Define quantities

$$S=(2\alpha r_s/\pi)1/yy', \tag{A1}$$

$$X_1^{\pm}=(2-y^2+y'^2)/2yy'\pm(1-y^2+y'^2)^{1/2}/yy', \tag{A2}$$

$$X_2^{\pm}=(2+y^2-y'^2)/2yy'\pm(1+y^2-y'^2)^{1/2}/yy', \tag{A3}$$

$$\phi(X)=X^{1/2}/S(S+X)+(1/S^{3/2})\tan^{-1}(X/S)^{1/2}, \tag{A4}$$

$$\psi(X)=\frac{1+\frac{1}{2}(y^2-y'^2)}{(2yy')^{5/2}}\phi(X)-\frac{1}{4}\frac{(y^2-y'^2)^2}{(2yy')^{7/2}}\times\left(-\frac{2}{S(S+X)X^{1/2}}-\frac{3X^{1/2}}{S^2(S+X)}-\frac{3\tan^{-1}(X/S)^{1/2}}{S^{5/2}}\right)-\frac{1}{4}\frac{1}{(2yy')^{3/2}}\left(-\frac{X^{1/2}}{S+X}+\frac{1}{S^{1/2}}\tan^{-1}(X/S)^{1/2}\right). \tag{A5}$$

Then for $y, y'>1$ and $y>y'$

$$W(y,y')=\theta(y^2-y'^2-1)[\psi(X)]_{X=X_2^-}^{X=X_2^+}+\theta(1-y^2+y'^2)\left\{\frac{y^2-y'^2}{(2yy')^{5/2}}[\phi(X)]_{X=X_1^-}^{X=X_1^+}+[\psi(X)]_{X=X_1^+}^{X=X_2^+}+[\psi(X)]_{X=X_2^-}^{X=X_1^-}\right\}, \tag{A6}$$

where the θ's are step function, and we have used the notation

$$[\psi(X)]_{X=b}^{X=a}=\psi(a)-\psi(b).$$

Note that the kernel is continuous across the boundary curve $y^2-y'^2=1$.

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Low-Temperature Electrical Resistivity of Pure Niobium*

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The temperature dependence of the normal-state electrical resistivity of very pure niobium is reported here. The measurements were carried out in the temperature range from the superconducting transition ($T_c=9.25$°K) to 300°K in zero magnetic field and from 2–22°K in a magnetic field strong enough to quench all superconductivity. The resistance-versus-temperature data were analyzed in terms of the possible scattering mechanisms likely to occur in niobium. To fit the data a single-band model was assumed. The best fit can be expressed as

$$\rho=(4.98\pm0.7)\times10^{-5}+(0.077\pm3.0)\times10^{-7}T^2+(3.10\pm0.23)\times10^{-7}[T^3J_3(\Theta/T)/7.212]+(1.84\pm0.26)\times10^{-10}[T^5J_5(\Theta/T)/124.4],$$

where T is in °K; J_3 and J_5 are integrals occurring in the Wilson and Bloch theories, respectively; and the best value for Θ, the effective Debye temperature, is (270±10)°K. The data are normalized so that $\rho(298\text{°K})=1$. The fitting scheme, which might be best described as a least-squares fractional-error fit, yielded a standard deviation of 2.6% per datum. The limits on the coefficients were obtained by varying each coefficient separately so as to make the fit worse by 1 standard deviation. In this analysis the Bloch term contributes about 55% to the total resistivity at room temperature and the Wilson term about 45%. Over most of the temperature range below 300°K, the T^3 Wilson term dominates. Thus it is concluded that *inter*band scattering is quite important in niobium. Because of the large magnitude of interband scattering, it was difficult to determine the precise amount of T^2 dependence in the resistivity. Several schemes for establishing an upper bound to this term were employed. The smallest, but still reliable, upper bound for the coefficient of this term BT^2 was found to be $B\leq5.7\times10^{-7}$ in the normalized units. This corresponds to about $B\leq8\times10^{-12}$ Ω cm/deg², which is more than an order of magnitude smaller than previously thought for niobium. There is an interesting relation between the *intra*band term in niobium and the total resistivity of molybdenum; it is found that they are nearly equal at their respective Debye temperatures. This result is briefly discussed in terms of their respective *d*-band densities of states.

I. INTRODUCTION

ONE of the most informative and fundamental properties of a metal is the behavior of its electrical resistivity as a function of temperature. The temperature dependence of the resistivity is a good indicator of important scattering mechanisms for the conduction electrons; it can also suggest in a general way what the solid-state electronic structure is like. Of the possible scattering mechanisms for metals, most have distinguishable temperature dependences below room temperature in the range between 1 and

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100°K. However, at these low temperatures, impurity scattering can easily mask the intrinsic behavior of the material.

The usual test for the purity of a metal is that it have a low residual resistance or, equivalently, a high residual resistance ratio. When, by further reduction of the temperature, the resistance of a metal sample cannot be significantly lowered it is said to be in the residual resistance region. The residual resistance ratio (RRR) is the ratio of the room-temperature resistance to the resistance in the residual region. One usually assumes Matthiessen's rule; that is, assume a single-conduction-band model, subtract the residual resistivity from the measured resistivity, and call the new quantity the intrinsic resistivity. If, however, the residual resistivity is a large number relative to the intrinsic resistivity, then any errors in measurement, or even slight deviations from Matthiessen's rule, will give misleading results. For example, in one[1] of the other reported measurements[1–5] of this type performed on niobium a sample was used with a RRR=33. These authors found that their measured resistivity could equally well be fit to either $\rho(T)=A+BT^2+CT^5$ or $\rho(T)=A+BT^3$. A large value of A, the residual resistivity, precluded any test between the two expressions. The highest RRR measured in this work was about 16 500 (a correction for magnetoresistance implies RRR>20 000). The low-temperature form of the experimental results to be reported here would best be described by $\rho(T)=A+BT^3+CT^5$, where A is 500 times smaller than in the previous work just mentioned. This temperature dependence will allow us to say something definite about the solid-state electronic structure of niobium.

II. EXPERIMENTAL

A. Sample Preparation

During the course of this work, samples were prepared using starting material obtained from several sources. The best samples, as determined from their residual resistance ratios, were prepared from niobium obtained from Union Carbide. This material, which had a particularly low W and Ta concentration,[6] came in the form of $\frac{1}{8}$-in.-thick sheets.

In order to prepare samples of the proper shape, the sheets were rolled to a thickness of $\frac{1}{4}$ mm and then were sheared along the rolling direction into parallel-sided strips from $\frac{1}{4}$- to $\frac{3}{4}$-mm widths and about 3 in. in length. After cutting, the rectangular-cross-sectioned wires were chemically polished with a dilute solution of Hf and HNO_3. The chemical polishing removed about 10^{-2} mm from the surface of the samples in order to prepare the surface for other measurements[7] and to preclude any surface contamination picked up in the rolling and shearing operations. The samples were then washed in distilled water followed by ethyl alcohol and then allowed to air dry. Plastic tipped tweezers were used to install them in a high vacuum system for outgassing.

The vacuum system was pumped by an oil diffusion pump and two liquid-nitrogen cold traps. The base pressure of the system, measured by a nude ion gauge in the working chamber, was about 3×10^{-9} mm Hg. The pressure during most of the outgassing was near 5×10^{-9} mm Hg.

When mounted in the vacuum system, the sample was surrounded by a liquid-nitrogen-cooled heat shield. Both ends of the sample were in good thermal contact with the heat shield; however, one end was electrically isolated so that the sample could be resistively heated by passing a current down its length. By observing the sample with an optical pyrometer, its center portion was maintained about 50°C below the melting point for several hours. A hot spot would eventually develop because of niobium evaporation and it would melt through in the central portion. The sample cooled to below room temperature in less than 40 sec and eventually to 77°K. In order to prevent surface contamination,[7] the samples were kept at 77°K while being transferred into a sample holder for measurement.

The two best samples had measured residual resistance ratios of 11 000 and 16 500. Resistance-versus-temperature data for these two samples are presented. It will be seen that the results for the two samples are quite similar. More extensive measurements were carried out on the RRR=16 500, sample and the analysis of these data are described in detail.

After the outgassing, it was found that this sample had recrystallized into large grains each extending across the cross section of the wire. The grains had interfaces which were nearly perpendicular to the wire axis.

Rotating sample x-ray photographs[8] were taken for this sample at three arbitrarily selected points along the 1-cm length of sample over which the resistance was measured. These photographs show highly oriented

[1] G. K. White and S. B. Woods, Phil. Trans. Roy. Soc. London Ser. **A251**, 273 (1959).

[2] G. W. Webb, Ph.D. thesis (unpublished). The data of this paper are the same as in the thesis except that a slight source of scale to scale systematic error in the voltmeter has been corrected. In addition, the data analysis of this paper is more complete. The general behavior of these results has been previously reported in J. J. Engelhardt, G. W. Webb, B. T. Matthias, Science **155**, 191 (1967); G. W. Webb, Bull. Am. Phys. Soc. **12**, 519 (1967).

[3] H. H. Potter, Proc. Phys. Soc. (London) **53**, 695 (1941).

[4] W. Meissner and B. Voigt, Ann. Phys. Leipzig, **7**, 892 (1930).

[5] K.-H. Berthel, Abstracts of L.T. 11, Saint Andrews, Scotland (unpublished). He states that, "the ideal resistivity (of niobium, molybdenum, and tantalium) can generally be approximated by the relation $\rho(T)=aT^2+bT^5$," in contradiction to our results for niobium. The probable answer to this contradiction is that his temperature range of measurement, from "1.8 to 30°K," is too small.

[6] I would like to thank G. Dunnifer for determining the Ta and W content of this material: Ta 3.8 atomic ppm and W 2.1 atomic ppm.

[7] G. W. Webb, Solid State Commun. **6**, 33 (1968).

[8] It is a pleasure to thank E. Vielhaber for helping me take these measurements.

grains whose crystallographic direction along the wire axis is [100]. The maximum deviation of this crystallographic direction from the wire axis is about 8°.

B. Measurement Technique

The conventional four-probe alternating current technique was used to measure the sample resistance. A constant-amplitude current source provided a sinusoidal sample current in the low audio range from 17–270 cps. Root-mean-square sample current densities between 3 and 60 A/cm² were used; the corresponding total sample currents were in the range 1–100 mA. The sample voltage, proportional to its resistance, was measured by a voltmeter whose impedance was high compared to the input circuit.

Almost all the measurements were carried out as a function of temperature with the magnetic field held at some constant value, usually either zero or great enough to quench superconductivity at the lowest temperatures which could be reached. The temperature was measured by a calibrate germanium resistance thermometer in good thermal contact with the sample. In practice, point-by-point sample resistance measurements were taken as the temperature was slowly swept both up and down. The rate of change of temperature was kept slow enough so that the measurements taken on heating and cooling coincided.

The main part of the sample holder was a quartz single crystal of semicircular cross section about 1½ in. long and 0.3 in. wide across the flat portion. A single crystal of quartz was chosen since it is an electrical insulator with high thermal conductivity at cryogenic temperatures. The sample was pressed against the quartz with four pure-indium-tipped Be-Cu electrical contacts. The pressure contacts did not deform the sample to an extent that was observable under a 40-power microscope.

The sample holder was placed in a stainless-steel vacuum-jacketed Dewar which fitted through a solenoidal magnet immersed in the liquid-helium bath. The sample holder chamber was filled with helium gas to a pressure of about 20 mm Hg to ensure thermal equilibrium. A heater could be used to vary the sample-holder temperature.

The thermometer was a Honeywell Class II uncalibrated germanium resistance thermometer. It was used for the temperature range 2–80°K. Calibration of the resistor was carried out between 1.5 and 4.2°K in boiling liquid helium, between 13.8 and 20.3°K in boiling liquid hydrogen, and between 63 and 77.4°K in boiling liquid nitrogen. In addition, the superconducting transition of pure lead furnished a calibration point at 7.19°K.

The virtue of these germanium thermometers is that a plot of the logarithm of the resistance versus the logarithm of the absolute temperature is almost a straight line, especially below 20°K. So, using the calibration points mentioned above and interpolating between the lead point and the liquid-hydrogen points, the T_c of niobium was found to be about 9.45°K. However, other workers[9] using a constant volume gas thermometer have measured $T_c = 9.25$°K on niobium samples with RRR of 2000. Since their samples are pure enough, and their thermometry more exact, the transition point of niobium was taken for the present experiment to be 9.25°K and was used as a calibration point. From the known behavior of germanium resistance thermometers, this deviation of 0.2°K at 9°K is not unreasonable. Sample resistance measurements between 80 and 300°K were taken in stirred constant temperature baths at 195, 273, and 298°K. The temperature error due to magnetoresistance in the thermometer was negligible. It was less than 0.02°K.

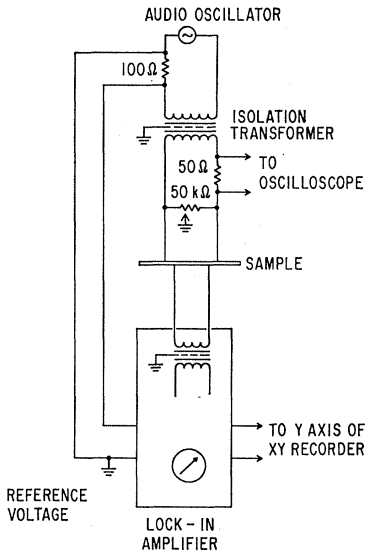

FIG. 1. Sample resistance measuring circuit. The sample current was driven by the audio oscillator through the isolation transformer. The Princeton HR8 lock-in amplifier utilized a type-B preamplifier with a transformer first stage. The 50-kΩ grounding potentiometer was adjusted for the lowest noise setting. It was found that No. 40 twisted pair current and input leads gave the lowest pickup voltages.

The sample measurement circuit is shown in Fig. 1. By tuning the potentiometer, one, in effect, moves the ground along the length of the sample. This grounding arrangement provides much less noise than single-ended operation. With care taken in lying out the input leads and experimenting with ground arrangements, this circuit provided a noise level of less than 5×10^{-10} V in the low audio-frequency range. This noise figure refers to a time constant of about 3 sec. The lowest voltage used for taking data was about 15×10^{-9} V; thus, the worst signal-to-noise ratio encountered was 30:1. However, most of the data were taken with the experimental parameters such that the signal-to-noise ratio was at least 60:1.

[9] D. K. Finnemore, F. T. Stromberg, and C. A. Swenson, Phys. Rev. **149**, 231 (1966).

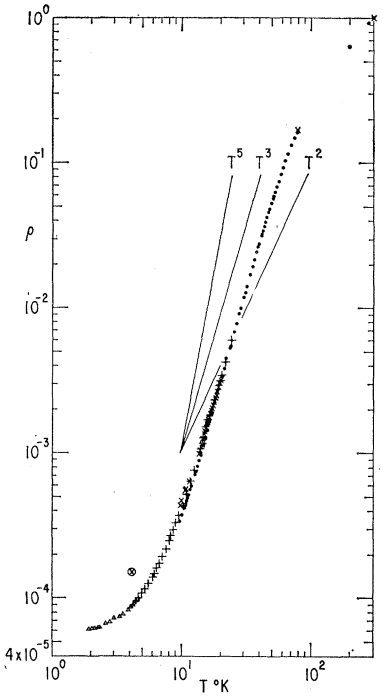

FIG. 2. Resistivity-versus-temperature data for Nb29 RRR ~11 000 and Nb30 RRR~16 500; × is Nb29 $H=0$, ⊗ is Nb29 $H=5.4$ kG; ● is Nb30 $H=0$, + is Nb30 $H=5.4$ kG, △ is Nb30 $H=7.0$ kG. The data have been normalized so that ρ ($T=298$°K) $=1.0$ for both samples. No correction for magnetoresistance has been made yet. The estimated point-to-point error in the resistance is ±2% except in the temperature range 2–4°K where it is ±4%. Over most of the range the temperature uncertainty is ±0.1°K except near 35°K where it is ±0.5°K.

III. RESULTS

Data for the two purest samples are shown in Fig. 2 for zero magnetic field and for two values of the longitudinal magnetic field strong enough to quench all superconductivity. The lines on the figures indicate the power laws T^2, T^3, and T^5. It is evident that between 10 and 50°K the slope lies very close to 3. The steepest portion of the data corresponds to a power law of about $T^{3.2}$.

The data for this sample have been normalized so that the sample resistance equals 1 at 298°K. It was not possible to obtain an accurate measurement of the specific resistivity of niobium because of uncertainties in sample cross-sectional area and the separation of voltage contacts on the samples. A rough estimation did yield a value between 13 and 15 $\mu\Omega$ cm at room temperature. From the literature it seems that a value between 13.2[10] and 14.5[1] should be assumed. For any calculation in this paper requiring a knowledge of the specific resistivity, we will assume $\rho(295°K)=14.5$ $\mu\Omega$ cm.

In Fig. 2, data for the less pure sample, RRR≃11 000, are also shown. These data were also normalized to one at 298°K. Again it is evident that slope is very close to 3. Thus it is concluded that the intrinsic behavior of the two samples is similar.

Measurements of the longitudinal magnetoresistance were made at a few selected temperatures. The magnetoresistance was found to be negligible at 77 and 25°K ($\Delta\rho/\rho\leq3\%$) in a 5-kG field. At 9.36°K the magnetoresistance in 5 kG was found to be 17.3%±2.5% and saturating with field as is shown in Fig. 3. The dashed curve fitted to the data is discussed later. By making a slight extrapolation, the magnetoresistance was also measured just below the superconducting transition temperature of 9.25°K for pure niobium.[9] At 9.10°K in 5 kG the magnetoresistance was found to be 20% ±2.5%. At lower temperatures, ~4°K, during the course of other measurements,[7] it was observed that above H_{c3} there seemed to be little field variation of the normal-state resistance. Although there is no way to determine the total magnetoresistance of "normal" niobium at a temperature this far below T_c, this observation supports the view that the magnetoresistance for this sample was near saturation.

IV. DISCUSSION

In this section, the measured resistivity is analyzed in terms of those scattering mechanisms which have been proposed for nonmagnetic transition metals such as niobium. Most of the analysis is based on the assumption that only one band of electrons carries the current (this assumes that other unfilled bands have much lower Fermi velocities). It is shown that this approximation yields excellent agreement with experiment (of course, the agreement does not rule out the unlikely possibility that there are several distinct condition bands with the same temperature dependences to their resistivities).

In order to facilitate the discussion we give a brief description of the possible scattering terms and point

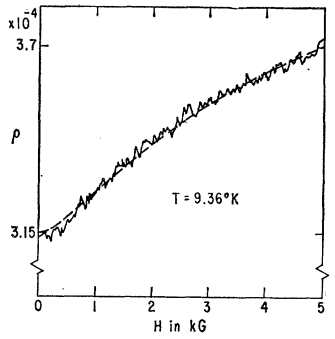

FIG. 3. Magnetoresistance of the purest sample RRR≈16 500 just above T_c. The ρ scale is greatly expanded. The dashed curve, in units where $\rho(298°K)=1$, is the function

$$\Delta\rho/\rho=8.6\times10^{-4}(H/\rho)^{4/3}/1+2.6\times10^{-3}(H/\rho)^{4/3},$$

where ρ in the equation is the resistivity in zero magnetic field and H is in G. There was little reason to choose the exponent $\frac{4}{3}$ instead of $\frac{3}{2}$. The asymptotic value of $\Delta\rho/\rho$ is 33%.

[10] G. Perriot, J. Phys. (Paris) 28, 472 (1967).

out some of the more serious approximations which have gone into the calculations.

A. Possible Scattering Mechanisms for Niobium

(i) At temperatures between 1 and 10°K the resistance of a metal is unsually dominated by impurity and dislocation scattering. This scattering arises from the disturbance of periodicity of the lattice potential. Its contribution to the electrical resistance is found to be independent of temperature for most metals. However, when the sample temperature cannot be neglected in comparison with the Fermi temperature then some temperature dependence of the impurity scattering could occur. However, for the temperature range of this experiment, and the impurity content of these samples, the temperature dependence of impurity scattering should be a negligible effect.

(ii) Within the framework of a single conduction band, electron-electron scattering has been predicted[11] to give a resistivity contribution proportional to T^2. The electrons scatter off each other via a screened Coulomb interaction. Provided there are electrons of different effective masses, a net loss of velocity along the current direction results. This T^2 dependence ought to be experimentally observable at either very low temperatures or at high temperatures roughly twice room temperature. In the transition metals where one has another band of relatively high effective-mass electrons this term ought to be especially large. There is evidence for it in some metals at low temperatures but it seems to be definitely absent at high temperature. In order to explain this discrepancy, Appel[12] has invoked a two-band model. The verification of these ideas still seems unclear especially in the light of recent work[13] (seemingly inapplicable to niobium) which would ascribe the T^2 term, observed in some transition metals with a relatively large magnitude, to a different scattering mechanism. The magnitude of this term is much smaller in nontransition metals.[14]

(iii) Another type of electron scattering has been proposed for the transition metals. This scattering mechanism, which seems to be very important for niobium, was first suggested by Mott.[15] For this scattering mechanism to be important one requires a high Fermi velocity conduction band, for simplicity called the s or s-p band, and another band of low Fermi velocity itinerant electrons, called the d band. The latter band can accept conduction electrons scattered into it by lattice vibrations, and thus it acts like a trap. This is usually called s-d scattering. At temperatures higher than the Debye temperature the mechanism leads to a resistance proportional to the first power of the temperature. With one restriction on the electron distribution, to be discussed in a moment, this mechanism will lead to a resistance proportional to the number of quanta of lattice vibrations; thus at low temperatures, low enough to decompose the lattice vibrations into a system of sound waves, the resistance will vary like the temperature cubed. In these two limits the behavior of the resistivity is independent of details in the phonon spectra.

In order to calculate the magnitude and behavior of the resistivity over the full temperature range Wilson[16] assumed a Debye phonon distribution. Furthermore, he assumed a spherical conduction band, the s band, and a spherical band of low Fermi velocity electrons, the d band. The phonons cause transitions between the two sheets of the Fermi surface. (Of course, hybridization could cause both sheets to have "s" and "d" properties in different directions of k space; and it would seem that along a given ray in k space one sheet would display s-like properties and the other "d"-like properties.) Wilson observed that, for this model, there could be a minimum phonon wave vector $q_{\min}$ required to cause transitions between the two bands; this defines a minimum temperature $\Theta_{\min}$ below which these s-d transitions should exponentially disappear. The form of his result for this contribution to the resistivity is

$$\rho_{sd}=\frac{CT^3}{7.212}\int_{\Theta_{\min}/T}^{\Theta/T}\frac{x^3dx}{(e^x-1)(1-e^{-x})}.$$

The constant C contains the electron-phonon interaction energy between s and d states. The constant $\Theta_{\min}$ is defined by

$$k\Theta_{\min}=u_0|\mathbf{k}_d-\mathbf{k}_s|,$$

where u_0 is the velocity of sound and $|\mathbf{k}_d-\mathbf{k}_s|$ defines the minimum phonon wave vector needed to cause s-d transitions. The Θ in the upper limit on the integral can be regarded as an effective Debye temperature for resistivity. In this approximation only the longitudinal phonons produce potential fluctuations in the lattice and thus cause transitions. Therefore, we might expect Θ to be somewhat different from the Debye temperature.

For small enough values of $\Theta_{\min}$ we can define three temperature ranges for ρ_{sd}. Let us set $\Theta_{\min}=\Theta/20$. Then, from high temperatures down to about $T=\frac{1}{2}\Theta$, ρ_{sd} is proportional to T. From $T=\frac{1}{5}\Theta$ down to about $T=\Theta/40$, ρ_{sd} is proportional to T^3. For temperatures below $\Theta/40$, ρ_{sd} drops away exponentially with temperature. If, on the other hand, we set $\Theta_{\min}=0$, then the T^3 behavior would be observed down to zero temperature. This will be done in our analysis.

(iv) The last type of scattering to be considered here is the well-known Bloch-Grüneisen term. This term

[11] W. G. Baber, Proc. Roy. Soc. (London) **A158**, 383 (1937).
[12] J. Appel, Phil. Mag. **8**, 1071 (1963).
[13] A. I. Schindler and B. R. Coles, J. Appl. Phys. **39**, 956 (1958).
[14] J. C. Garland and R. Bowers, Phys. Rev. Letters **21**, 1007 (1968).
[15] N. F. Mott, Proc. Roy. Soc. (London) **A153**, 699 (1935).
[16] A. H. Wilson, Proc. Roy. Soc. (London) **A167**, 580 (1938).

arises from phonons scattering electrons within a single conduction band. If one assumes a Debye phonon spectrum and a spherical Fermi surface, the well-known result is

$$\rho_{ss}=\frac{D}{124.4}T^5\int_0^{\Theta/T}\frac{x^5dx}{(e^x-1)(1-e^{-x})},$$

where Θ is the effective Debye temperature for resistivity and D is a constant containing among other things the electron-phonon interaction constant.

From high temperatures down to about $T=\frac{1}{2}\Theta$, ρ_{ss} is proportional to T. For temperatures below about $T=\frac{1}{5}\Theta$, ρ_{ss} displays a T^5 dependence. Thus it should be easily distinguishable from the T^3 term of Sec. III. There are some well-known suspected deficiencies to this calculation; however, this term has been found to fit at least the form of the experimental results for the nontransition metals remarkably well.

B. Analysis of Data

The data were analyzed assuming a single-conduction-band model. Therefore, the measured resistivity was fit by a sum of the terms which were discussed, namely, impurity scattering, electron-electron scattering, interband *s-d* scattering, and intraband *s-s* scattering:

$$\rho=A+BT^2+\frac{T^3C}{7.212}\int_0^{\Theta/T}\frac{x^3dx}{(e^x-1)(1-e^{-x})}+\frac{T^5D}{124.43}\int_0^{\Theta/T}\frac{x^5dx}{(e^x-1)(1-e^{-x})}.$$

With this choice of constants at low temperature, the function reduces to

$$\rho+A+BT^2+CT^3+DT^5$$

at low temperatures.

The Θ which appears in J_3 and J_5 is the "effective Debye temperature for resistivity." Although it might reasonably be taken as different for the two types of scattering processes, the same Θ was used in each integral. Θ was varied in steps.

The variable parameters A, B, C, and D were adjusted to give the best fit for a modified least-square fit. Because the data varied over many decades, the usual least-squares fit was inappropriate. A better scheme was found to be a least-square fractional-error fit. That is, the deviation of the curve from the experimental value is divided by that value. With this routine a standard deviation can be expressed as a percentage error per datum. This scheme weights all data points equally. As a slight refinement, the data points taken at temperatures of 298, 273.2, 195.8, 77.35, and 20.25°K were each included five times, while all other points were only included once. These points were treated as special because they are either well-known fixed points or calibration points for the thermometer. The expression for the resistivity is only valid in the absence of a magnetic field. If we are to include the data below T_c in the fit, and we must if we are to determine A and B, then the magnetoresistance must be estimated and corrected for. To make this estimation, we will apply Kohler's rule.

Kohler's rule states that the fractional increase of the resistance of a given metal, in a magnetic field, is a universal function of the magnetic field and the resistance at that temperature in zero field

$$\Delta\rho/\rho=F(\omega_c\tau)=f(H/\rho),$$

where ω_c is the cyclotron frequency and τ is the transport mean-free time. From Fig. 3, we see that $f(H)$ at $T=9.36$°K is saturating. We assume that for lower temperatures the sample is simply being driven closer to saturation. So, by using the $f(H)$ determined above T_c, from Fig. 3, we can estimate the "zero-field intrinsic normal-state resistivity" of Nb.

At low temperatures, with very pure metals, it is possible for boundary scattering to contribute a significant amount of resistance. This boundary scattering can be partially or almost entirely suppressed under the application of a longitudinal magnetic field, possibly generating a negative magnetoresistance. Of course, the magnetic field contributes a bulk positive term. A rough estimation of the boundary scattering in the presence of a magnetic field,[17] assuming a free-electron Fermi surface containing one electron per atom, indicates an additional positive contribution to the total resistance in a 5-kG magnetic field of about 7%.

In fitting the data, we make the simplest possible correction for magnetoresistance and boundary scattering, namely, that below about 9°K it provides a constant, temperature-independent fractional increase to the resistance. Within this approximation it is clear that the best choice of this constant magnetoresistance factor must lie between the amount observed in Fig. 3 and the saturation value (we can neglect the boundary scattering).

The results of this analysis scheme are shown in Fig. 4. These results were obtained by fixing g, the magnetoresistance factor, and then determining the value of Θ, A, B, C, and D which gave the least-square-fractional-error fit. None of the terms in this fit is expected to be negative. Therefore, we conclude that the best fit under the constraint of positive coefficients is

$$\rho=(4.98\pm0.7)\times10^{-5}+(0.077\pm3.0)\times10^{-7}T^2+(3.10\pm0.23)\times10^{-7}(T^3/7.212)J_3(\Theta/T)+(1.84\pm0.26)\times10^{-10}(T^5/124.4)J_5(\Theta/T)$$

(T in °K). The T^2 term is negligible over any temperature range covered in this experiment, thus it can be

[17] E. Koenigsberg, Phys. Rev. **91**, 8 (1953).

neglected; so in effect we remove an adjustable parameter.

The range of values g might take on can be determined by fairly plausible arguments. Clearly, g ought to be smaller than 0.85 (giving 17% magnetoresistance) which was determined by the measured magnetoresistance at 9.36°K as shown in Fig. 3. Secondly, we can consider the saturation magnetoresistance extrapolated from Fig. 3 as a lower bound on g, namely, 0.75 (giving about 33% magnetoresistance; we neglect the 7% boundary scattering term mentioned earlier). The best value of g was found to be 0.833 (giving 20% magnetoresistance).

We have to deal with B separately in order to establish a reliable upper bound for it in niobium. In doing this, we shall stay within the framework of a single-conduction-band model. Furthermore, it is instructive to try several schemes for establishing upper bounds starting with the crudest and most reliable scheme.

For the first upper bound on B, let us consider the data taken in zero magnetic field. As has been shown, the data vary quite closely as T^3 below about 35°K. Therefore, if we obtain the best fit to the data without any T^3 dependence, we establish an upper bound $B<5.8\times10^{-6}$. The results are shown in Fig. 5. Clearly, the curve is a poor representation of the data.

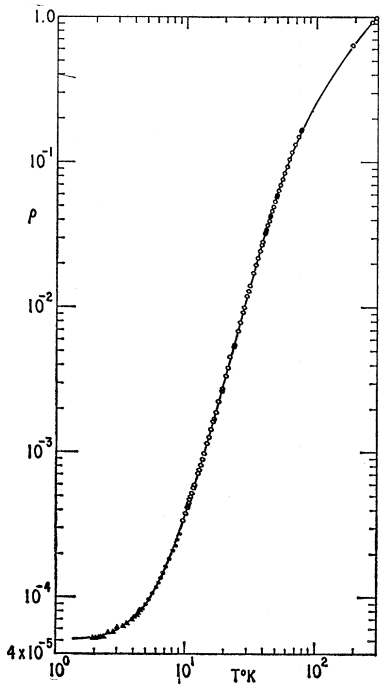

FIG. 4. Some of the data for the RRR∼16 500 sample: ○ is $H=0$, ● is $H=5.4$ kG, △ is $H=7.0$ kG. The data taken in a magnetic field have been multiplied by 0.833 providing a constant correction of 20% for magnetoresistance. The curve is the function

$$\rho=4.98\times10^{-5}+7.7\times10^{-9}T^2+3.10\times10^{-7}(T^3/7.212)J_3(270.5/T)+1.84\times10^{-10}(T^5/124.4)J_5(270.5/T),$$

where J_3 and J_5 are the standard Grüneisen integrals.

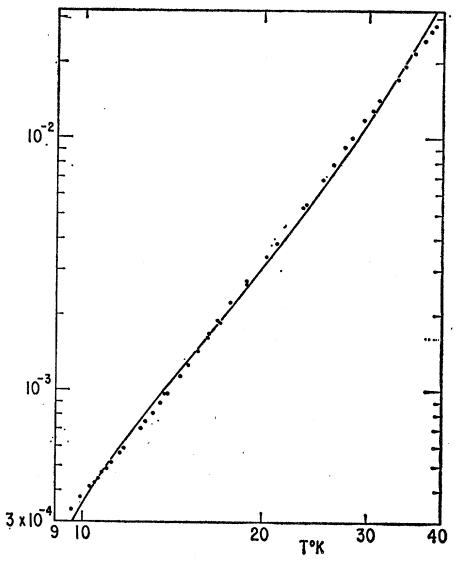

FIG. 5. Data from the purest sample is shown between 9.5 and 40°K. The curve is a least-square-fractional-error fit yielding

$$\rho=-3.0\times10^{-4}+6.3\times10^{-6}T^2+2.5\times10^{-10}T^5.$$

It is seen that the omission of the T^3 term is a serious deficiency. The negative residual-resistivity term is meaningless. The coefficient of the T^2 term should be regarded as an upper limit.

Another upper limit for B can be obtained from the low-temperature data taken in a magnetic field. We can use the data up to 9°K and for the moment ignore any multiplicative factors which would approximate magnetoresistive effects. However, the magnetoresistance is expected to alter the temperature dependence of the "intrinsic normal-state resistance." In fact, experience (and the unsaturated magnetoresistance of Fig. 3 together with Kohler's rule) leads one to believe that the fractional increase of the resistance will be largest at low temperatures. Consequently, one expects the measured data, taken in a magnetic field, to fall less rapidly with decreasing temperature than the "intrinsic zero-field normal-state resistivity"; it is concluded that the value of B obtained in this way is an upper limit. Furthermore, from the coefficients of Fig. 4 we see that at 9°K DT^5 provides less than 4% of the total resistivity thus we can ignore it in the fit and reduce the number of variable parameters to

$$\rho=A+BT^2+CT^3.$$

The fitted curve is shown in Fig. 6, where it is seen that $B\leq6.7\times10^{-7}$. It seems perfectly fair to correct the upper limit on B obtained by this scheme for at least the amount of magnetoresistance found in Fig. 3. Making this correction for magnetoresistance we obtain our most reliable upper limit of $B\leq5.6\times10^{-7}$.

One of the usual schemes for obtaining the coefficients of a resistivity curve is to estimate the residual resistivity ρ_0 from Fig. 1 and plot $(\rho-\rho_0)/T^2$ versus T as in Fig. 7. To do this we have used $\rho_0=6.0\times10^{-5}$ and then

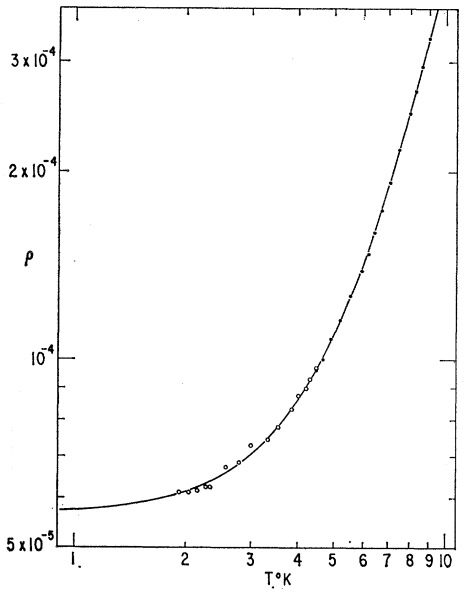

FIG. 6. Data are taken from the purest sample over the range 1.9–9°K: ● is $H=5.4$ kG, ○ is $H=7.0$ kG. The curve is the function

$$\rho=5.64\times10^{-5}+6.7\times10^{-7}T^2+2.9\times10^{-7}T^3,$$

obtained from a least-square-fractional-error fit. No corrections have been made for magnetoresistance. Meter fluctuations of ±2% were observed during the lowest-temperature resistance measurements.

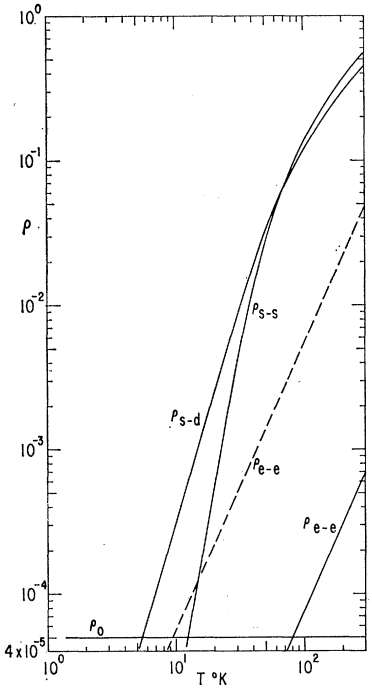

FIG. 8. The solid curves are the separate contributions to the best fit discussed in the text. The dashed curve is the upper limit to electron-electron scattering discussed in the text; its equation is $\rho_{ee}\leq5.6\times10^{-7}\,T^2$.

estimated the best straight line through the data. The chief source of error, which was noise at the lowest temperatures, has been shown with a few error bars on the graph. Estimates of B and C obtained this way are less reliable because of uncertainties in ρ_0. The data do not warrant any speculation about the drop below about 3°K. The coefficients obtained this way are considered to be upper limits for the same reason as the last scheme.

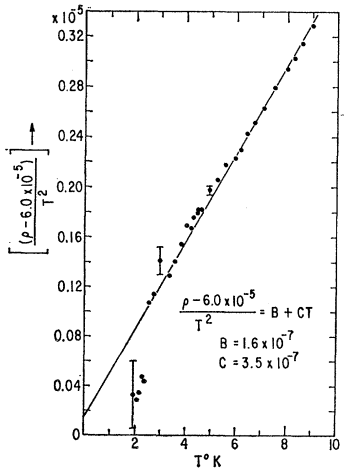

FIG. 7. From Fig. 1 the residual reisistvity was estimated to be 6.0×10^{-5}. This number was subtracted from the data of Fig. 6 and plotted here as shown. The straight line through the data is $(\rho-6.0\times10^{-5})/T^2=1.6\times10^{-7}+3.5\times10^{-7}T$. The error bars indicate resistance uncertainties due to noise.

Let us now assume that a single-conduction-band model is adequate for niobium and that the coefficients of the fit in Fig. 4 are the correct ones. It is interesting to compute the relative importance of the different scattering mechanisms in the resistivity. These results are shown in Fig. 8 as a function of temperature. Clearly, the T^3 term dominates over most of the temperature range below room temperature.

It was previously mentioned that the lower limit $\Theta_{\min}$ on the integral J_3 had been set equal to zero. From Fig. 8 we can estimate an upper bound to $\Theta_{\min}$. From the figure we observe that a sizable fraction of the low-temperature resistivity is due to the T^3 term. Clearly, we ought to be able to see a 30% reduction in ρ_{sd}. From Fig. 8 it is evident that this reduction has not occurred down to at least 10°K. From this a simple calculation gives $\Theta_{\min}\leq23$°K. A bolder estimate would be to set an upper limit to any observable ρ_{sd} reduction at 10°K of two standard deviations, i.e., 6%. This assumption gives $\Theta_{\min}\leq9.5$°K.

We estimate what $\Theta_{\min}=9.5$°K implies in the way of a longitudinal phonon wave vector $q_{\min}$. We make the usual assumption that $k\Theta_{\min}=h\nu_{\min}$. Then from the measured phonon spectrum of niobium[18] we find that

[18] Y. Nakagawa and A. D. B. Woods, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 39.

$(q_{\min}/q_{\max})_l = 1.25\%$ where $q_{\max}$ in this case is the distance ΓH in the niobium Brillouin zone. The transverse phonons have a much lower measured velocity of sound which gives $(q_{\min}/q_{\max})_t = 3.3\%$ for $\Theta_{\min} = 9.5°\text{K}$. Ordinarily in the Debye approximation one assumes that only longitudinal phonons produce potential fluctuations which can cause scattering in non-umklapp processes. However, to include umklapp process one must also consider transverse phonon scattering[19] which is why we mention it here. The ticklish question of umklapp processes and electrical conductivity has not been solved in as general a way as Bloch-Grüneisen scattering or Wilson interband scattering. Thus there seems to be very little that can be said about umklapp processes in niobium until a genuine calculation, including the complicated geometrical factors involved has been done. In this regard it is worth mentioning that umklapp processes have been over estimated in past calculations. For a discussion of this point see Sham and Ziman.[20]

We briefly consider a different procedure from what has been done up to now. From Fig. 1 we noticed that the slope of the data was close to 3. We could completely ignore the ρ_{ss} term and regard the measured resistivity as arising entirely from ρ_{sd}. The data could be then fit exactly by regarding Θ as a continuously variable parameter. When this is done,[2] it is found that a 15% variation of Θ will fit the data between 300 and 20°K. However, it is felt that this scheme is unrealistic.

One of the reasons why it is felt to be unrealistic is apparent when we compare our Nb results with what is known about Mo. The temperature dependence of the resistivity of pure Mo[1,21] is fairly close to T^5. Thus we expect its resistivity to arise mainly from ρ_{ss} (this is supported by the low total density of states at the Fermi surface).[22] The measured resistivity[1] of Mo at its Debye temperature is about 7.3 $\mu\Omega$ cm. From the fit for Nb as represented in Fig. 8, we find that ρ_{ss} for Nb at its Debye temperature, as determined here, is about 7.4 $\mu\Omega$ cm. The agreement of ρ_{ss} for Nb with the resistivity of Mo is expected if the Fermi level lies within a d-sub band in niobium but between two d-sub bands in molybdenum. We also expect the s-p band occupation to be about the same for the two metals.

[19] See, for example, J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960).
[20] L. J. Sham and J. M. Ziman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., 1963), Vol. 15, p. 233.
[21] N. V. Vol'kenshteyn, Ye. P. Romanov, L. S. Starostina, and V. Ye. Startsev, Phys. Metals Metallog. USSR, English transl.: **17**, 152 (1964).
[22] F. J. Morin and J. P. Maita, Phys. Rev. **129**, 1115 (1963).

V. CONCLUSIONS

From the excellent fit to the data, obtained here on the basis of a single-conduction-band model, we conclude that *inter*band T^3 scattering is the dominant scattering term for the low-temperature resistivity in niobium. The *intra*band T^5 scattering term is small at low temperatures, however, it rises more rapidly with temperature so that at room temperature it comprises approximately 55% of the total resistivity, the remaining 45% being furnished by s-d scattering. As for the electron-electron scattering, proportional to the square of the temperature at low temperatures, we conclude that its magnitude is much smaller than previously thought.[1]

During the last few years a great deal of information on niobium has accumulated. Among the measurements with bearing on the electrical resistivity we might include the room-temperature phonon dispersion curves,[18] room-temperature elastic constants,[23] the thermal expansion data[24] above room temperature, and, of course, the data presented in this paper. Furthermore, Mattheiss[25] has recently made an augmented plane-wave (APW) calculation of the niobium Fermi surface. He finds most of the Fermi surface confined to two sheets, which, in the reduced zone scheme, intersect each other along twelve closed curves and are tangent at eight points. These intersections and tangencies would likely yield a very low average value of $\Theta_{\min}$. With these data, it seems that a more rigorous calculation of the resistivity could be done for niobium than has yet been done for any transition metal. In turn, this calculation could shed some light on the possibility of two-band superconductivity[26] in niobium.[27] It would also have bearing on the question of whether or not there are mechanisms other than the electron-phonon mechanism leading to superconductivity in the transition metals.[28]

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[27] L. Y. L. Shen, N. M. Senozan, and N. E. Phillips, Phys. Rev. Letters **14**, 1025 (1965).
[28] B. T. Matthias (private communication).