The Dependence of the Upper Critical Field of Niobium on Temperature and Resistivity

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The upper critical field H_{c2} at which the magnetization M of a group II superconductor goes to zero may also be obtained from its resistive behavior.[1–3] For alloys having a relatively high H_{c2}, the field at which some arbitrarily low current density such as 10 A/cm² [1,2] produces a measurable voltage may be identified with H_{c2} with adequate precision. For niobium, however, the situation is more complex.

Figure 1 shows the current density vs applied field for annealed polycrystalline samples of Nb having different normal resistivities. For most of these samples the value of the field is sensitive to current even at low densities. All these samples show a "peak"[4] followed by a more or less steep drop in current which we have previously[3] identified with H_{c2}. This is a better indication of H_{c2} in niobium than the 10-A/cm² criterion.

This is demonstrated in Fig. 2 where magnetization vs H and log (R/R_{normal}) vs H are shown for the same sample. M goes to zero at 2.9 kG, within 0.1 kG of the field at which is found the striking resistance "dip" of several orders of magnitude. The position of this "dip" is independent of current and field orientation and coincides with the zero magnetization field for all samples for which magnetization data has also been taken.[5] The origin of this dip is not known and it is not found in all samples. However, it has been observed in "niobium" samples having a range in resistance ratio, $r = R_{300}/R_{4.2}$ from $r = 500$ to $r = 2.5$. For those samples in which it is observed it provides a relatively simple and accurate way of measuring the upper critical field.

We have determined H_{c2} by this method, for samples ranging in normal resistivity ρ_n from 3.5×10^{-8} Ω cm ($r = 500$) to 1.0×10^{-5} Ω-cm ($r = 2.5$), at temperatures T from 1.5°K to 9°K. The samples were prepared by heating niobium wires to temperatures between 1000°C and over 2000°C *in vacua* of varying degrees of perfection. As shown by De Sorbo[5,6], this results in varying amounts of interstitial oxygen and nitrogen which he has correlated with T_c and H_{c2} as determined by magnetization and resistance measurements.

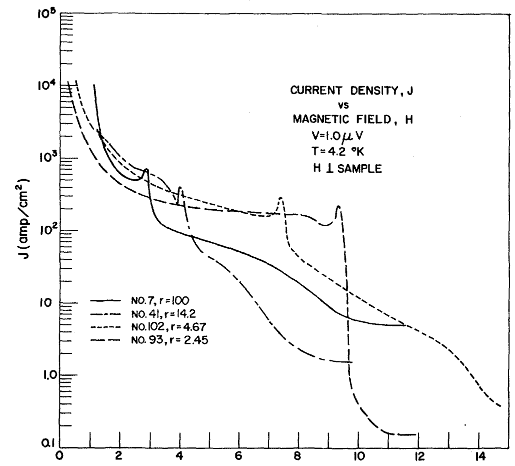

FIG. 1. Current density vs magnetic field with voltage across samples held constant at 10^{-6} V. $r = R_{300}/R_{4.2}$.

Figure 3 summarizes the measurements of H_{c2} vs T for three of our samples. As impurities are added the form becomes less linear and T_c is reduced from 9.1°K to 7.7°K. The data from these and other samples can be used as an experimental test of the GLAG[7] theory. As expressed by Goodman,[8] this takes the form

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* Operated with support from the U. S. Army, Navy, and Air Force.

† Operated with support by the U. S. Air Force through the Air Force Office of Scientific Research.

[1] T. G. Berlincourt and R. R. Hake, Phys. Rev. Letters 9, 293 (1962).

[2] B. S. Chandrasekhar, J. K. Hulm, and C. K. Jones, Phys. Letters 5, 18 (1963).

[3] S. H. Autler, E. S. Rosenblum, and K. H. Gooen, Phys. Rev. Letters 9, 489 (1962).

[4] T. G. Berlincourt, Phys. Rev. 114, 969 (1959). T. G. Berlincourt and R. R. Hake have also reported peak effects in cold-rolled alloys which may be related. See Phys. Rev. 131, 141 (1963).

[5] W. De Sorbo has also confirmed this agreement. See Bull. Am. Phys. Soc. 8, 294 (1963).

[6] W. De Sorbo, Phys. Rev. 132, 107 (1963).

[7] See Berlincourt and Hake (Ref. 4) for bibliography.

[8] B. B. Goodman, IBM J. Res. Develop. 6, 63 (1962).

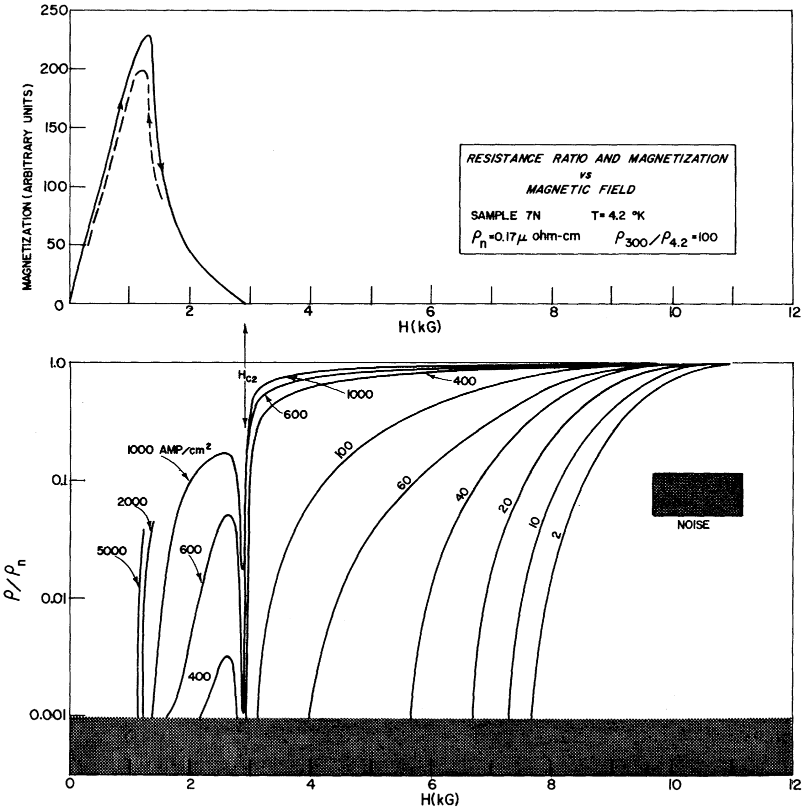

Fig. 2. Magnetization and resistance vs magnetic field for sample 7 N. The field was longitudinal for the magnetization measurements; transverse for the resistance measurements.

$$H_{c2} = \sqrt{2}H_{cb}(\kappa_0 + 7.53 \times 10^3\gamma^{\frac{1}{2}}\rho_n)\,, \qquad (1)$$

where H_{cb} is the bulk critical field, κ_0 is the G.L. parameter for the pure material, γ is the electronic specific heat coefficient in erg/cm³ deg², and ρ_n is the normal resistivity in Ω-cm.

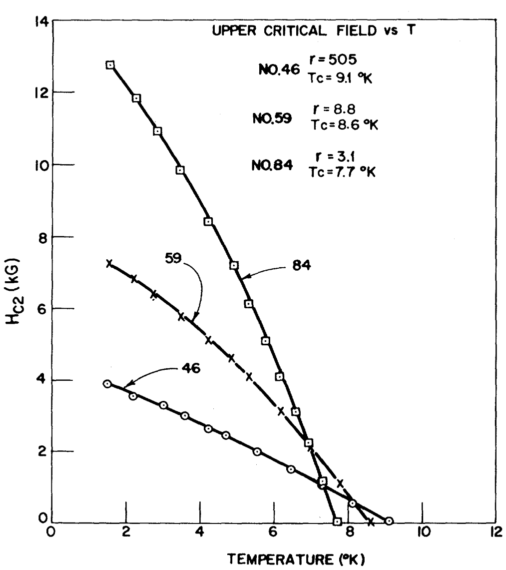

Fig. 3. Upper critical field vs temperature for samples of different resistivities.

Since T_c varies with impurity concentration, it may be expected that H_{cb} and γ will also vary. Assuming H_{cb} to be a quadratic function of the reduced temperature $t = T/T_c$,

$$H_{cb} = H_0(1 - t^2)\,. \qquad (2)$$

Well-known thermodynamic arguments show that

$$H_0 = (2\pi\gamma)^{\frac{1}{2}}T_c\,. \qquad (3)$$

We also write

$$(\gamma/\gamma_0)^{\frac{1}{2}} = T_c/T_{c0}\,, \qquad (4)$$

where γ_0 and T_{c0} are properties of the pure material which have been measured. Equation (4) implies that the electronic specific heat in the superconducting phase is not significantly changed by the addition of impurities.

Using (2), (3), and (4) to eliminate γ and H_{cb} from (1), we obtain

$$H_{c2} = \frac{2(\pi\gamma_0)^{\frac{1}{2}}}{T_{c0}}T_c^2(1 - t^2) \times \left[\kappa_0 + 7.53 \times 10^3\frac{\gamma_0^{\frac{1}{2}}}{T_{c0}}T_c\rho_n\right]. \qquad (5)$$

Using[9] $T_{c0} = 9.1$°K, $\gamma_0 = 6.8 \times 10^3$ erg/cm³ deg²,

[9] A. T. Hirshfeld, H. A. Leupold, and H. A. Boorse, Phys. Rev. 127, 1501 (1962).

Eq. (5) becomes

$$H_{c2} = 0.0321\ T_c^2(1 - t^2)(\kappa_0 + 0.068\ T_c\rho_n)\ , \quad (6)$$

where H_{c2} is in kG and ρ_n is in $\mu\Omega$-cm.

To test the validity of Eq. (6), our data were replotted as $H_{c2}/0.0321\ T_c^2$ vs $T_c\rho_n$ (Fig. 4). Analysis

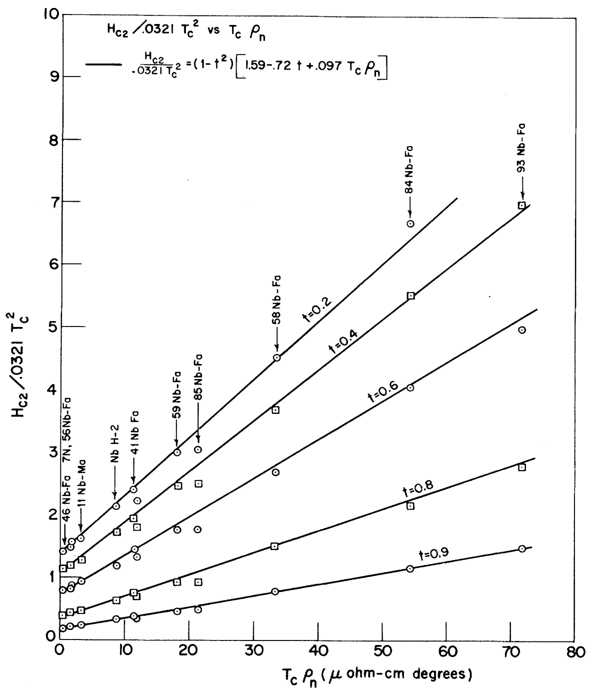

FIG. 4. $H_{c2}/0.0321T_c^2$ vs $T_c\rho_n$ at several values of reduced temperature.

of this figure shows that our data are well fitted by a family of straight lines with slopes equal to $0.097(1 - t^2)$. Values for κ_0 are obtained by dividing the $\rho_n = 0$ intercepts by $(1 - t^2)$. Figure 5 shows these values but the accuracy is not great enough to determine exactly the best functional relationship between κ_0 and t. Purely empirically, we will use $\kappa_0 = 1.59 - 0.72t$ which fits a little better than any of the other forms tried, including $\kappa_0 = 1.58/(1 + t^2)$,[10] which is also shown in Fig. 5.

The solid lines in Fig. 4 correspond to

$$H_{c2} = 0.0321\ T_c^2(1 - t^2)\ (1.59 - 0.72t + 0.097\ T_c\rho_n) \quad (7)$$

[10] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **30**, 593 (1956) [English transl.: Soviet Phys.—JETP **3**, 621 (1956)].

which fits our data quite well. It has exactly the form of Eq. (6) with the 0.068 replaced by 0.097 in the last term.

Conclusions. Since the derivation of Ginsburg–Landau theory involved an expansion of the free energy about T_c, there is some question whether it is valid at lower values of T. Our results seem to indicate that the GLAG theory can predict quite well the temperature and resistivity dependence of the upper critical field for temperatures as low as $0.2T_c$. The results also confirm that the assumptions in Eqs. (2) and (4) are not seriously in error. The discrepancy between the constants in the last term of Eqs. (6) and (7) remains to be explained.

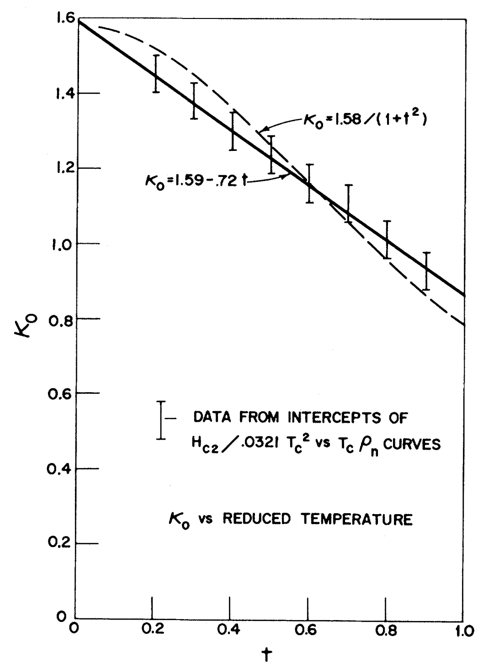

FIG. 5. κ_0 vs reduced temperature. Length of bars represents our estimate of uncertainty in determining κ_0 from intercepts of Fig. 4.

Finally, as seen in Fig. 5, pure niobium should be a group II superconductor for all $T < T_c$, with $\kappa_0 = 1.24 \pm 0.05$ at $T = 4.2°K$.[11] Our best estimate for κ_0 at $T = 0$ is 1.6.

[11] This compares with $\kappa_0 \approx 1.3$ estimated in Ref. 3 and $\kappa_0 \approx 1.1$ estimated by T. F. Stromberg and C. A. Swenson [Phys. Rev. Letters **9**, 370 (1962)].

Discussion 8

LYNTON: You mention towards the end that the temperature variation of κ_0, the Gor'kov variation I believe, is less in any case than that obtained from the Ginzburg–Landau expression. Therefore, if the Ginzburg–Landau variation fits, more or less, the Gor'kov expression should have fit better.

EARL S. ROSENBLUM, *Massachusetts Institute of Technology:* Didn't Gor'kov predict about a 25% change over the temperature range? We tried it and it didn't look any better than any of the others. Our data show an 80% increase in κ_0 from T_c to zero.

MENDELSSOHN: When you measure these peaks in the current at the upper critical field, what exactly is the procedure? How long does it take you to go over this peak? Can you stay at different points pinning out that peak?

ROSENBLUM: This is quite stable. We measured resistance against field with the current kept constant, and could vary the field as slowly as we wanted. As a matter of fact, our bandpass was less than a couple of cycles per second. We could sit right at the bottom of this curve, and with few exceptions we detected almost no noise except that residual in the system.

GOODMAN: I'd like to know, first of all, in what sort of vacuum your specimens were annealed.

ROSENBLUM: The vacuum ranged from the high 10^{-5} region down to 10^{-9}.

GOODMAN: The second question I'd like to ask you is why did you assume that gamma depends on the transition temperature, and how are your conclusions modified if you drop this assumption?

ROSENBLUM: If you assume that the electronic specific-heat coefficient of the superconducting phase is a constant, then thermodynamic arguments show that gamma will vary in this way.

GOODMAN: I would remind you that early measurements of Lock, Pippard, and Shoenberg on the isotope effect in tin show that, while the transition temperature and the critical field at the absolute zero varied as a function of the isotopic mass, the variation of gamma was much less than that, and, in fact, too small to be detected.

G. RICKAYZEN, *University of Liverpool:* I'd like to point out that the upper critical field is the field at which the normal state becomes unstable to the formation of Cooper pairs. One can predict it completely without any detailed theory of the structure of the superconducting state. The results are in agreement with Gor'kov's results.

CHANDRASEKHAR: I'd like to make a general comment on the measurement of upper critical fields resistively. It would be desirable to get a clean-cut experimental measurement which either confirmed or disproved the equality of the upper critical field measured resistively and the straightforward thermodynamic measurements. This is not a great problem for low-field superconductors, but it may be for many of these alloys which have extreme high critical fields. I imagine magnetization measurements are going to be difficult because the magnetization will approach the H axis with a small angle. Perhaps since the group at Atomics International is able to do both specific-heat measurements and critical-field measurements, they might carry out this crucial experiment if they have a 100- or 150-kG magnet.

Superconducting Tantalum Films

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I. INTRODUCTION

As reported previously,[1] it is possible to sputter thin films of niobium and tantalum in which the mean free path is limited by the grain size of the film. If the mean free path is reduced below the coherence length ξ_0 of the pure bulk metal, this results in an enhancement of the upper critical field. A knowledge of the grain size of the film permits an experimental estimate of the effective coherence length in the bulk material to be made. As the grain size controls such a fundamental property as the coherence length, it becomes interesting to study the grain size as a function of sputtering temperature.

II. EXPERIMENTAL PROCEDURE

The tantalum thin films were sputtered by a new technique called getter-sputtering.[2] This technique uses the gettering action of part of the sputtered tantalum atoms to produce an atmosphere very low in the type of interstitials (O_2, N_2, $\cdots$) which are detrimental to superconducting films. The substrates used in all experiments were MgO single crystals, except at 1700°K where sapphire single crystals were used. The substrate is located on a hot or cold table, situated between two tantalum cathodes. The table and the two cathodes are placed in a grounded cylindrical stainless steel can which can be cooled by such refrigerants as water or liquid nitrogen. At the beginning of each run, sputtering proceeds with a shield over the substrate in order to produce in the can an atmosphere low in interstitials.

The transition fields of the films were obtained using a resistance measuring equipment sensitive to 10^{-6} V at a current density of a few A/cm^2. The magnetization curves were plotted directly using a Foner type vibrating sample magnetometer.[3] For this purpose, the output of the pick-up coils was fed into the Y-input of an X–Y recorder, while a voltage proportional to the magnetic field was used for the X-input.

[1] J. J. Hauser and H. C. Theuerer, Phys. Rev. (to be published).

[2] H. C. Theuerer and J. J. Hauser, J. Appl. Phys. (to be published).

[3] S. Foner, Rev. Sci. Instr. 30, 548 (1959).