PHYSICAL REVIEW VOLUME 140, NUMBER 5A 29 NOVEMBER 1965

Upper Critical Fields of Nb-Ti Alloys: Evidence for the Influence of Pauli Paramagnetism

Y. Shapira and L. J. Neuringer
National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts*

(Received 28 June 1965)

Resistivity, flow-resistance, and ultrasonic-attenuation measurements were carried out on Nb–37 at.% Ti and Nb–56 at.% Ti in dc magnetic fields up to 150 kG. The transition temperatures and the dependence of the upper critical field on temperature were measured by the resistive method. The transition temperatures are: $T_c=9.2\pm0.2$°K for Nb–37 at.% Ti and $T_c=9.0\pm0.2$°K for Nb–56 at.% Ti. Flow-resistance measurements gave the following values for the Ginzburg-Landau-Abrikosov-Gor'kov upper critical field at $T=0$: 111 ± 7 kG for Nb–37 at.% Ti and 188 ± 9 kG for Nb–56 at.% Ti. Changes in the ultrasonic attenuation were observed near the upper critical field. The data support the view that the Pauli paramagnetism plays a role in determining the upper critical field. However, the effect of the Pauli paramagnetism is found to be smaller than predicted by Maki.

I. INTRODUCTION

One of the parameters which characterize type-II superconductors is the upper critical field H_{c2}. Recent experimental investigations[1,2] have shown that for some high-field superconductors the measured upper critical field H_{c2} is lower than the upper critical field H_{c2}^* which is expected on the basis of the Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory.[3] Clogston[4] had shown previously that the Pauli spin paramagnetism places an upper limit H_p on the field at which superconductivity can exist. The difference between H_{c2} and H_{c2}^* was therefore attributed to the Pauli paramagnetism. More recently Maki,[5] and Helfand and Werthamer,[6] have calculated the temperature variation of H_{c2}. In particular, Maki has considered the influence of the Pauli paramagnetism and has shown that this effect reduces the value of H_{c2} and modifies its temperature variation. In this paper we compare experimental data on the temperature variation of H_{c2} in Nb–37 at.% Ti and Nb–56 at.% Ti with Maki's theory. The second of these alloys has a measured upper critical field which is comparable to the field H_p determined by the Clogston criterion, so that one expects a noticeable effect due to the Pauli paramagnetism. While several authors[1,2,7,8] have reported on measurements of upper critical fields in the Nb–Ti alloy system, the present work presents more complete data on the temperature variation of H_{c2} and consequently allows a detailed comparison with a theory which was not available to the earlier workers.

Flow-resistance measurements have been recently reported by Kim, Hempstead, and Strnad.[2,9] These authors have suggested that the GLAG upper critical field at $T=0$, $H_{c2}^*(0)$, can be determined from this type of measurement. A comparison of $H_{c2}^*(0)$ with the actual upper critical field at $T=0$, $H_{c2}(0)$, then indicates whether or not a paramagnetic effect exists. In the present paper we apply the flow-resistance technique to investigate the two niobium-titanium alloys. The results are compared with those obtained from the temperature variation of the upper critical field.

Ultrasonic techniques have been very useful in the study of superconductors.[10] However, virtually no ultrasonic work has been reported on high-field superconductors. Recently[11] we have reported the existence of an ultrasonic absorption edge near the upper critical field of Nb–25 at.% Zr. Here we report on a different type of ultrasonic behavior near the upper critical field of the niobium-titanium alloys.

The variety of measurements reported in the present paper (transition temperatures, resistive transitions, flow resistance, and ultrasonic attenuation) were carried out on the same samples. The extensive data collected in these experiments allow a meaningful comparison between the results of the various measurements as well as a detailed comparison with several predictions of Maki's theory.

II. EXPERIMENTAL TECHNIQUE

Two niobium-titanium ingots of different compositions were kindly provided by Dr. S. H. Autler of the Westinghouse Research Laboratories. These ingots had been annealed at 1300°C for 16 h. Stoichiometric analysis, performed by D. L. Guernsey of M.I.T., gave the following compositions: Ingot I: Nb–37 at.% Ti, Ingot II: Nb–56 at.% Ti. All the samples used in the present work were cut from these ingots.

---

* Supported by the U. S. Air Force Office of Scientific Research.

[1] T. C. Berlincourt and R. R. Hake, Phys. Rev. **131**, 140 (1963).

[2] Y. B. Kim, C. F. Hempstead, and A. R. Strnad, Phys. Rev. **139**, A1163 (1965).

[3] References to the GLAG theory are found in Ref. 1. In the present paper we follow the notation of Ref. 2.

[4] A. M. Clogston, Phys. Rev. Letters **9**, 266 (1962).

[5] K. Maki, Physics **1**, 21 (1964); **1**, 127 (1964).

[6] E. Helfand and N. R. Werthamer, Phys. Rev. Letters **13**, 686 (1964), and private communication.

[7] J. H. Wernick, F. J. Morin, F. S. L. Hsu, D. Dorsi, J. P. Maita, and J. E. Kunzler, *High Magnetic Fields* (John Wiley & Sons, Inc., New York, 1962), p. 609.

[8] B. S. Chandrasekhar, J. K. Hulm, and C. K. Jones, Phys. Letters **5**, 18 (1963); Rev. Mod. Phys. **36**, 74 (1964).

[9] A. R. Strnad, C. F. Hempstead, and Y. B. Kim, Phys. Rev. Letters **13**, 794 (1964).

[10] For a short review see A. R. Mackintosh, *Phonons and Phonon Interactions* (W. A. Benjamin, Inc., New York, 1964), p. 181.

[11] L. J. Neuringer and Y. Shapira, Solid State Commun. **2**, 349 (1964).

Ultrasonic attenuation measurements were carried out with conventional pulse techniques. The samples, which were cubes with an edge about 1 cm long, were polished to obtain good acoustical reflections. Acoustical bonds were made with Nonaq stopcock grease or with Dow Corning 200 silicone fluid of 30 000 centistoke viscosity at 25°C. The details of the ultrasonic equipment have been described elsewhere.[12]

Two types of resistance measurements were performed: superconducting-to-normal transition and flow resistance. Both types of measurements were made with a four-probe arrangement. Current and voltage leads were ultrasonically soldered to the samples with indium. The specimens were bars about 1 cm long and 10^{-2} cm^2 in cross section. In studying the superconducting-to-normal transition, the current was produced by a constant current supply and the voltage was detected by a Keithley microvoltmeter. When measuring the flow resistance a voltage proportional to the measuring current was fed to the X terminals of a Moseley X-Y recorder, and the voltage probes of the sample were connected directly to the Y terminals.

Measurements at liquid-helium temperatures, extending down to 1.3°K, were made with the samples immersed directly in the liquid helium. The temperature was determined from the helium vapor pressure. Experiments above 4.2°K were conducted with the sample mounted inside a closed chamber which was immersed in liquid helium. The temperature of the sample was regulated by a heater and was measured with an Allen Bradley 0.1-W carbon resistor which was calibrated against a Honeywell germanium thermometer. Special care was taken to ensure good thermal contact between the specimen and the carbon resistor. Corrections for the slight magnetoresistance of the carbon thermometer were applied whenever necessary. The accuracy of the temperature measurements above 4.2°K is estimated to be better than 0.2°K. The reproducibility of the temperature measurements in this range was better than 0.1°K.

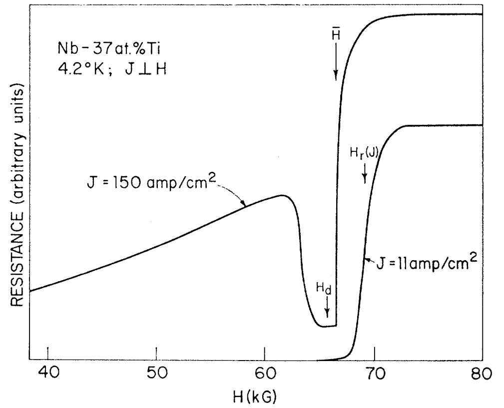

Fig. 1. Variation of the electrical resistance of Nb–37 at.% Ti with magnetic-field intensity at 4.2°K. The ordinate scale is different for the two curves, and the curve for $J=150$ A/cm^2 is displaced upward for clarity. The resistance at the bottom of the dip in the curve for $J=150$ A/cm^2 is below the detectable level.

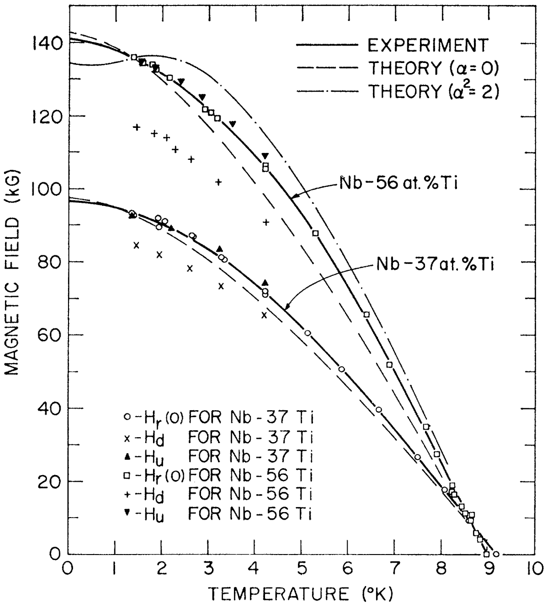

Fig. 2. Temperature variation of $H_r(0)$, H_d, and H_u. The solid curves represent the observed variation of $H_r(0)$ with temperature. The theoretical curves are normalized to the value of $H_r(0)$ measured at the lowest temperature.

Steady magnetic fields up to 150 kG were generated in $2\frac{1}{8}$- and $1\frac{1}{4}$-in.-bore water-cooled solenoids. The magnetic field in each solenoid as a function of current through the solenoid was measured prior to each run with a Newport type J flux integrator which had been calibrated against an NMR probe. During the run, the current through the solenoid was recorded and the magnetic field was deduced from the field-versus-current characteristic of the magnet. The accuracy of the magnetic field measurements is estimated to be better than 2%. Some experiments were also conducted at low fields, up to 18 kG, in a Harvey Wells 12-in. electromagnet.

III. RESULTS

A. Normal-to-Superconducting Resistive Transitions

The variation of the electrical resistance of the two niobium-titanium alloys with temperature was measured at zero magnetic field using current densities $J\sim0.2$–2 A/cm^2. Sharp normal-superconducting transitions were observed. The width of the transition, defined as the temperature interval in which the resistance R changes from 0.1 to 0.9 R_n, were R_n is the normal resistance, was ~0.1°K in both Nb–37 at.% Ti and Nb–56 at.% Ti alloys. The temperature at which $R=0.5\,R_n$ was taken to be the transition temperature T_c. The values of T_c determined in this fashion were independent of the current density. The

---

[12] Y. Shapira and B. Lax, Phys. Rev. **138**, A1191 (1965).

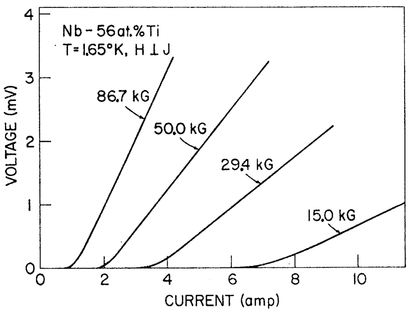

FIG. 3. Voltage-versus-current characteristics of Nb–56 at.% Ti at 1.65°K. The magnetic field is normal to the direction of current flow.

measured transition temperatures are $T_c=9.2\pm0.2$°K for Nb–37 at.% Ti and $T_c=9.0\pm0.2$°K for Nb–56 at.% Ti. The first of these values is close to the one obtained by Wernick *et al.*[7] for Nb–33 at.% Ti, but it is somewhat lower than the value given by Hulm and Blaugher[13] for Nb–37 at.% Ti. Our value for the transition temperature of Nb–56 at.% Ti is, on the other hand, in good agreement with that reported by Hulm and Blaugher for the same composition. The normal resistivities at $T\approx10$°K are 33 $\mu\Omega$ cm for Nb–37 at.% Ti, and 53 $\mu\Omega$ cm for Nb–56 at.% Ti. The resistivity ratio $\rho_{300}/\rho_{10°\mathrm{K}}$ is 1.4 for Nb–37 at.% Ti, and 1.2 for Nb–56 at.% Ti.

Resistance measurements were also carried out at constant temperature as a function of the magnetic-field intensity H. The current densities were varied from ~1 A/cm^2 to ~1000 A/cm^2 and the magnetic field was normal to the direction of current flow. When the current density was low ($J\sim1$–30 A/cm^2) sharp resistive transitions were observed at temperatures below T_c. This type of resistive behavior is illustrated in Fig. 1 by the curve for $J=11$ A/cm^2. The width of the transition, defined as the field interval in which R changes from 0.1 to 0.9 R_n, was ~3 kG in both alloys, depending only slightly on the temperature and the current density. The field at which $R=0.5\,R_n$ was defined as the resistive transition field $H_r(J)$. At any given temperature the value of $H_r(J)$ was found to decrease slightly as the current density J was increased, obeying very closely the relation

$$H_r(J)=H_r(0)-AJ^{1/2}, \tag{1}$$

where $H_r(0)$ and A are constants. The resistive transition field at zero measuring current $H_r(0)$ was determined by plotting $H_r(J)$ versus $J^{1/2}$ and extrapolating to zero current. The temperature variation of $H_r(0)$ is shown in Fig. 2. The value of $H_r(0)$ for Nb–56 at.% Ti, measured at ~1.3°K, is close to the one reported by Berlincourt and Hake for a sample of the same composition.[1] However, our value for Nb–37 at.% Ti is lower than the one measured by these authors. The difference in the resistive transition field in the latter case is probably due to a difference in the purity and method of preparation of the specimens. The normal resistivities of our alloys at $H>H_r(J)$ agree very closely with the resistivities measured at ~10°K in zero magnetic field. The magnetoresistance of the samples at $H>H_r(J)$ was too small to be detected; e.g., for Nb–37 at.% Ti at 4.2°K the change in the resistance between 80 and 105 kG was less than 1%.

Measurements of $H_r(J)$ carried out at temperatures just below T_c show that at these temperatures $H_r(0)$ varies linearly with $(T-T_c)$. The following values for the temperature derivative $-[dH_r(0)/dt]_{t=1}$, where $t=T/T_c$, were obtained: 146 kG for Nb–37 at.% Ti and 227 kG for Nb–56 at.% Ti. The estimated uncertainty of these values is $\pm7\%$.

Resistance measurements as a function of the magnetic-field intensity, carried out with high current densities at liquid-helium temperatures, gave quantitatively different results from those at lower current densities. With current densities of 70 A/cm$^2\lesssim J\lesssim700$ A/cm^2 the resistance rose above the detectable level of about 0.01 R_n at fields well below $H_r(0)$. This resistance first increased gradually with magnetic field, then dropped substantially, often to an undetectable level, and finally increased sharply to its normal value. This type of resistance behavior is illustrated in Fig. 1 by the curve for $J=150$ A/cm^2. A similar type of resistance behavior was observed in niobium by Autler *et al.*[14] and in other materials.[2,15] For a certain range of J the resistance at the bottom of the dip in our experiments, was below the detectable level. The field $\bar{H}$ at which the resistance increases sharply (see Fig. 1) decreased as J increased. Over the range of J in which the resistance minimum was below the detectable level, this decrease in $\bar{H}$ amounted to $\sim5\%$. On the other hand, the field H_d at the middle of the resistance dip was constant to $\sim1\%$ over the same range of measuring current. The variation of H_d with temperature is shown in Fig. 2. For each of the two niobium-titanium alloys the ratio $H_d/H_r(0)$ was constant, to within $\sim1\%$, at liquid-helium temperatures. For Nb–37 at.% Ti, $H_d/H_r(0)=0.91$, while for Nb–56 at.% Ti, $H_d/H_r(0)=0.86$. When current densities higher than ~700 A/cm^2 were used the resistance increased monotonically with field. No resistance dips, as a function of H, were observed at these very high current densities.

Resistance measurements were also carried out at 4.2°K using low current densities ($J\sim1$–30 A/cm^2) with **H** parallel to the direction of the current flow. The results were similar to those obtained at the same current densities with the magnetic field perpendicular to the current except that the value of $H_r(0)$ was about 1% higher for $\mathbf{H}\|\mathbf{J}$ than for $\mathbf{H}\perp\mathbf{J}$. This small dependence of $H_r(0)$ on the relative orientation of **H** and **J** is

---

[13] J. K. Hulm and R. D. Blaugher, Phys. Rev. **123**, 1569 (1961).

[14] S. H. Autler, E. S. Rosenblum, and K. H. Gooen, Phys. Rev. Letters **9**, 489 (1962); Rev. Mod. Phys. **36**, 77 (1964).

[15] W. DeSorbo, Rev. Mod. Phys. **36**, 90 (1964).

within the experimental error, although it may be genuine.

B. Flow Resistance

The resistance of the two niobium-titanium alloys was measured as a function of current at fixed temperature and magnetic field. These measurements were carried out at liquid-helium temperatures with $\mathbf{H}\perp\mathbf{J}$. The measuring current was varied from 0 to 15 A which corresponds to current densities $0\leq J\lesssim 1500$ A/cm^2. Typical voltage-versus-current characteristics are shown in Fig. 3. As this figure indicates, no voltage is observed until the current exceeds a certain value. At somewhat higher currents the voltage V varies linearly with the current I. Following Kim *et al.*[2,9] we define the flow resistance R_f as the slope $\Delta V/\Delta I$ of the straight-line portion of the V-I curve. The type of V-I characteristic shown in Fig. 3 was observed only at fields below $\sim 0.7\ H_r(0)$. At fields above $\sim 0.7\ H_r(0)$, but well below $H_r(0)$, the flow resistance could not be defined meaningfully since the V-I characteristic curved upward slightly and had no well-defined linear portion. At fields just below $H_r(0)$ the resistance, as a function of I, jumped abruptly from zero to its normal value R_n. As a consequence, the flow resistance could be determined only for $H\lesssim 0.7\ H_r(0)$.

According to Kim *et al.*,[2] at fields well below $H_r(0)$, the ratio of the flow resistance R_f to the normal resistance R_n obeys the relation

$$R_f/R_n=H/H_{c2}^*(0)\,, \tag{2}$$

where $H_{c2}^*(0)$ is the GLAG upper critical field at $T=0$ in the absence of the Pauli spin paramagnetism. The measured ratio R_f/R_n as a function of H for the Nb–56 at.% Ti alloy is shown in Fig. 4. We note that R_f is, in fact, approximately proportional to H in accordance with Eq. (2). By extending the linear portion of the R_f/R_n-versus-H curve to the field at which $R_f/R_n=1$, we obtain $H_{c2}^*(0)=188\pm 9$ kG for Nb–56 at.% Ti and $H_{c2}^*(0)=111\pm 7$ kG for Nb–37 at.% Ti.

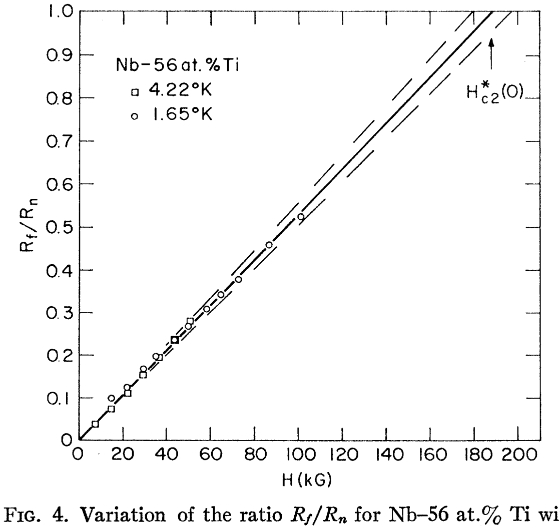

FIG. 4. Variation of the ratio R_f/R_n for Nb–56 at.% Ti with magnetic-field intensity. The solid line is a fit of the data to Eq. (2). The dashed lines represent the uncertainty of this fit.

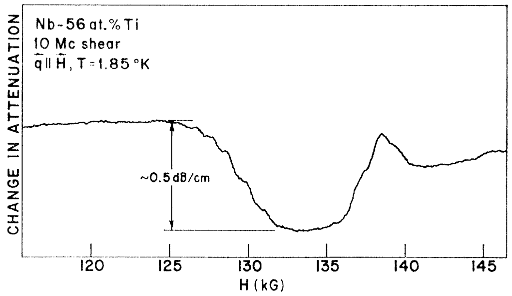

FIG. 5. Recorder tracing of the ultrasonic attenuation of 10-Mc/sec shear waves in Nb–56 at.% Ti as a function of the magnetic-field intensity at 1.85°K. The magnetic field is parallel to the direction of sound propagation.

C. Ultrasonic Attenuation

The attenuation of ~10-Mc/sec shear waves in both niobium-titanium alloys was measured at liquid-helium temperatures in a magnetic field up to 150 kG. The magnetic field was oriented parallel to the direction of sound propagation. A dip in the attenuation coefficient was observed in both alloys at high magnetic fields. This is illustrated in Fig. 5. We define the ultrasonic transition field H_u as the field at the middle of this dip. Values of H_u at several temperatures in the liquid-helium range are plotted in Fig. 2. The close agreement between the values of H_u and those of $H_r(0)$ indicates that the dip in the ultrasonic attenuation coefficient occurs near or at the upper critical field. The magnitude of the dip at 4.2°K was ~0.1 dB/cm for Nb–37 at.% Ti and ~0.2 dB/cm for Nb–56 at.% Ti. This magnitude increased as the temperature was lowered.

Measurements of the attenuation of 10-Mc/sec longitudinal waves propagated in Nb–37 at.% Ti were also carried out at liquid helium in fields up to 110 kG. With the magnetic field perpendicular to the direction of sound propagation the attenuation coefficient showed a dip at a field which was within 2% of H_u for shear waves. This dip had a magnitude of ~0.04 dB/cm at 4.2°K, and was superimposed on a monotonic increase of the attenuation coefficient with H. A typical experimental trace is shown in Fig. 6. As the angle θ between $\mathbf{H}$ and the direction of sound propagation was varied gradually from 90° to 0°, the magnitude of the attenuation dip diminished but the magnetic field at which the dip occurred remained unchanged to within 2%. Figure 7 shows the variation with θ of the attenuation change $\Delta\Gamma$, which is defined in Fig. 6.

IV. DISCUSSION

In order to compare our resistivity data with Maki's theory it is necessary to choose a criterion by which

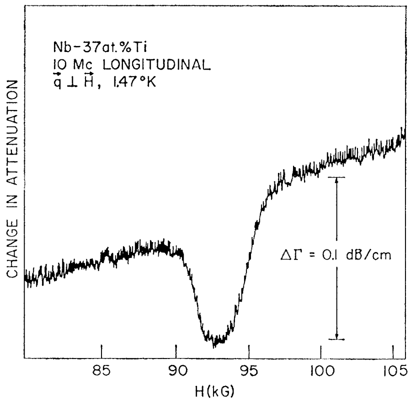

FIG. 6. Recorder tracing of the ultrasonic attenuation of 10-Mc/sec longitudinal waves in Nb–37 at.% Ti as a function of the magnetic-field intensity at 1.47°K. The magnetic field is normal to the direction of sound propagation.

the upper critical field H_{c2} can be determined from the resistance measurements. Two different criteria of this type were used by previous workers. The first criterion[8] identifies H_{c2} with the field at which the smallest detectable voltage appears across a sample carrying some low current (usually 10 A/cm^2). The second criterion[14,15] is based on measurements with moderately high current densities when a sharp dip in the resistance is observed. The upper critical field H_{c2} is then identified with the field at which this dip occurs. The first criterion is somewhat arbitrary since it depends on the smallest voltage which can be detected as well as on the current density which is used. Moreover, it is not clear why the field at which the resistance first appears, rather than the field at which the resistance is restored to its normal value, should be chosen as H_{c2}. While the field $H_r(0)$, as defined in the present work, is close to the field determined by the first criterion, we believe that it is more meaningful to identify $H_r(0)$ with the *resistive* transition field. We shall therefore interpret our data first on the assumption that H_{c2} coincides with $H_r(0)$. A second interpretation in which H_{c2} is taken to be equal to the field H_d at the center of the resistive dip will be presented subsequently. Several attempts to determine H_{c2} from magnetization measurements have been made by S. Foner and E. J. McNiff, Jr., by S. J. Williamson, and by the authors. However, the results of all the magnetization measurements were inconclusive. Consequently, we cannot say on the basis of the magnetization measurements which of the two interpretations [$H_{c2}=H_r(0)$ or $H_{c2}=H_d$] is more nearly correct.

A. Interpretation I: $H_{c2}=H_r(0)$

The temperature variation of the upper critical field H_{c2}, in the absence of the Pauli spin paramagnetism, was calculated recently by Maki[5] and by Helfand and Werthamer.[6] The former assumed that the electronic mean free path is very short (dirty limit) while the latter considered the case of an arbitrary mean free path. The two calculations agree in the dirty limit. In Fig. 2 the predicted temperature variation of H_{c2}, in the dirty limit, is shown by the theoretical curves labeled by $\alpha=0$. The theoretical curve for each alloy was normalized to the value of $H_r(0)$ measured at the lowest temperature. We proceed to compare our experimental findings with theory under the assumption $H_{c2}=H_r(0)$. As can be seen, the experimental curves in Fig. 2 differ somewhat from the theoretical curves with $\alpha=0$, the difference being more pronounced for Nb–56 at.% Ti. The agreement between experiment and theory can be improved only slightly by assuming different values for the electronic mean free path.[6] However, for Nb–56 at.% Ti, the discrepancy between experiment and theory is too large to be accounted for in this fashion. The most plausible explanation for this discrepancy lies in the effect of the Pauli paramagnetism. Such an effect is expected to be pronounced for Nb–56 at.% Ti where the upper critical field is comparable to the field H_p obtained from the Clogston criterion.[4]

Maki[5] has considered the effect of the Pauli paramagnetism on the temperature variation of the upper critical field H_{c2}. In Maki's theory the relative importance of this effect is characterized by the parameter α which is defined as

$$\alpha=\sqrt{2}H_{c2}^*(0)/H_p\,, \tag{3}$$

where H_p is given by

$$H_p=18\,400\;T_c\;(\text{gauss})\,. \tag{4}$$

At low temperatures the slope $-(dH_{c2}/dT)$ of the H_{c2}-versus-T curve is expected to decrease as α increases. As Fig. 2 indicates, the experimental curves for $H_r(0)$ are, in fact, flatter at low temperatures than the theoretical curves with $\alpha=0$. Moreover, Nb–56 at.% Ti which has a higher value of α than Nb–37 at.% Ti shows a greater departure from the theoretical curve with $\alpha=0$. Further evidence for the existence of a paramagnetic effect in both niobium-titanium alloys is found in the values of $H_{c2}^*(0)$ which were obtained from the flow-resistance measurements by using Eq. (2). These values are higher than the corresponding values of $H_r(0)$ extrapolated to $T=0$. Identifying the latter values with the upper critical field at $T=0$, $H_{c2}(0)$, we obtain $H_{c2}^*(0)/H_{c2}(0)=1.15\pm0.07$ for Nb–37 at.% Ti and $H_{c2}^*(0)/H_{c2}(0)=1.33\pm0.07$ for Nb–56 at.% Ti. Thus the actual values of $H_{c2}(0)$ are lower than those of $H_{c2}^*(0)$ — a result which is expected when the paramagnetic effect is present.

In the preceding paragraph we have seen that both the discrepancy between $H_{c2}(0)$ and $H_{c2}^*(0)$ and the departure of the observed temperature variation of $H_{c2}(0)$ from the theoretical curves with $\alpha=0$ can be understood *qualitatively* on the basis of Maki's theory for the effect of the Pauli paramagnetism. However, a *quantitative* comparison of the experimental results with Maki's theory indicates that this theory overestimates the effect of the Pauli paramagnetism. Under the assumption that the superconducting-to-normal transition is a second-order transition, Maki has predicted that the ratio $H_{c2}(0)/H_{c2}^*(0)$ is given by

$$H_{c2}(0)/H_{c2}^*(0) = (1+\alpha^2)^{-1/2}. \qquad (5)$$

Substituting the values of $H_{c2}^*(0)$, as determined from the flow-resistance measurements, in Eq. (3) we obtain $\alpha = 0.93$ for Nb–37 at.% Ti and $\alpha = 1.61$ for Nb–56 at.% Ti. Substituting these values of α into Eq. (5) we then obtain the following values for the ratio $H_{c2}(0)/H_{c2}^*(0)$, 0.73 for Nb–37 at.% Ti and 0.53 for Nb–56 at.% Ti. These calculated values are substantially lower than the corresponding experimental values 0.87 ± 0.06 and 0.75 ± 0.04 obtained by assuming $H_{c2} = H_r(0)$. The disagreement between the experimental results and Maki's theory becomes more striking when one calculates the values of $H_{c2}^*(0)$ on the basis of Eqs. (3)–(5) using the measured values of T_c and setting $H_{c2}(0)$ equal to the value of $H_r(0)$ extrapolated to $T = 0$. For Nb–37 at.% Ti one obtains $H_{c2}^*(0) = 164$ kG, as compared with the experimental value of 111 ± 7 kG, while for Nb–56 at.% Ti the calculated value of $H_{c2}^*(0)$ turns out to be imaginary!

The temperature variation of $H_r(0)$ for Nb–56 at.% Ti also deviates from Maki's prediction. In Fig. 2 the temperature variation of H_{c2} predicted by Maki for $\alpha = 0$ and $\alpha^2 = 2$ is plotted. These curves are normalized in such a way that they pass through the value of $H_r(0)$ measured at the lowest temperature. A comparison of the experimental results with the theoretical fits would indicate that $0 < \alpha^2 < 2$. However, the value of α^2, as calculated from the flow-resistance value of $H_{c2}^*(0)$ and the measured value of T_c, is 2.6.

A further comparison with Maki's theory can be made by considering the temperature derivative $H_0 \equiv -(dH_{c2}/dt)_{t=1}$. According to the theory $H_{c2}^*(0)$ and $H_{c2}(0)$ are related to H_0 in the following way:

$$H_{c2}^*(0)/H_0 = 0.69, \qquad (6)$$

and

$$H_{c2}(0)/H_0 = 0.69(1+\alpha^2)^{-1/2}. \qquad (7)$$

The last two equations were derived for the case of a short electron mean free path. In the case of $\alpha = 0$ the calculations of Helfand and Werthamer indicate that the right-side of Eq. (6) increases only slightly ($\sim 5\%$) as the electron mean free path l increases from zero to infinity.[6] While the general case of arbitrary l and arbitrary α has not been treated theoretically thus far, the calculations for the case $\alpha = 0$ suggest that the ratios $H_{c2}^*(0)/H_0$ and $H_{c2}(0)/H_0$ do not depend strongly on l. Using Eq. (6) and substituting the measured value of $-[dH_r(0)/dt]_{t=1}$ for H_0 we obtain $H_{c2}^*(0) = 101 \pm 7$ kG for Nb–37 at.% Ti and $H_{c2}^*(0) = 157 \pm 11$ kG for Nb–56 at.% Ti. The value for Nb–37 at.% Ti is in fair agreement with the value of $H_{c2}^*(0)$ obtained from the flow-resistance measurements, but in the case of Nb–56 at.% Ti the flow-resistance value of $H_{c2}^*(0)$ is some 20% higher than the one obtained on the basis of Eq. (6). This difference in the value of $H_{c2}^*(0)$ for Nb–56 at.% Ti is outside the estimated experimental error. We believe that the flow-resistance values of $H_{c2}^*(0)$ are the more reliable ones since we have already noted deviations from Maki's theory. To test Eq. (7) we substitute the value of $H_r(0)$ at $T = 0$ for $H_{c2}(0)$, and $-[dH_r(0)/dt]_{t=1}$ for H_0. We then obtain: $H_{c2}(0)/H_0 = 0.66 \pm 0.05$ for Nb–37 at.% Ti and $H_{c2}(0)/H_0 = 0.62 \pm 0.04$ for Nb–56 at.% Ti. Note that the lower of these two ratios corresponds to the material with the higher value of α. This agrees qualitatively with Maki's prediction for the effect of the Pauli paramagnetism. On the other hand, both ratios are substantially higher than predicted by Eq. (7).

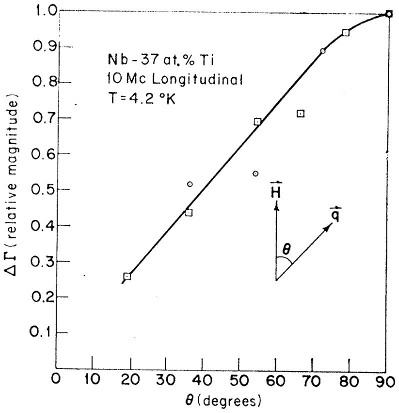

FIG. 7. The variation of the attenuation change $\Delta\Gamma$ (defined in Fig. 6) with the angle θ between the magnetic field and the direction of sound propagation.

B. Interpretation II: $H_{c2} = H_d$

In interpreting our data we have assumed, so far, that $H_{c2} = H_r(0)$. We now remove this assumption and assume instead that $H_{c2} = H_d$. At liquid-helium temperatures the ratio $H_d/H_r(0)$ was found to be constant for both alloys. Thus, aside from a scale factor, the temperature variation of H_d is (at least for $T \leq 4.2°\text{K}$) the same as that of $H_r(0)$. The same conclusions which were drawn from the temperature variation of $H_r(0)$, under the assumption $H_{c2} = H_r(0)$, can also be drawn therefore from the temperature variation of H_d under the assumption $H_{c2} = H_d$. By setting $H_{c2}(0)$ equal to the value of H_d extrapolated to $T = 0$, and by using the flow-resistance values of $H_{c2}^*(0)$ we obtain $H_{c2}(0)/H_{c2}^*(0) = 0.79 \pm 0.05$ for Nb–37 at.% Ti and $H_{c2}(0)/H_{c2}^*(0) = 0.65 \pm 0.03$ for Nb–56 at.% Ti. These values are smaller than the corresponding values obtained by assuming $H_{c2} = H_r(0)$. However, in the case of Nb–56 at.% Ti, the ratio $H_{c2}(0)/H_{c2}^*(0)$ is still larger than predicted by Eq. (5). For Nb–37 at.% Ti the ratio predicted by Eq. (5) is barely outside the experimental error. Thus, our data support the view that: (1) in both alloys the Pauli paramagnetism lowers the value of the upper critical field at $T=0$, (2) the paramagnetic effect in Nb–56 at.% Ti is smaller than predicted by Maki. It should be pointed out that for Nb–56 at.% Ti, the value of α is slightly larger than 1.47 so that the superconducting-to-normal transition at very low temperatures may be of first order.[5] This circumstance may account for some of the observed deviations from Maki's theory which assumes a second-order transition. However, in the case of Nb–37 at.% Ti, the value of α is certainly lower than 1.47 so that Maki's theory should be valid. Under the assumption $H_{c2}=H_d$ the data for Nb–37 at.% Ti are, in fact, in fair agreement with Maki's theory. This is not the case if one assumes $H_{c2}=H_r(0)$. Deviations from Maki's theory have been reported by Kim *et al.*,[2] who have studied the Ti-V alloy system. These authors have suggested that the discrepancy between theory and experiment may be due to the spin-orbit interaction, which tends to reduce the paramagnetic effect.[16]

C. Ultrasonic Attenuation

The physical origin of the changes in the ultrasonic absorption near the upper critical field is not understood at present. Nevertheless it is interesting to compare the present ultrasonic attenuation results with those obtained with 10-Mc/sec shear waves in Nb–25 at.% Zr.[11] In the latter case an ultrasonic absorption edge, rather than a dip in the attenuation coefficient, was found near the upper critical field H_{c2}. There is a similarity between the ultrasonic behavior and the resistive behavior at moderately high current densities in both niobium-zirconium and niobium-titanium alloys. In the Nb–25 at.% Zr sample no dip in the resistance can be observed at any current density.[17] Rather the resistance as a function of H always increases abruptly from zero to R_n at a field $H_r(J)$. In the niobium-titanium alloys, on the other hand, a dip in the resistance is observed at moderately high current densities. It is somewhat disconcerting, however, that in the niobium-titanium alloys H_u agrees with $H_r(0)$ rather than with H_d.

The ultrasonic technique enjoys one advantage over many other techniques, namely, it measures a bulk property. The close agreement between H_u and $H_r(0)$ suggests therefore that $H_r(0)$ represents a bulk property which is independent of surface effects. Further support for this inference is found in the agreement of the low current resistive measurements for $\mathbf{H}\|\mathbf{J}$ with those for $\mathbf{H}\perp\mathbf{J}$.

V. CONCLUSION

The temperature variation of the upper critical field and the flow-resistance measurements, reported in this paper, both support the view that the Pauli spin paramagnetism plays an important role in determining the upper critical field. The detailed comparison of the data with Maki's theory depends on whether one assumes $H_{c2}=H_r(0)$ or $H_{c2}=H_d$. Either assumption leads to the conclusion that this theory overestimates the effect of the Pauli paramagnetism in the case of Nb–56 at.% Ti. The same conclusion applies to Nb–37 at.% Ti if one assumes $H_{c2}=H_r(0)$. However, the data for Nb–37 at.% Ti are in fair agreement with the theoretical predictions if one assumes $H_{c2}=H_d$. In the case of Nb–56 at.% Ti the superconducting-to-normal transition at very low temperatures may be of first order, which could account for some of the discrepancies with Maki's theory. It is also possible that the discrepancy between theory and experiment is due to the presence of a spin-orbit interaction which tends to reduce the paramagnetic effect.

ACKNOWLEDGMENTS

The authors are grateful to S. H. Autler for kindly providing the samples, and to Y. B. Kim for a stimulating and informative discussion. We wish to thank S. Foner, E. J. McNiff, Jr., and S. J. Williamson for performing the magnetization experiments. The authors are also indebted to E. Helfand and D. B. Montgomery for several helpful discussions. The technical assistance of M. Kelly and B. Perry throughout the course of this work is greatly appreciated.

---

[16] K. Maki and T. Tsuneto, Progr. Theoret. Phys. (Kyoto) **31**, 945 (1964).

[17] L. J. Neuringer and Y. Shapira (to be published).