to be applied with caution. Nevertheless, a tentative model is proposed for the conduction which is consistent with the experimental results. Ionic current can be ruled out because the number of monovalent charge carriers needed in typical experiments exceeds by many orders of magnitude the number of crystal lattice points in the current path. Space-charge-limited currents are reported to cause dc negative resistance,[7] but the experiments described here are not limited to dc; at 20 cps the anomalous behavior is still observed, and moreover, the current decreases with crystal thickness much faster than the third power.[8] This strong dependence of current on thickness and the region of negative resistance are suggestive of current tunneling which is observed between degenerate $p$ and $n$ semiconducting regions[9] and between superconductors.[10]

The tentative model for the systems studied here describes the inner region of the crystal as a perfect lattice with large energy gap, and the outer layers as thin imperfect crystals consisting of the chain folds. The energy states of these layers are ionized by metal electrodes, depending upon the contact potential, and hence act as injector electrodes.

The current through the single crystal consists of two main parts: on one hand, tunneling from catwhisker to substrate through the whole crystal, and on the other hand, charge injection from the catwhisker into the surface states, tunneling through the perfect part of the crystal into the opposite surface states and finally into the metal substrate. If the applied voltage lowers the energy levels in the surface layer adjacent to the substrate to a position equal to or lower than the energy levels in the surface layer at the catwhisker, then the second part of the current will be enhanced and give rise to a negative resistance region. For any given crystal, the peak voltage will be determined by the difference in contact potential at the two surfaces while the total current depends upon the difference in barrier height; i.e., the energy level difference between the inner part of the crystal and the surface states.

When the current passes through two single crystals in series, a decrease in total current density and a decrease of the negative resistance effect is consistent with the model described. The two contacting surface layers form an area with strong carrier scattering and thus can be described as an energy barrier of considerable height. As the transmission coefficient of a barrier is exponentially dependent upon the barrier height, it follows that the current through two crystals is smaller than that through a single crystal of the same total thickness. Furthermore, as the total current is given by the product of the transmission coefficient and the density of surface states in the layers near the metal electrodes, the effect of the current leading to the region of negative resistance is reduced simultaneously.

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## NEGATIVE SURFACE FREE-ENERGY EFFECTS IN SUPERCONDUCTING NIOBIUM*

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The transition metals such as niobium, vanadium, and tantalum have been classified in the past as "hard" superconductors, since they customarily exhibit irreversible magnetization curves, locked-in flux and broad superconducting transitions.[1] This type of classification is quite arbitrary, however, since the work of Ittner, Budnick, Seraphim, and others has shown that tantalum exhibits soft rather than hard superconducting behavior if it is made sufficiently pure.[2-7] There is no reason to believe that tantalum is unique in its behavior, and a similar relationship between sample purity and superconducting properties should exist for other transition metals. Very roughly, the procedure which was used in the treatment of the tantalum samples was first to obtain the highest purity raw metal available, and then to degas the samples by heating them close to the melting

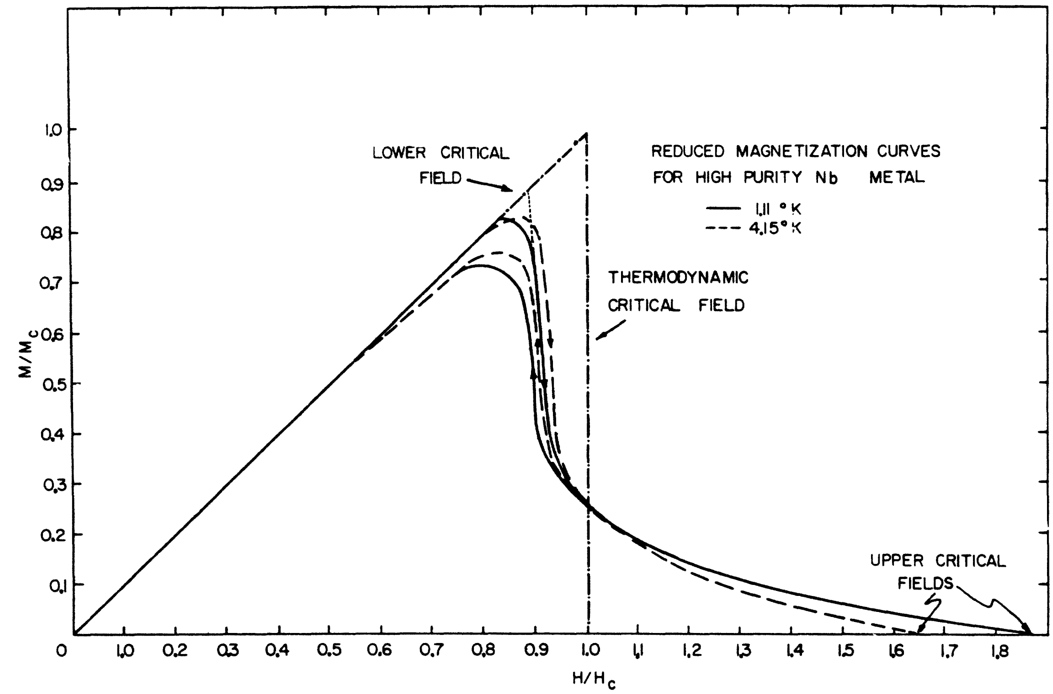


FIG. 1. Reduced magnetization curves for a high-purity niobium sample. The lower critical field was defined by ignoring the rounding of the magnetization curve in this region, and extrapolating the almost vertical portion of the curve to lower fields, as is shown for the 1.11°K $S$-$N$ transition.

point in as good a vacuum as possible (preferably close to $10^{-9}$ Torr).[3,7] The results which are described below were obtained with a polycrystalline wire sample of niobium (0.6-mm diam by 10-mm long) which was prepared in the same general manner as were our previous tantalum samples.[7] The resistivity ratio as measured for this sample, $R_{300}/R_{4.2}{}^N = 1900$, is perhaps as good as has ever been obtained for niobium metal.

Reduced magnetization curves for the previously mentioned sample are shown in Fig. 1 for two temperatures, 4.15°K and 1.11°K. The magnetic moment of the sample was measured directly as a ballistic galvanometer deflection when the sample was moved rapidly in a uniform magnetic field from one 10 000-turn coil to a second identical but oppositely wound coil.[8] This was done for suitable magnetic field increments at constant temperature, and the resulting relative magnetic moment $M$ vs external field $H$ relationship was mapped out as shown in Fig. 1. Previous tests of the apparatus with tin and high-purity tantalum samples had shown behavior which could be represented by the "thermodynamic" curve shown. The galvanometer sensitivity, roughly ±0.003 on the vertical scale, was the limiting factor in the precision of these data.

The display of the data in a reduced plot was accomplished as follows. Since the magnetization curves are approximately reversible, it is possible to use the shape of these curves to obtain the free-energy difference between the normal and superconducting states,[9,10]

$$F_n - F_s = H_c{}^2 V/8\pi = -\int_0^\infty M dH. \qquad (1)$$

This relationship serves as a definition of $H_c$, which then can be calculated either from calorimetric data or from magnetization data. The left-hand side of Eq. (1) was used to calculate $H_c$ for the field-increasing ($S$-$N$) and field-decreasing ($N$-$S$) magnetization curves for each temperature. The various values of $H_c$ which were obtained in this manner are plotted in Fig. 2 as $H_c{}^2$ vs $T^2$. An average value of $H_c$ was used for a given temperature to obtain reduced magnetic fields $H/H_c$ and reduced values of the magnetization $M/M_c$, where $M_c$ is the extrapolated value of $M$ at $H_c$. Additional data which were obtained at three intermediate temperatures between 4.15°K and 1.11°K showed a smooth change in the shape of the $M$ vs $H$ curve as the temperature was

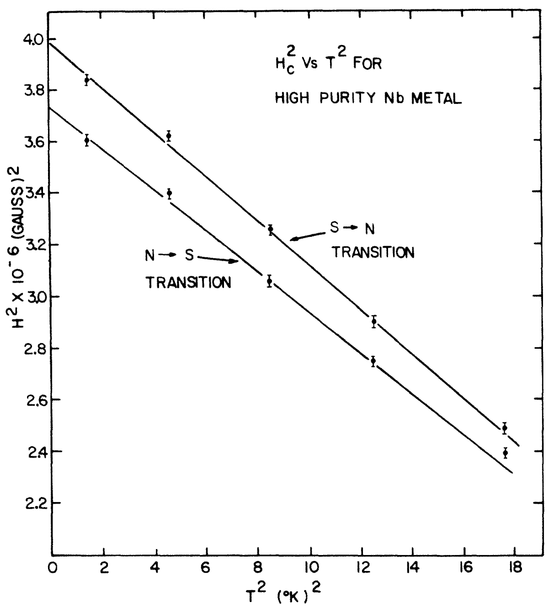


FIG. 2. A plot of $H_c^2$ vs $T^2$ for a high-purity niobium sample. Two values were obtained for each temperature depending on whether the field was increasing or decreasing. The vertical separation of the curves is a measure of the hysteresis which was observed.

decreased.

This type of behavior for superconductors has been discussed previously by Abrikosov, Goodman, Gor'kov, and others.[9-13] In general, the theories predict that if a negative surface free energy exists between the normal and superconducting states, there will be an initial penetration of the magnetic field into the sample at some field smaller than $H_c$ ($H_1$, the lower critical field), and a final complete penetration of the flux and a restoration of the electrical resistance at a field greater than $H_c$ ($H_2$, the upper critical field). The magnetization curve for positive surface free energies would resemble the "thermodynamic" curve of Fig. 1 when demagnetization effects are ignored. The region between $H_1$ and $H_2$ is characterized by a "mixed" state which resembles the more usual intermediate state in many respects. Any theoretical calculations must postulate a model for the distribution of the normal and superconducting regions in this mixed state. Previous experimental evidence for the existence of a negative surface free energy in superconductors has been based on the behavior of alloys where the electronic mean free path is much smaller than the superconducting penetration depth.[9,11,13] The mean free path for this sample of niobium metal, where the resistivity at 4°K is $7\times10^{-9}$ ohm-cm, was estimated to be about 25 $\mu$ using a Fermi surface area which is 20% of the free-electron value for five electrons. Thus, we believe that the present experiments show negative surface free-energy effects for the first time in a substance where the mean free path is much longer than the penetration depth. Dobbs and Perz have commented on similar effects which they observed in ultrasonic measurements on a high-purity niobium sample.[14]

The reasons why we believe that this behavior is characteristic of pure niobium metal and is not simply an impurity effect are as follows:

(1) The electronic mean free path is so much longer than usually quoted coherence lengths (about one micron),[15] that it would appear to be difficult to attribute this behavior to the nature of the impurities present in the sample.

(2) Virtually no change in the hysteresis or the locked-in flux was observed as the temperature was decreased. In addition, the raw data superposed perfectly below $H_1$ for the various temperatures, implying that the deviations from linear behavior for the $M$ vs $H$ curve on decreasing field are a temperature-independent characteristic of the sample.

(3) Preliminary data were obtained a year ago using a sample which was prepared in the same manner from metal which came from another source. As compared with the present measurements, these earlier $M$ vs $H$ curves showed the same amount of locked-in flux (0.5% of the flux at $H_c$), slightly greater hysteresis, and the same values of $H_1$, $H_2$, and $H_c$. The major difference between the two samples was presumably in tantalum content (1000 ppm vs 200 ppm), and this was reflected in a smaller residual resistivity ratio (about 500) for the earlier sample.

(4) If the values of $H_c$ as defined by Eq. (1) are correct, a plot of $H_c^2$ vs $T^2$ should be linear with a slope which is proportional to the temperature coefficient of the electronic specific heat $\gamma$ and an intercept at $T=0$ which is equal to $H_0^2$.[7] Both of these quantities can be obtained independently from calorimetric data for comparison. The data shown in Fig. 2 can be analyzed to give $\gamma=(1.71\pm0.04)\times10^{-3}$ joule/(°K)$^2$-mole with a molar volume of 10.80 cm$^3$, and $H_0=1960\pm40$ gauss. These are in good agreement with those calculated from the calorimetric data, namely $(1.75\pm0.03)\times10^{-3}$ joule/(°K)$^2$-mole[16,17] and 1944 gauss.[16] The deviation of the 4.15°K points from the linear relationship is roughly as would be expected.[7] If the initial pen-

etration fields $H_1$ had been used as the definition of $H_C$, our calculated values of both $\gamma$ and $H_0$ would have been at least 10% low.

It is of interest to compare the curves which we have obtained with the behavior suggested by the various theories. Here it is customary to introduce from the Ginzburg-Landau theory a dimensionless parameter $\kappa$ which is of the order of the superconducting penetration depth divided by the Pippard coherence length.[9-11] This parameter can be related to the upper critical field in both the high-temperature[9] and low-temperature[12] limits, and if $\kappa$ is truly a constant for a superconductor, $H_2/H_C$ should decrease with increasing temperature.[12] Our data indeed verify this, with $H_2/H_C$ varying from an extrapolated value of 1.93 at absolute zero to 1.90 at 1.11°K to 1.65 at 4.15°K. $H_1/H_C$ shows a much smaller temperature dependence, with an increase from 0.88 at both absolute zero and 1.11°K to 0.90 at 4.15°K. Both $(H_1/H_C)^2$ and $(H_2/H_C)^2$ appear to satisfy a linear relationship with respect to $T^2$ to better than 2%. It can be concluded that our data imply a value of $\kappa \cong 1.1$, and hence that the coherence length and the penetration depth are of the same order of magnitude for high-purity niobium metal.[12]

The linear form of the magnetization curve as $H$ approaches $H_2$ is in much closer agreement with the predictions of Abrikosov[9] than those of Goodman.[10,11] The independent values of $\kappa$ which can be calculated from the slope and intercept at $H_2$ both appear to approach at high temperatures the value of 1.1 which was calculated from $H_2$ at absolute zero using Gor'kov's theory.

Both Abrikosov and Goodman predict a rapid decrease in magnetization with increasing field at lower critical field $H_1$, and this is evident in Fig. 1. Goodman has extrapolated Abrikosov's results to values of $\kappa$ near unity, and has suggested a possible shape of the magnetization curve in this limit. The experimental and theoretical curves differ in shape with our observed curves showing a much greater decrease in $M$ at $H_1$ than is predicted. No significance should be placed on this difference, however.

The question can be raised as to whether or not a value of $\kappa$ of the order of unity is reasonable for niobium in view of the much smaller numbers which are found for soft (nontransition metal) superconductors. Gor'kov gives two relationships involving $\kappa$ which involve other electronic properties. First, a rearrangement and combination of several of his equations gives the effective number of free electrons per cubic centimeter as

$$n = 0.188 \times 10^{18} (H_{C0}^3/\kappa T_C^2)^{0.75} = 1.72 \times 10^{23}, \quad (2)$$

using $T_C = 9.2$°K and $\kappa = 1$. The numerical constant involves only fundamental constants and numbers which arise in the theory. This value for the density of free electrons corresponds to a Fermi surface area which is roughly 18% of the free-electron value for five electrons per atom, and is slightly greater than the fraction which Fawcett finds for tungsten, chromium, and molybdenum which have six electrons per atom.[18] Second, the London penetration depth at absolute zero $\lambda_0$ can be calculated to be about 250 Å. Thus it appears that for niobium, where $\kappa$ is roughly unity, both the coherence length and the penetration depth are of the same magnitude as the penetration depth for the nontransition metal superconductors. This, in turn, implies a much smaller value for the electron velocity at the Fermi surface than the free-electron model would predict.[19]

The results which have been discussed here are only preliminary in nature and obviously must be extended to temperatures much closer to 9°K, where Abrikosov's theory is applicable. Heat capacity measurements on high-purity samples in magnetic fields of the order of $H_C$ would be useful to verify the prediction that the transition at $H_1$ is of second order.[9] Detailed theoretical calculations of the shape of the magnetization curve in the difficult region where $\kappa$ is of the order of unity also would be of value. Finally, we have obtained preliminary data for the magnetization curve for a vanadium sample with a resistivity ratio of about 400. These data indicate that even with considerable hysteresis present, flux penetration occurs in increasing magnetic fields considerably below the calorimetric value of $H_C$,[20] and the values of $H_2/H_C$ imply a value of $\kappa$ of the order of 1.4. These results have not been reproduced with another sample and must be verified before much reliance can be placed upon them. There exists, unfortunately, a serious problem for tantalum, niobium, and vanadium, in particular, which involves both the difficulty of obtaining high-purity starting material and a tremendous sensitivity of the electronic properties to gaseous contamination. These make sample preparation tedious.

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## MAGNETIC-FIELD DEPENDENCE OF THE ENERGY GAP IN SUPERCONDUCTORS

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The effect of a magnetic field on the energy gap of a superconductor was first obtained from the theory of Bardeen, Cooper, and Schrieffer[1] by Gupta and Mathur (GM).[2] It has also been worked out from the Ginzburg-Landau-Gor'kov[3] theory by Douglass.[4] Douglass finds that for thin films the energy gap $\epsilon$ varies with magnetic field $H$ according to the formula

$$\epsilon(H)=\epsilon(0)[1-(H/H_c)^2]^{1/2}, \tag{1}$$

where $H_c$ is the critical field for the film. He also finds that the transition to the normal state is of second order for films of thickness $d<5^{1/2}\lambda$, but becomes first order for thicker specimens. Here $\lambda$ is the penetration depth. These results are in very good agreement with the experiments of Douglass[5] and of Morris and Tinkham.[6] Since the calculations of Douglass are based on the Ginzburg-Landau-Gor'kov theory, they are reliable only for temperatures $T\sim T_c$, the critical temperature. Indeed Morris and Tinkham find that for $T\sim 0$, the experimental points fit a formula of the type

$$\epsilon(H)=\epsilon(0)[1-(H/H_c)^2] \tag{2}$$

rather than Eq. (1).

The purpose of this note is to point out that this formula can be derived from the results of GM, which are valid for $T=0$. The GM expressions also reproduce the experimentally observed small decrease in the energy gap for bulk matter. Finally, the change in the nature of transition at thickness $d\sim 5^{1/2}\lambda$ can also be understood on the basis of these calculations.

We shall be working in the local limit of London. The GM equation[7] for the energy gap in this limit is given by

$$\epsilon(H)=\epsilon(0)\{1-\tfrac{1}{3}(e^2/m^2)(k_f^{\,2}/\epsilon^2)(H^2/2\mu^3 d) \times[(\sinh\mu d-\mu d)/\cosh^2(\tfrac{1}{2}\mu d)]\}, \tag{3}$$