predicted by Shapoval[15] for H_{c2}.

If the Abrikosov-type mechanism were the only one present, the samples should be completely normal for $H > H_2$. However, Fig. 1 shows that the sample remains superconducting above H_2 if the current is low enough. This may be due to the existence of a few defects similar to those which carry currents in less-annealed samples. The 2000°C curve in Fig. 3 also shows that this sample, 7*N*, can carry some current for $H > H_2$. The form of this high-field tail is seen to be similar to the other curves. We therefore propose that there are two distinct mechanisms at work in Nb. One is of the Abrikosov type; in transverse fields it allows current densities of the order of 10^3 amp/cm^2 at fields near H_{c2}. In longitudinal fields, H_{c2} is the same, but the current density is somewhat greater. The second mechanism allows higher current densities than these and predominates if the sample has not been annealed, being probably associated with defects, possibly dislocations, which are removed by annealing. In cold-worked relatively pure Nb, this overrides the vortex or negative surface energy (Abrikosov) mechanism. However, extrapolation of Fig. 4 to higher values of ρ_n indicates that H_2 should be much higher in less pure Nb or alloys. H_2 may then be greater than the fields at which the exponential tails of Fig. 4 occur and will dominate the high-field behavior, at least at relatively low current densities. We would then have the situation observed by Berlincourt and Hake.[9]

Actually, the two mechanisms should not be considered as independent except as a first approximation, for they probably interact. The Abrikosov picture would be altered in the presence of defects and the two mechanisms may merge when the defects are sufficiently dense. Further work is certainly needed on many aspects of the behavior described in this Letter. In particular, an attempt should be made to account for the peculiar form of the dependence of resistance on field near H_2 in the presence of a current. Hopefully, including a transport current in an Abrikosov-type calculation would permit one to explain the stability in the presence of transport currents observed near H_{c2} and to estimate the magnitude of the current density.

We would like to express appreciation for the help of John Burke and George Ajootian, who contributed to many phases of the experiments.

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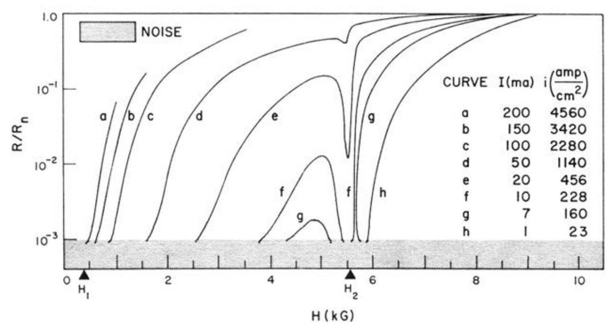

FIG. 1. R/R_n vs H for sample Nb-H-6 (Table I) at 4.2°K. This, and Fig. 2, are tracings of an x - y recorder plot. The voltage across the sample, after preamplification, was fed into a logarithmic converter, whose output was adjusted at each current to the same ordinate on the y axis of the recorder at a field high enough to make the sample entirely normal. Thus, ordinates are proportional to $\log(R/R_n)$. H_2 was determined from plots such as this one, while H_1 was obtained from a series of runs at high currents in which the preamplifier gain was greatly increased to allow sample voltages smaller than 0.1 μV to be observed. The samples were perpendicular to the field in all experiments illustrated by Figs. 1 and 2.

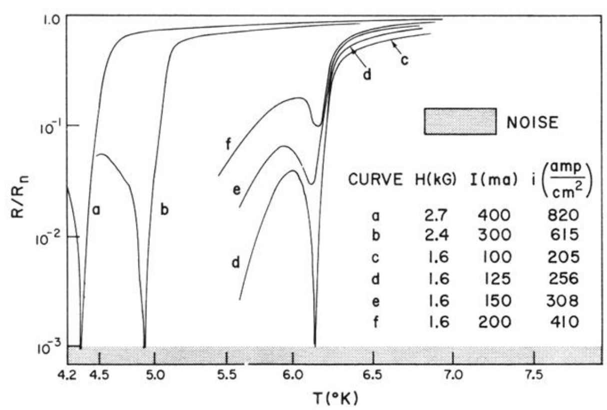

FIG. 2. R/R_n vs T for sample 7N (Table I) at several values of H, with the current in each case adjusted for a maximum "dip" in $\log(R/R_n)$. Also shown is a series of curves at 1.6 kG and various currents.