Thermal Conductivity of Superconducting Niobium*

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Thermal-conductivity measurements on niobium of intermediate purity ($l \simeq \xi_0$) were performed in the normal, superconducting, and mixed states. The lattice and electronic components of the conductivity in the superconducting state are separated. The critical temperature and the energy gap are found to be $T_c = (9 \pm 0.1°\text{K}$ and $2\epsilon(0) = 3.96kT_c$. The temperature dependence of the minimum in the thermal conductivity in the mixed state suggests a decrease in both the phonon and the electron conductivities just above H_{c1}. The comparative importance of each depends on a combination of temperature range and purity of the sample. The slope $\partial K_m/\partial H$ and upper-critical-field parameter $\kappa_1(t)$ are found to change with temperature much faster than predicted by relevant theories.

I. INTRODUCTION

THE purpose of this work is the study of the thermal conductivity of niobium in the normal (K_n), superconducting (K_s), and mixed states. The focus of the work is on the behavior of the thermal conductivity in the mixed state and its dependence on magnetic field and temperature.

Previous extensive work on the thermal conductivity of niobium is mainly that of Mendelssohn and coworkers.[1] Their data do not extend into the temperature region above 4.2°K—a shortcoming that leaves the upper half of the reduced temperature range unexplored —and their study of the influence of an applied magnetic field is lacking in interpretation for the reasons that the existence of a mixed state and the nature of niobium as an intrinsic type-II superconductor were not recognized at that time. It is on these two points that the present work intends to bring more complete results and interpretations. More recently, Lindenfeld *et al.*[2] reported mixed-state thermal conductivity measurements on pure and impure specimens of niobium at the Cleveland Conference, Lowell and Sousa[3] have published a mixed-state measurement for only one temperature, and Muto *et al.*[4] and Noto[4] have reported a more complete investigation of a scope similar to the present work.

Recent theoretical and experimental results were mainly concerned with the extreme limits of dirty ($l/\xi_0 \ll 1$) and pure ($l/\xi_0 \gg 1$) type-II superconductors, these limits depending on the relative magnitudes of the electronic mean free path l and the coherence length ξ_0. Formulas have been obtained for the upper critical field $H_{c2}(t)$ or the corresponding parameter $\kappa_1(t)$ by Gorkov[5] for the pure limit and by Maki[6] and de Gennes[7] for the dirty limit, while the general case was treated by Helfand and Werthamer[8] and by Eilenberger[9] in an effort to extend the results to all temperatures and impurity concentrations. Anisotropy of H_{c2} in cubic materials such as niobium was attributed by Hohenberg and Werthamer[10] to nonlocal corrections to the Ginzburg-Landau-Abrikosov-Gorkov (GLAG) theory, with the conclusion that for pure polycrystalline niobium, Eilenberger's curves represent only a lower limit for $H_{c2}(t)$ and $\kappa_1(t)$.

Detailed theoretical treatment of the thermal conductivity K_m in the mixed state, for the gapless region where the applied field is close to the upper critical field, is due to the work of Caroli and Cyrot[11] for the limit of dirty superconductors and of Maki[12] for the limit of pure type-II superconductors. This leaves the intermediate range still without a theory. There are also very few experimental results on superconductors of this intermediate category.[13] It is, therefore, notable that the samples studied here are in this intermediate range which makes the comparison of the results to existing theory and to measurements on purer niobium[4] interesting. Limited agreement is found with the dirty-limit theory[11] in the sense that linear behavior of $K_m(H)$ is found in the region close to H_{c2}, with a finite slope

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[4] Y. Muto, K. Noto, and T. Fukuroi, in *Proceedings of the Eleventh International Conference on Low-Temperature Physics*, edited by J. F. Allen *et al.* (University of St. Andrews Printing Department, St. Andrews, Scotland, 1969), Vol. 2, p. 930; Y. Muto, K. Noto, T. Mamiya, and T. Fukuroi, J. Phys. Soc. Japan **23**, 130 (1967); K. Noto, *ibid.* **26**, 710 (1969).

[5] L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **37**, 833 (1959) [English transl.: Soviet Phys.—JETP **10**, 593 (1960)].

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[7] P. G. Gennes, Physik Kondensierten Materie **3**, 79 (1965). See also C. Caroli, M. Cyrot, and P. G. de Gennes, Solid State Commun. **4**, 17 (1966).

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[10] P. C. Hohenberg and N. R. Werthamer, Phys. Rev. **153**, 493 (1967).

[11] C. Caroli and M. Cyrot, Physik Kondensierten Materie **4**, 285 (1965).

[12] K. Maki, Phys. Rev. **158**, 397 (1967).

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at H_{c2}, and the slope $\partial K_m/\partial H$ does go through a maximum as the temperature is varied. But experimental slopes have a much steeper variation with temperature, leading to values up to 10 times larger than expected from theory. The earlier treatment by Dubeck *et al.*[14] inserting in the results of Bardeen, Rickayzen, and Tewordt[15] (hereafter referred to as BRT) a field-dependent gap parameter, though it is open to serious objections[11] in the gapless region, is still found to be quite successful for the description of the minimum of K_m, but only at temperatures where phonon conduction is predominant ($K_{gs}>K_{es}$). A detailed comparison of the present work with the results of Ref. 4 reveals that a sudden decrease of the electronic conductivity K_{em}, upon entry in the mixed state, has to be postulated in addition to the decrease of the phonon conductivity K_{gm}.

In Sec. II we review briefly the techniques of measurements; Sec. III covers the results on thermal conductivity in (A) the superconducting and normal states and (B) the mixed state; and Sec. IV is the conclusion.

II. EXPERIMENTAL METHOD

The annealed sample was supplied by Materials Research Corporation[16] in the form of a plate $0.01\times3.0\times0.435$ in. from triple zone refined material (Marz grade). A typical analysis shows 170 ppm total impurities, of which 100 ppm of tantalum, 8 ppm of carbon, 6.4 ppm of tungsten, 23.4 ppm of nitrogen, and 4 ppm of oxygen are the largest contributions. The resistance ratio was found to be $\Gamma=R_{300}/R_N=29$, and the residual resistance ρ_0 was measured to be 5.2×10^{-7} Ω cm. This low value of the resistance ratio suggests high concentration of structural defects and incomplete annealing. From the measurement of $\rho_0=\sigma^{-1}$, the electronic mean free path l was estimated by using the relation $D=\sigma/2e^2N(0)=\frac{1}{3}V_F{}^2\tau$, where D is the diffusion constant. We get $l=V_F\tau=3\sigma/2e^2N(0)V_F$, where σ is the residual electrical conductivity, $N(0)$ is the density of states, and[17,18] $V_F=3\times10^7$ cm/sec is the Fermi velocity. $N(0)$ was calculated by using the relation $N(0)=3\gamma/\pi^2\kappa^2$, where $\gamma=7.85$ mJ/mole deg^2 is the electronic specific-heat constant. This yields a value of $l=328$ Å which is of the same order of magnitude as $\xi_0=390$ Å reported by French[17] and 430 Å by Finnemore, Stromberg, and Swenson[18] (hereafter referred to as FSS).

The main apparatus and measuring techniques were an evolved and extended form of those used in the earlier work of Grenier *et al.*,[19] and their description will be brief. The sample inside a vacuum calorimeter was clamped in a brass sample holder which itself was screwed into a copper post extending up into the liquid-helium bath. The temperature of the sample could be raised to 10°K with the brass sample holder acting as a thermal resistor between sample and heat sink. Two heaters of Constantan wire No. 40 were wound, one at the bottom of the sample and the other on the sample holder. The heater on the sample holder was used to raise the temperature of the sample in the range 4.2–10°K and also to drive the sample normal thermally after each field cycle to eliminate the trapped flux. The sample heater was used to establish a thermal gradient along the sample for the heat-conductivity measurements. The thermal gradient along the sample varied from 20 m°K at the lowest temperature to about 100 m°K at the highest temperature. A "well-matched" pair of 50-Ω $\frac{1}{10}$-W Allen-Bradley carbon resistors was used for thermal-conductivity measurements, and the thermometers were calibrated against the vapor pressure of liquid helium in the temperature range of 1.4–4.2°K and against a calibrated germanium thermometer[20] in the range 4.2–10°K. The temperature measuring circuit was in the form of a bridge, two arms of which were carbon thermometers, and a difference of temperature would result in an unbalance voltage in the measuring arm of the bridge. All measurements were done with dc methods. The circuit was designed so that the voltage and current of each thermometer could also be measured separately. Current in the thermometers was varied from 4 μA at $T<4$°K to about 10 μA at higher temperatures. At each temperature T the bridge was balanced by adjusting the current in the two thermometers so that to a zero heat current in the absence of the magnetic field there corresponded a zero signal on the recorder. The temperature of the bath was then lowered to $T-\Delta T_0$ where ΔT_0 ranged from around 150 m°K at higher temperature to about 30 m°K at the lower temperature. The sample heater was then switched on, and the heat current was adjusted so that the thermometer closest to the sample heater read the same voltage as at T. This procedure has the advantage that the temperature difference ΔT can be computed from the unbalance voltage ΔV through the use of the characteristic $R(T)$ curve of only one thermometer, in this case the one closest to the heat sink. Measurements over a period of months showed that the slopes $\Delta T_0/\Delta R$ were reproducible within 4%. For this reason, we plotted $\Delta T_0/\Delta R$ against T on a semilog paper and used the values from the smoothed-out curve. Point-by-point measurements of K_m were made in the same way as those of K_s at increasing values of

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[15] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959).
[16] Materials Research Corp., Orangeburg, N. Y.
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[20] Texas Instruments Inc., Dallas, Tex.

TABLE I. Temperature dependence of thermal-conductivity parameters. K is in mW cm^{-1} °K^{-1}; H_{c2} is in G.

T	t	K_s	K_{gs}	K_{es}	H_{c2}	κ_1	$[K_{\min}]_{\text{expt}}$	$[K_{\min}]_{\text{calc}}$	$K_{\min}/K_s$
9.0	1.0	423		423		1.14	...	...	...
8.4	0.933	374		380.0	421.0	1.209	...	...	...
8	0.888	341		342.5	765.4	1.348	...	...	...
7.3	0.811	286.5		286.54	1238.4	1.344	285.0	...	0.994
6.8	0.755	247.0	4.0	242.94	1548.0	1.337	244.0	...	0.987
6	0.666	180.0	2.87	177.13	2253.2	1.504	174.0	...	0.972
5.45	0.605	146.0	13.0	133.0	2597.2	1.521	142.0	...	0.965
4.47	0.497	95.0	24.0	71.0	3250.8	1.603	88.0	...	0.916
4.1	0.455	78.0	27.89	50.11	3474.4	1.627	71.0	...	0.916
3.09	0.343	70.0	55.72	14.28	3930.2	1.643	37.0	52.0	0.528
1.95	0.216	122.0	122.0		4420.4	1.722	14.5	14.0	0.118

magnetic field until it was found that K was constant at $H>H_{c2}$.

It was observed that at temperatures above 3.5°K carbon resistors had considerable magnetoresistance. This was measured by balancing the thermometers at the temperature T and then recording the signal ΔV as a function of the applied magnetic field without setting the thermal gradient across the sample. This signal was added or subtracted from the conductivity signal depending on whether the magnetoresistance was negative or positive. All measurements were made with the direction of the magnetic field parallel to the large face of the sample in order to minimize demagnetization effects.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Thermal Conductivity in Superconducting and Normal States

The temperature dependence of the thermal conductivity of niobium in the superconducting state K_s and in the normal state K_n is plotted in Fig. 1 and partly tabulated in Table I. The temperature at which the K_s and K_n curves intersect one another is taken as the critical temperature T_c and is found to be 9.0±0.1°K.

The straight line which very nearly fits the normal-state points is obtained from the residual resistance ρ_0 by assuming the validity of the Wiedemann-Franz relation $K_n=L_0T/\rho_0$ ($\rho_0=5.2\times10^{-7}$ Ω cm, $K_n=47.01T$ mW cm^{-1} °K^{-1}). A slight tendency of the experimental points to fall below the Lorentz line at temperatures close to T_c seems genuine and corroborates the results obtained by Muto *et al.*[4] and can be attributed to the existence of a small resistive component due to scattering of electrons by phonons. In the major remaining part of the temperature range, the nearly exact fit of the experimental points to the Lorentz relation indicates that scattering of electrons by impurities is predominant in the normal state.

In the superconducting state, the presence of a local maximum in K_s, already observed by Calverley, Mendelssohn, and Rowell[1] and Connolly and Mendelssohn[1] (hereafter referred to as CM) in niobium, tantalum, and vanadium, and by Sharma[21] in tantalum, is recognized as being due to the lattice contribution to the thermal conductivity which becomes prominent as the electronic contribution becomes smaller with decreasing temperature and scattering of the phonons by the conduction electrons in the superconducting state decreases.

The conductivity in the superconducting state can be divided into three temperature regions. The results indicate that between T_c and 3.5°K electron conduction is dominant; between 3.5 and 2°K it is mostly due to phonons scattered by electrons; and below 2°K the heat conduction can be assumed to be due to phonons scattered by imperfections and boundaries, as was demonstrated by the measurements of CM below 1°K.

The temperatures at which the local minimum and maximum in K_s occur, 3.5 and 2°K, respectively, are in fortuitous agreement with the results found by CM. In the recent measurements of K_s by Muto *et al.*[4] on a niobium specimen with resistance ratio of 1900, it is interesting to note the apparent absence of any significant phonon contribution at lower temperatures, as shown by the smallness of the local maximum in their results. A possible explanation is that as the purity

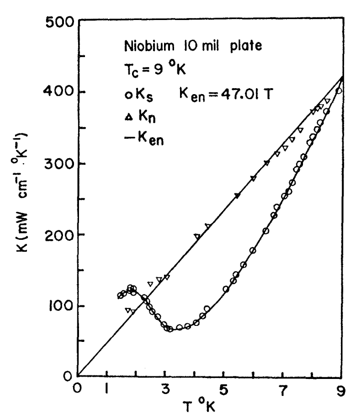

FIG. 1. Thermal conductivity of niobium in the normal and the superconducting states. The straight solid line is obtained from the residual electrical resistivity ρ_0 through the Wiedemann-Franz law $K_{en}=L_0T/\rho_0$.

[21] J. K. N. Sharma, Cryogenics 7, 195 (1967).

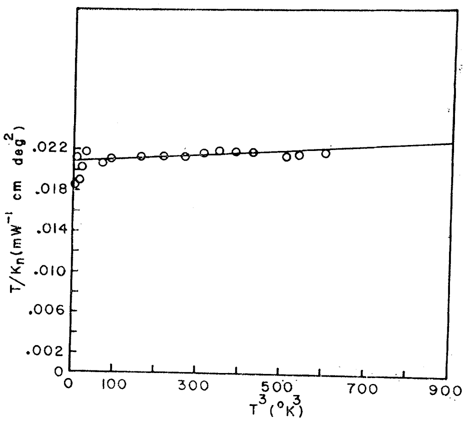

FIG. 2. Plot of T/K_n versus T^3. A straight-line fit determines the coefficients a and b in $1/K_{en}=aT^2+b/T$.

increases, the electron contribution K_{es} to the conductivity, which is limited by impurity scattering, increases accordingly, while the phonon contribution K_{gs} which is limited by electron scattering stays unchanged to a first approximation. As a result, the increase of K_{gs} with decreasing temperatures becomes comparatively less important and the associated local maximum tends to flatten out.

Analysis of the normal-state conductivity in terms of the different scattering mechanisms is made by using the formula given by Makinson[22] for a free-electron model. The electronic thermal conductivity K_{en} at temperatures $T<\frac{1}{10}\Theta$ (Θ is the Debye temperature) is given by

$$1/K_{en}=aT^2+b/T, \quad (1)$$

where $a=95.3\ N_a^{2/3}/K_\infty\Theta^2$ and $b=\rho_0/L_0$. N_a is defined as the effective number of conduction electrons per atom, K_∞ is the limiting value of the electronic thermal conductivity at high temperature, ρ_0 is the residual electrical resistivity, and L_0 is the Lorentz number. The first term on the right in Eq. (1) represents the electronic thermal resistivity limited by phonon scattering, and the second term represents the electronic thermal resistivity due to impurity scattering. Figure 2 gives a plot of T/K_n against T^3, which within the experimental scatter has been approximated by a straight line. The slope of the straight line gives the value of the constant $a=2.3\times10^{-6}$ cm mW^{-1} °K^{-1}. The intercept on the T/K_n axis gives $b=20.8\times10^{-3}$ cm °K^2 mW^{-1} which differs by 2% from the result obtained from the residual resistivity measurements. These values of a and b indicate that for temperatures very close to T_c, the contribution of phonon scattering to the resistivity is at most 8% of the total thermal resistivity. The experimentally determined value of a, using[23] $\Theta=275$°K and[24] $K_\infty=580$ mW cm^{-1} °K^{-1}, indicates an effective number of conduction electrons per atom $N_a=1.0891$; but if one uses the value $\Theta=241$°K found[23] in the temperature range 3–10°K, then $N_a=0.733$ is obtained. We do not find any phonon conductivity in the normal state, as seen in Fig. 1. The preponderance of impurity scattering for both K_s and K_n allows us to make a direct comparison of the temperature dependence of K_s/K_n to the theory of BRT. The BRT relation for the case of elastic impurity scattering of electrons is[15]

$$K_{es}/K_{en}=2F_1(-y)+2y\ln(1+e^{-y}) +y^2(1+e^y)^{-1}/2F_1(0), \quad (2)$$

where $y=\epsilon(t)/kT=[\epsilon(t)/\epsilon(0)][\epsilon(0)/kT_c](1/t)$, $\epsilon(t)$ being the half-width of the energy gap at temperature T in the Bardeen, Cooper, and Schrieffer[25] theory (hereafter referred to as BCS). The temperature dependence of $\epsilon(t)/\epsilon(0)$ has been calculated by Mühlschlegel[26] based on the BCS theory, and from this a temperature dependence of y has been calculated for different values of $\epsilon(0)/kT_c$. The term $F_1(-y)$ is given by the expression

$$F_n(-y)=\int_0^\infty \frac{z^n dz}{(1+e^{z+y})}.$$

$F_1(-y)$ has been tabulated by Rhodes[27] for $-y$ from 0 to 4 and has been extrapolated in the present work to higher values. In Fig. 3 we have plotted the experi-

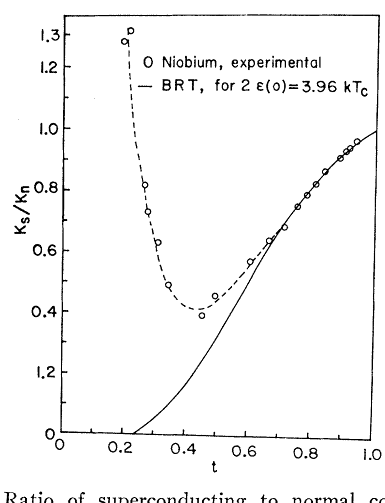

FIG. 3. Ratio of superconducting to normal conductivities versus reduced temperature. The solid line is the theoretical BRT ratio for $2\epsilon(0)=3.96\ kT_c$.

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[27] P. Rhodes, Proc. Roy. Soc. (London) **A204**, 396 (1950).

TABLE II. Comparison of experimental results on the energy gap in Nb.

Authors	Technique used	$2\epsilon(0)/KT_c$
Present work	Thermal conductivity	3.96
Connolly and Mendelssohn[a]	Thermal conductivity	3.5
Muto *et al.*[b]	Thermal conductivity	3.80
Goodman[c]	Specific heat	3.7–4.0
Leupold and Boorse[d]	Specific heat	3.69
Da Silva *et al.*[e]	Specific heat	3.72
Van Der Hoeven and Keesom[f]	Specific heat	3.70
French[g]	Magnetization	3.62
Perz and Dobbs[h]	Ultrasonic attenuation	3.75
Levy *et al.*[i]	Ultrasonic attenuation	3.5
Townsend and Sutton[j]	Tunneling (Nb/Sn)	3.84
Gaiever[k]	Tunneling (Nb/Sn)	3.6
Sherrill and Edwards[l]	Tunneling (Nb/Pb)	3.59
Bonnet *et al.*[m]	Tunneling (Nb/Sn)	2.8
Richards and Tinkham[n]	Infrared absorption	2.8

[a] See Ref. 1.
[b] See Ref. 4.
[c] B. B. Goodman, Compt. Rend. **246**, 3031 (1958).
[d] See Ref. 34.
[e] See Ref. 35.
[f] See Ref. 23.
[g] See Ref. 17.
[h] E. R. Dobbs and J. M. Perz, Proc. Roy. Soc. (London) **A296**, 113 (1967).
[i] M. Levy, R. Kagiwada, and I. Rudnick, Phys. Rev. **132**, 2039 (1963).
[j] P. Townsend and J. Sutton, Phys. Rev. **128**, 591 (1962).
[k] J. Gaiever, in *Proceedings of the Eighth International Conference on Low Temperature Physics*, edited by R. Davies, (Butterworth Publishing Co., London, 1962).
[l] M. D. Sherrill and H. H. Edwards, Phys. Rev. Letters **6**, 460 (1961).
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[n] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).

mental values of K_s/K_n against the reduced temperature. We find a good fit of the upper range to the BRT expression for $2\epsilon(0)=3.96\ kT_c$ as represented by the solid line in Fig. 3. This value of the energy gap at absolute zero obtained for our sample has been compared with previous results, and these are shown in Table II. A comparison between K_s/K_n and the BRT expression for $2\epsilon(0)=3.96\ kT_c$ shows that there is an agreement from $t=1.0$ to $t=0.65$. This confirms that at higher temperatures the contribution of phonon conductivity in the superconducting state is negligible. Below $t=0.65$, the experimental curve K_s/K_n departs

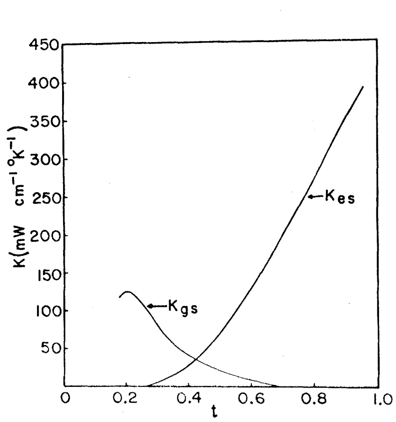

FIG. 4. Separated lattice K_{gs} and electronic K_{es} components of the thermal conductivity in the superconducting state versus reduced temperature.

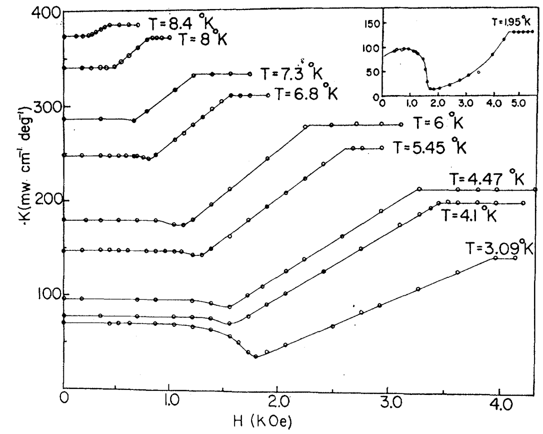

FIG. 5. Thermal conductivity in the mixed state K_m versus the applied magnetic field strength H, at different temperatures. The insert shows K_m at the lowest temperature investigated.

from the theoretical curve K_{es}/K_{en} because of the increasing contribution of the phonon conductivity.

The electronic thermal conductivity in the superconducting state K_{es} has been calculated from Eq. (2) with the energy gap $2\epsilon(0)=3.96\ kT_c$ by substituting for K_{en} the value obtained from the residual resistivity using the Wiedemann-Franz law. The phonon conductivity K_{gs} in the superconducting state has been obtained by subtracting the electronic component K_{es}, as obtained from BRT theory, from the total thermal conductivity K_s. This has been plotted against the reduced temperature in Fig. 4 along with K_{es} and tabulated in Table I. As explained earlier, it shows that K_{gs} is maximum at $t=0.22(T=2°K)$. It decreases with increasing temperature, and at $t=0.65$ it represents less than 4% of K_s. BRT have pointed out that in the temperature region $t=0.4$ to $t=0.6$, the ratio K_{gs}/K_{gn} may be proportional to T^{-5}. This has been observed by Laredo.[28] Experimentally it has been found by Sladek[29] that K_{gs}/K_{gn} is proportional to T^{-n} where $3<n<6$. Assuming K_{gn} to be proportional to T^2 implies that, from BRT's theory, K_{gs} should be proportional to T^{-3}. We find that between $t=0.3$ to $t=0.55$, K_{gs} is proportional to $T^{-(2.4\pm0.1)}$ which appears to be significantly different from the theory but falls within limits that corroborate Sladek's results.

B. Mixed-State Conductivity

1. *Minimum of K_m in the Mixed State*

The thermal conductivity of niobium as a function of the applied field has been measured from $T=8.64$ to $T=1.95°K$, and representative results are shown in Fig. 5. For all temperatures above and excluding $T=1.95°K$, it is found that the thermal conductivity remains constant up to the lower critical field H_{c1}. A

[28] S. J. Laredo, Proc. Roy. Soc. (London) **A229**, 473 (1955).
[29] R. J. Sladek, Phys. Rev. **97**, 910 (1955).

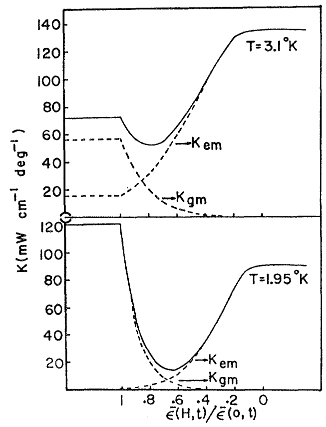

FIG. 6. Lattice and electronic components of the mixed-state conductivity, and their sum, versus the reduced field-dependent energy gap according to the "effective-gap approximation" of Ref. 14.

decrease in the conductivity occurs at H_{c1}, where the magnetic field starts penetrating the sample. This decrease reaches a minimum at fields slightly above H_{c1}, then starts increasingly slowly until it attains a constant value at the upper critical field H_{c2}. The depth of the minimum as well as the sharpness of the drop become more pronounced as the temperature is lowered. Similar behavior in the mixed state has also been observed on In-Tl alloys by Sladek,[29] on In+3% Bi alloys by Dubeck *et al.*,[14] on $Nb_{0.8}Mo_{0.2}$ alloy and pure niobium by Lowell and Sousa,[3] on pure niobium by Muto *et al.*[4] and Noto,[4] and on Pb-In alloys by Muto *et al.*[30] and Mamiya.[30]

The existence of a minimum of the thermal conductivity in the mixed state is generally explained, on the basis of the mechanism proposed in the "effective-gap approximation,"[14] as the result of the decrease of the lattice conductivity K_{gm} concomitant with the increase of the electronic conductivity K_{em} as the applied magnetic field is increased from H_{c1} to H_{c2}. Representative curves, calculated on the basis of this approximation—introducing a reduced field-dependent energy gap $\epsilon(H,t)/\epsilon(0,t)$ and using the tables given by Lindenfeld and Rohrer[31]—are shown in Fig. 6, and predicted values of the minimum are listed in Table I together with the corresponding experimental values. One notes that the existence of a minimum, in this model, depends on the algebraic sum of the slopes of the monotonic field-dependent curves $K_{gm}(H)$ and $K_{em}(H)$. Table I shows that the value of the minimum calculated in this approximation agrees fairly well with experiment for lower temperatures where phonon conductivity is preponderant. For increasing temperatures, a minimum is still found experimentally where the calculated value is zero. This persistence of the minimum is not trivial, as explained below.

The comparison of our results with those of Muto *et al.*[4] and Noto[4] leads to a fundamental remark: The data of Ref. 4, concerning the minimum of the thermal conductivity in the mixed state, cannot be explained by a decrease of the phonon contribution as has been done above. The reason is that, from the data,[4] it is clear that the phonon contribution K_{gs}, even at its maximum value, is much smaller than the decrease in conductivity $(K_s-K_{\min})$ observed at all temperatures above $t=T/T_c=0.365$. It is, therefore, imperative to postulate that the decrease $(K_s-K_{\min})$ is due, at least in part, to a decrease in the electronic contribution K_{em} upon entry in the mixed state, a possibility mentioned recently by other authors.[32] Possibly a scattering of the electrons by the Abrikosov flux lines can be conjectured, which the comparison between the average flux-line separation ($\sim 0.1\ \mu$) and electron mean free path in the sample of Ref. 4 ($\sim 1\ \mu$) does not rule out. With the postulated decrease in K_{em}, one can write $K_m=K_{gm}+K_{em}=K_{gm}+(W_{ei}+W_{ef})^{-1}$, where W_{ei} is a thermal-resistivity term due to the scattering of uncondensed electrons by impurities and possibly phonons, and W_{ef} is a resistive term due to scattering of these electrons by the flux lines. The term W_{ei} decreases smoothly as the field is increased from H_{c1} to H_{c2}, while W_{ef} would increase, go through a maximum $(W_{ef})_{\max}$ and decrease back to zero at H_{c2}. One can distinguish three possible experimental situations: (1) The impurity scattering is very large, $W_{ei}\gg(W_{ef})_{\max}$, which would be the case of alloys,[14] and the minimum is then fairly accounted for by the drop in K_{gm} as in the effective-gap approximation[14];

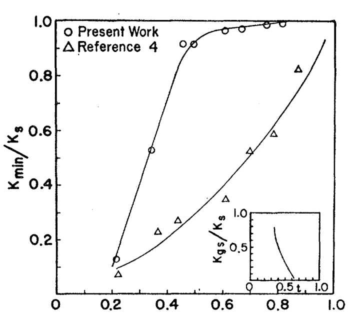

FIG. 7. Ratio of the thermal conductivity at the minimum in the mixed state $K_{\min}$ to the conductivity in the superconducting state versus reduced temperature for both this work and the work of Ref. 4. The insert shows the rapid decrease of K_{gs}/K_s versus temperature observed in the present work.

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[32] E. M. Forgan, C. E. Gough, J. M. Hood, and W. F. Vinen, in *Proceedings of the Eleventh International Conference on Low-Temperature Physics*, edited by J. F. Allen *et al.* (University of St. Andrews Printing Department, St. Andrews, Scotland, 1968), Vol. 2, p. 934; E. Umlauf, Z. Physik **206**, 415 (1967).

(2) the impurity scattering is very small, $W_{ei} \ll (W_{ef})_{\max}$ and $K_{em} \gg K_{gm}$, which would be the case of very pure intrinsic type-II samples, like the pure niobium of Ref. 4; the minimum is then due to the field dependence of W_{ef}; (3) the impurity scattering is of intermediate strength and $W_{ei} \sim (W_{ef})_{\max}$. We believe this third case to correspond to the results of the present work, and the origin of the minimum may then depend on the temperature range. At low temperatures where $K_{gs} > K_{es}$, the minimum is mostly due to the drop in the phonon conductivity, and good agreement is found with the effective gap calculations. At higher temperatures, $K_{gs} < K_{es}$, the influence of a drop in K_{gs} becomes negligible, but a minimum might still appear because of the influence of the variation in W_{ef}. Table I shows evidence of this transitional behavior since one can see that the minimum at temperature $t > 0.5$ is unaccounted for by the effective-gap approximation. In Fig. 7, we have plotted $K_{\min}/K_s$ for our data and that of Ref. 4; the presence of two distinct regions above and below $t = 0.5$ is characteristic of our results, and we conjecture that below $t = 0.5$ the influence of the decrease in the phonon conductivity is predominant, while above this temperature it is the variation of the electronic conductivity which becomes responsible for the mixed-state behavior. The insert in Fig. 7 shows the steep decrease of K_{gs}/K_s as the temperature is raised from below to above $t = 0.5$.

This suggested scattering of the electrons by the flux lines deserves, in our opinion, some further investigation.

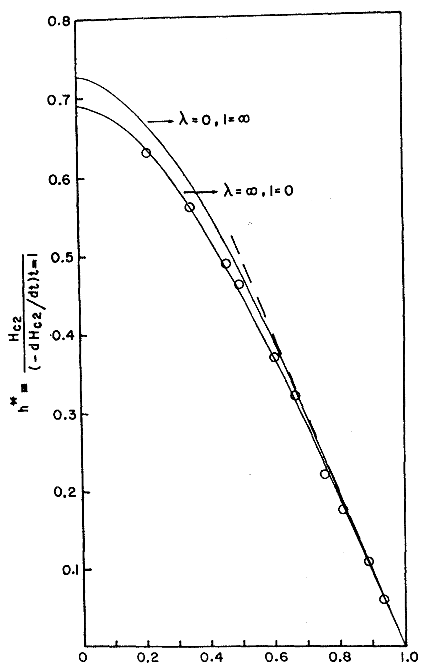

FIG. 8. Normalized upper critical field $h^* = H_{c2}[(dH_{c2}/dt)_{t=1}]^{-1}$ of Ref. 8 versus reduced temperature. The pure and dirty limits are shown together with the experimental values observed in the present work.

2. *Temperature Dependence of $H_{c2}(t)$ and $\kappa_1(t)$*

A theoretical study of the temperature dependence of the upper critical field has been made by Gorkov,[5] who has calculated a lower bound to H_{c2} at $T = 0$ for pure specimens and has proposed a simple interpolating polynomial for $H_{c2}(T)$ to link his $T = 0$ point with known results at higher temperatures. Maki[6] and de Gennes[7] have calculated the temperature dependence of $H_{c2}(t)$ and the corresponding ratio of the parameter $\kappa_1(t)/\kappa_1(1)$ for dirty specimen where $\kappa_1(t) = H_{c2}(t)/\sqrt{2}H_c(t)$. Helfand and Werthamer[8] have solved exactly the eigenvalue equation for $H_{c2}(t)$ for all temperatures and for all concentrations of the impurities. They have defined a parameter $h^* \equiv H_{c2}(t)/[-dH_{c2}(t)/dt]t = 1$ and have shown its temperature dependence for pure and dirty limits. This parameter has the advantage of being independent of any assumed temperature dependence for $H_c(t)$. In Fig. 8 we have plotted h^* against the reduced temperature t along with Helfand and Werthamer's theoretical results for pure and dirty superconductors. We find that our results agree more with the dirty limit in the plot, although, considering that the present sample has $l \simeq \xi_0$, we should expect the experimental points to fall closer to the pure-limit curve. This type of discrepancy using the h^*-versus-t plot has also been reported recently on Pb-In alloys by Dubeck, Aston, and Rothwarf,[33] who find that their results on a 28-at. % In-alloy sample falls closer to the pure limit than their 1.5-at.% In alloy, which falls closer to the dirty limit.

To find $\kappa_1(t)$ we need the thermodynamic critical field H_c. In the absence of magnetization measurements we have caclulated $H_c(0)$ by using the BCS relation $H_c(0) = \sqrt{2}\gamma^{1/2}T_c$, which connects $H_c(0)$ with the electronic specific-heat constant γ and the critical temperature T_c. The published values[23,34–38] of γ range from 7.50 to 7.85 mJ/mole deg^2. Using $\gamma = 7.85$ mJ/mole deg^2 and $T_c = 9.0$°K, we find $H_c(0) = 1940$ Oe. Assuming a parabolic temperature dependence, we have calculated $H_c(t)$, which has been used to calculate $\kappa_1(t) = H_{c2}(t)/\sqrt{2}H_c(t)$, where $H_{c2}(t)$ is the experimentally determined value of the upper critical field from thermal-conductivity measurements in the mixed state. Ohtsuka[39] has also followed this method to calculate $H_c(t)$ and

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[39] T. Ohtsuka, Phys. Letters **17**, 194 (1965).

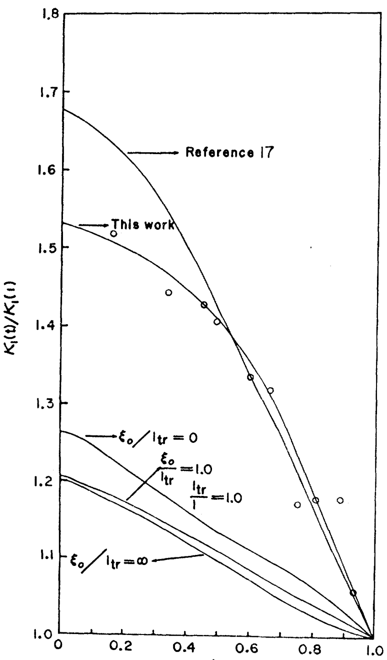

FIG. 9. Temperature dependence of the reduced upper critical field parameter $\kappa_1(t)/\kappa_1(1)$ for the dirty, intermediate, and pure limits. $\kappa_1(1)$ is 1.14. The points are our experimental results, and the experimental curve of Ref. 17 is also shown for comparison.

$\kappa_1(t)$ from the magnetocaloric measurements. The parabolic temperature dependence assumed for $H_c(t)$ has been recently confirmed by the magnetization measurements of French[17] and does not, as a consequence, introduce a source of error.

The extrapolated value of $\kappa_1(t)$ at $t=1$ is found to be $\kappa_1(1)=1.14\pm0.03$. This value is surprisingly large when compared to French's[17] $\kappa_1(1)=0.83$ for instance, but one can show that this reflects only the short electronic mean free path in the present sample. Theory requires that $\kappa_1(1)=\kappa(1)$ at $t=1$ where $\kappa(t)$ is the Ginzburg-Landau parameter connected to the weak-field penetration depth λ_0 and the thermodynamic critical field H_c by $\kappa(t)=2\sqrt{2}eH_c(t)\lambda_0^2/\hbar c$. Goodman[40] has extended Gorkov's theory and has shown that $\kappa(1)$ can be separated into two components, $\kappa(1)=\kappa_0+\kappa_l$. κ_0 is a constant characteristic of the pure metal, and κ_l is dependent on the electronic mean free path given by the relation $\kappa_l=7.53\times10^3\rho_0\gamma^{1/2}$, where γ is the specific-heat constant and ρ_0 is the normal-state resistivity in Ω cm. Using $\rho_0=5.2\times10^{-7}$ Ω cm and $\gamma=7.162\times10^3$ erg/cm^3 deg^2, we find $\kappa_l=0.331$ and $\kappa_0=0.81\pm0.03$. This value of κ_0 agrees very well with the value 0.815 reported by French[17] from magnetization measurements and is comparable to 0.87 by Rosenblum *et al.*[41] from resistivity measurements and 0.78 by FSS also from magnetization measurements. It is, therefore, the component κ_l, depending on the mean free path, which is responsible for the large value $\kappa_1(1)=1.14\pm0.03$ found here. Though it is large when compared to 0.78 by FSS, 0.83 by French,[17] 0.85 by McConville and Serin,[42] and 0.92 by Ikushima *et al.*,[43] in much purer samples ($\Gamma>500$) it is smaller than the value 2.37 found by Da Silva *et al.*[35] for an impure sample ($\Gamma=7$).

The ratio $\kappa_1(t)/\kappa_1(1)$ has been plotted in Fig. 9 along with the theoretical results of Eilenberger[9] for the pure case ($\xi_0/l_{tr}=0$, $l_{tr}=l$) and for the intermediate case ($\xi_0/l_{tr}=1$, $l_{tr}=l$). Theoretical results of Maki[6] for dirty alloys ($\xi_0/l=\infty$) and the experimental results of French[17] are also shown in the same figure. We find that as observed earlier,[17,18,39,42,43] $\kappa_1(t)/\kappa_1(1)$ increases with decreasing temperature at a much faster rate than the theory predicts. It is interesting to note that our results agree with McConville and Serin[42] on pure niobium ($\Gamma=500$). Since their curve is indistinguishable from this work, it has not been shown separately, to avoid confusion. The extrapolated value of $\kappa_1(t)/\kappa_1(1)$ at $t=0$ is found to be 1.53, which agrees with Ref. 42 but is 20% higher than the theory for the pure sample and 10% smaller than the experimental result[17] on one of the purest samples investigated so far. However, it is higher by 6% when compared to the results of Da Silva *et al.*[35] on less pure samples ($\Gamma=7$). It appears, therefore, that the experimental values of $\kappa_1(0)/\kappa_1(1)$ found for niobium cover a range which reflects the comparative purity of the samples, but all values are larger than expected from theory.

This systematic discrepancy may be related to the results obtained by Hohenberg and Werthamer.[10] They have shown that for cubic crystals like niobium the anisotropy in H_{c2} arises from the nonlocal corrections to the GLAG theory which would give a nonspherical Fermi-surface condition and not from the anisotropy of the normal-metal Fermi surface itself. From the calculation, they have shown that the anisotropy depends on the impurity and temperature; the anisotropy being higher for low t and high l, and that Eilenberger's[9] theory represents a lower limit for $H_{c2}(t)$ and $\kappa_1(t)$. Although the expression cannot be evaluated directly, it is expected that $\kappa_1(0)/\kappa_1(1)$ will be higher than 1.26 for pure specimens, but for our sample of intermediate purity the value of 1.53 might be too high to be explained on these grounds.

3. *Slope of K_m for H Close to H_{c2}*

Caroli and Cyrot[11] have predicted that for a dirty type-II superconductor ($l\ll\xi_0$) the electronic thermal conductivity in the mixed state is proportional to $H_{c2}-H$ near the upper critical field H_{c2}, which is the gapless region, and that the ratio of the slope of the

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thermal conductivity to the slope of the magnetization near H_{c2} is a universal function of temperature. For our sample which has $l\simeq\xi_0$, we find that $K_m\propto H_{c2}-H$ not only near H_{c2} but also over a wide range of the mixed state. This has also been observed by Lowell and Sousa[3] on $Nb_{0.08}MO_{0.2}$ alloys, by Lowell and Mendelssohn[44] on Nb-Ta alloys, and by Lindenfeld *et al.*[45] on In-Bi alloys. Maki[12] has shown that for a pure type-II superconductor ($l\gg\xi_0$) the thermal conductivity in the mixed state near the upper critical field H_{c2} is proportional to $(H_{c2}-H)^{1/2}$. We do not find any such field dependence of the conductivity, but it has been observed for pure niobium samples by Lowell and Sousa[3] and by Muto *et al.*[4] In the case of a sample of intermediate purity ($l\sim\xi_0$) like the one investigated here, it is interesting to note that we have unambiguous agreement with the constant-slope behavior predicted by the dirty-limit theory of Ref. 11 (see Fig. 5), but large discrepancies appear when a quantitative comparison is made of the temperature dependence of the slope $\partial K_m/\partial H$. Caroli and Cyrot's results[11] give

$$\left(\frac{dK_s}{dH}\Big/\frac{dM}{dH}\right)_{H=H_{c2}}=-\frac{2\pi ck_B}{e}\times\frac{x[\psi^{(1)}(\frac{1}{2}+x)+x\psi^{(2)}(\frac{1}{2}+x)]}{\psi^{(1)}(\frac{1}{2}+x)},\qquad(3)$$

where the slope of the magnetization dM/dH near H_{c2} is given by Abrikosov's theory[46] as

$$-4\pi dM/dH=1/1.16(2\kappa_2^2-1).\qquad(4)$$

The parameter x is related to the electron-pair lifetime τ_K by the relation $x=[4\pi k_BT\tau_K]^{-1}$ and is defined by

$$\ln T/T_c=\psi(\tfrac{1}{2})-\psi(x+\tfrac{1}{2}),\qquad(5)$$

where $\psi(x)$ is the digamma function, and $\psi^{(1)}(x)$ and $\psi^{(2)}(x)$ are defined by

$$\psi^{(1)}(x)=\sum_{n=0}^{\infty}\frac{1}{(n+x)^2}\qquad(6)$$

and

$$\psi^{(2)}(x)=-2\sum_{n=0}^{\infty}\frac{1}{(n+x)^3}.\qquad(7)$$

From Eq. (5) x has been calculated[47] and the right-hand side of Eq. (3) has been evaluated. To make a quantitative comparison of our experimental slopes with the theory, we have substituted our experimentally determined $\kappa_1(t)$ in place of $\kappa_2(t)$ in Eq. (4). This leads to a calculated value of dM/dH which is an upper limit of the actual value since it has been shown by Maki and Suzuki,[48] Eilenberger,[9] and Caroli, Cyrot, and de Gennes[7] that for any temperature t, $\kappa_2(t)\geq\kappa_1(t)$. This inequality was first observed by McConville and Serin[42] and later confirmed by FSS and French[17] in pure niobium, and the equality in alloys has also been observed by McConville and Serin[42] and later confirmed by Bon Mardion *et al.*[49]

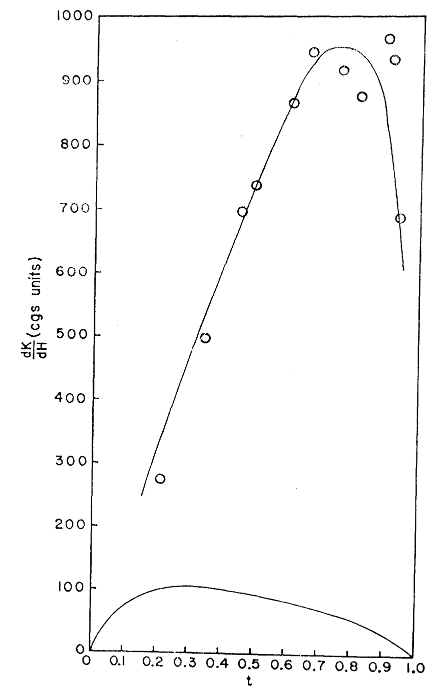

FIG. 10. Temperature dependence of the slope of the thermal conductivity in the mixed state, for $H\rightarrow H_{c2}$. The lower curve is calculated from the theory of Ref. 11. The points and upper curve are determined experimentally in the present work.

The upper limit for the theoretical value of dK/dH obtained in this manner and our experimental results are both plotted in Fig. 10 against the reduced temperature t. The theoretical results show a maximum at $t=0.3$, whereas the experimental results show a maximum at $t=0.75$. Also the magnitude of the observed maximum of dK/dH is about ten times higher than the theoretical prediction. This disagreement has been noted by Lowell and Mendelssohn[44] on Ta-Nb alloys. The Rutgers group[2] has also reported at the Cleveland Conference on Superconductivity that for their impure niobium sample the disagreement between the theory

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and experiment was about 30%, while for pure niobium the experimental result was higher by a factor of 40 as compared to the theoretical value. One can, therefore, conclude that the experimental evidence on intrinsic type-II superconductors, for samples which show a constant slope in the mixed state, points to larger values of dK/dH than expected from theory and to a steeper variation with temperature.

IV. CONCLUSION

The present study indicates that the mixed-state properties of the thermal conductivity K_m, in a niobium sample of intermediate purity ($l/\xi_0 \simeq 1$), are still in qualitative agreement with the dirty-limit ($l/\xi_0 \ll 1$) theory of Caroli and Cyrot[11] inasmuch as K_m increases linearly as H approaches H_{c2}. This linear behavior extends over an appreciable range of the mixed state. The slope $\partial K_m/\partial H$ varies with temperature much faster than predicted by theory, and this behavior seems characteristic of samples departing from the extreme dirty limit.

The parameter $\kappa_1(t) = H_{c2}(t)/\sqrt{2}H_c(t)$ is found, in agreement with other investigators, to increase with decreasing temperature much faster than expected from theory.

The temperature dependence of the minimum in the mixed state is thought to imply—in addition to the monotonic decrease of K_{gm} with increasing magnetic field—a nonmonotonic variation of K_{es}, viz., a decrease of the electronic conductivity upon entry in the mixed state followed by an increase as H approaches H_{c2}. This is strongly supported by the data of Muto *et al.*[4] The scattering mechanism responsible for this behavior of K_{em}, though it can be conjectured to be scattering by flux lines, merits further investigation.

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Magnetic Properties of Type-II Superconductors in the Two-Band Model

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It has been suggested previously by Wong and Sung that the present discrepancies between theory and experiments on the magnetic properties of some transition metals which are intrinsic type-II superconductors (e.g., Nb) may be caused by the overlapping-band effect of s and d bands. We present here the numerical results of this effect on the magnetic properties. It is shown that the overlapping-band effect in the pure limit can reduce the upper critical field H_{c2} about 30–60% at T close to temperature T_c, and thus enhance the over-all temperature dependence of H_{c2}. The amount of reduction decreases as the superconductors become dirtier. Reasonable parameters which characterize the overlapping-band effect are assumed. We also compute κ_2, which defines the slope of H_{c2} when the external field is slightly less than H_{c2}. It is found that κ_2 becomes smaller in comparison with the present theory as $T \to T_c$; thus a stronger temperature dependence is also associated with κ_2. The numerical value of this correction in κ_2, however, is very sensitive to the parameters used.

I. INTRODUCTION

THE magnetic properties of type-II superconductors close to the upper critical field H_{c2} were first studied by Abrikosov, using the phenomenological Ginzberg-Landau equation[1] near the transition temperature T_c. Later, Gorkov derived Abrikosov's theory in the BCS model throughout the whole temperature range at the "clean" limit (the mean free path l is much larger than the coherence length ξ). Actually, this problem is simpler in the "dirty" limit where it is unnecessary to solve an integral equation for the order parameter (the position-dependent energy gap). This was investigated by Maki and de Gennes,[2] who obtained the temperature dependence of κ_1 and κ_2 (parameters related to H_{c2} and the magnetization for the external field less than H_{c2}) for $l \ll \xi$. Helfand and Werthamer[3] investigated this problem and generalized the treatment given by Gorkov, Maki, and de Gennes to all temperature and purity ranges. Thus, a micro-

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