

the alloy is observed as is evident by the appearance of a sharp peak in the $\partial T/\partial C$ -vs- C curve. The critical concentration so determined is (0.27 ± 0.05) at. % of Os in Re.

(c) Small additions of nonmagnetic impurities to Re is found to enhance the T_c . This is explained in

terms of the effects of band-structure smearing by impurity scattering near a singularity below ϵ_F and the Fermi-surface-topology change at a singularity above ϵ_F . The anomalous impurity influence on T_c of slightly doped Tl is understood by using only the Fermi-surface-topology change mechanism.

*Present address: Physics Department, Cleveland State University, Cleveland, Ohio.

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¹For experimental studies on transition-metal alloy superconductors, see references in B. W. Roberts, *Progress in Cryogenics* (Heywood, London, 1964); Natl. Bur. Std. (U. S.) Technical Note No. 482, 1969 (unpublished).

²For theoretical studies on transition-metal alloy superconductors, see W. L. McMillan, *Phys. Rev.* **109**, 280 (1952), and references therein.

³C. W. Chu, T. F. Smith, and W. E. Gardner, *Phys. Rev. Letters* **20**, 198 (1968); *Phys. Rev. B* **1**, 214 (1970).

⁴L. F. Mattheiss, *Phys. Rev.* **151**, 450 (1966).

⁵F. Heiniger, E. Bucher, and J. Muller, *Physik Kondensierten Materie* **5**, 243 (1966).

⁶T. H. Geballe, *Rev. Mod. Phys.* **36**, 134 (1964).

⁷M. A. Tylkina, V. P. Polyakova, and E. M. Savitskii, *Russ. J. Inorg. Chem.* **7**, 755 (1962); **7**, 754 (1962); E. M. Savitskii, M. A. Tylkina, and V. P. Polyakova, *ibid.* **7**, 224 (1962).

⁸Re: E. Maxwell, M. Strongin, and T. B. Reed, *Phys. Rev.* **166**, 557 (1968); Os: T. H. Geballe and B. T. Matthias, *IBM J. Res. Develop.* **6**, 256 (1962); R. A. Hein and J. W. Gibson, *Phys. Rev.* **131**, 1105 (1963); Ru: T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, *Phys. Rev. Letters* **6**, 275 (1961).

⁹Values of $N_b(0)$ for Re, $\text{Re}_{0.88}\text{W}_{0.12}$, $\text{Re}_{0.70}\text{Os}_{0.30}$, and $\text{Re}_{0.30}\text{Os}_{0.70}$, first evaluated by McMillan in Ref. 2, are slightly different from ours because of the different α used by us.

¹⁰V. I. Makarov and V. G. Baryakhtar, *Zh. Eksperim. i Teor. Fiz.* **48**, 1717 (1965) [*Sov. Phys. JETP* **21**, 1151 (1965)].

¹¹A similar result is believed obtainable from the possible peculiar phenomenon in the phonon spectrum or in the electron-phonon interaction due to the sudden change in N . However, this anomaly in λ , if any, is not large enough to show up in our analysis.

¹²Recently J. E. Crow, M. Strongin, R. S. Thompson, and O. F. Kammerer, *Phys. Letters* **30A**, 161 (1969) found that T_c of W, Mo, and Re films are enhanced. They attributed this to the smearing of $N(0)$ where a valley was assumed to exist. However, it is not clear both from the band-structure calculation (Ref. 4) and specific-heat measurements (Ref. 5) that this valley is in existence at ϵ_F of Mo and Re. Also see D. Markowitz and L. Kadanoff, *Phys. Rev.* **131**, 563 (1963), and references therein.

¹³J. Doulat, B. B. Goodman, M. Renard, and L. Weil, *Compt. Rend.* **249**, 2017 (1959).

¹⁴B. G. Lazarev, L. S. Lazareva, and V. I. Makarov, *Zh. Eksperim. i Teor. Fiz.* **44**, 481 (1963) [*Sov. Phys. JETP* **17**, 328 (1963)]; B. G. Lazarev, L. S. Lazareva, V. I. Makarov, and T. A. Ignateva, *ibid.* **46**, 829 (1963); **48**, 1065 (1965) [*ibid.* **19**, 566 (1964); **21**, 711 (1965)]; N. B. Brandt, N. I. Ginzburg, T. A. Ignateva, B. G. Lazarev, and V. I. Makarov, *ibid.* **49**, 85 (1965) [*ibid.* **22**, 61 (1966)].

¹⁵D. J. Quinn and J. I. Budnick, *Phys. Rev.* **123**, 466 (1961).

¹⁶B. G. Lazarev, L. S. Lazareva, V. I. Makarov, and T. A. Ignateva, Ref. 14.

Thermal Conductivity of Superconducting Niobium[†]

A. C. Anderson, C. B. Satterthwaite, and S. C. Smith
Department of Physics and Materials Research Laboratory,
University of Illinois, Urbana, Illinois 61801
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The thermal conductivity of single-crystal superconducting niobium has been measured in the temperature range 0.04–4 K. No evidence is found either for thermal transport or for phonon scattering by electrons associated with a second energy gap.

The possibility that superconducting transition metals may exhibit two distinct energy gaps was suggested by Suhl *et al.*¹ This two-band model has since been used in the analysis of data on specific

heat,^{2–5} critical field,⁶ upper critical field,^{7,8} penetration depth,⁹ and tunneling.^{10–13} Generally, the data for Nb are consistent with $\Delta_s/\Delta_d \approx 10^{-1}$ and $N_s/N_d \approx 10^{-2}$ – 10^{-1} , where Δ is the energy gap and N

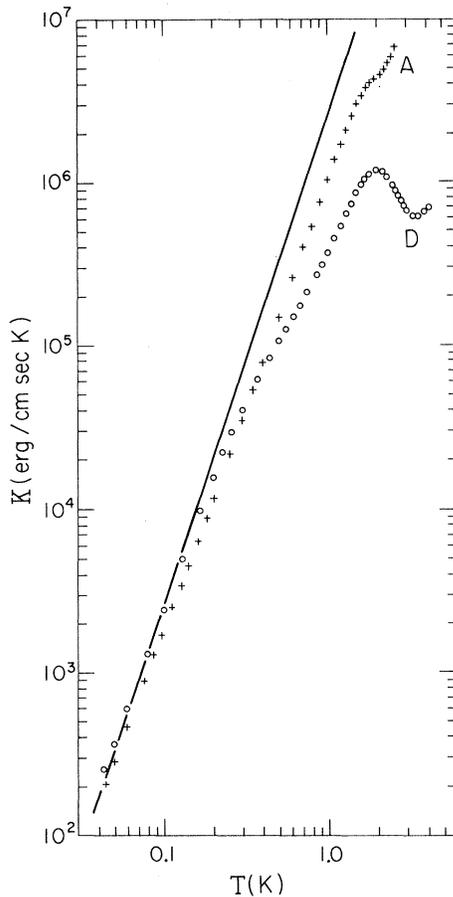


FIG. 1. Thermal conductivity K of two single crystals of Nb vs temperature. The straight line represents the calculated T^3 phonon conductance if the phonon mean free path were limited by diffuse scattering at the abraded surfaces of the sample.

the density of states associated with the respective "s" or "d" band.¹⁴ Recent measurements¹⁵ of the thermal conductivity of superconducting Nb suggested an anomalous or additional thermal transport near 0.5 K which was believed to be due to electrons associated with the small gap Δ_s , even though the calculated ratios Δ_s/Δ_d and N_s/N_d differed considerably from the above values. Subsequently, it was shown that these data were compatible with $\Delta_s/\Delta_d \approx 10^{-1}$ if interband coupling was taken into consideration.¹⁶ In the present paper, however, we show that there is no evidence for thermal transport by electrons associated with a second gap in superconducting Nb.

The Nb samples were single crystals, the surfaces of which had been roughened by 26- μ -diam air-borne abrasive. Sample A had diam 0.304 cm, length 14 cm, resistivity ratio ≈ 2000 , and a Ta impurity of $\lesssim 10^2$ ppm atomic. Sample D had diam 0.315 cm, length 14 cm, resistivity ratio ≈ 26 , and a Ta impurity of 10^4 ppm atomic. Carbon resistance

thermometers were mounted ~ 3.5 cm from the ends of the samples. The lower thermometer was calibrated against a single-crystal sphere of cerous magnesium nitrate, which in turn was calibrated against the vapor pressure of liquid ^3He . The uncertainty in the calibration was greatest ($\sim 2\%$) at the lowest temperatures because of the influence of a measured heat leak of 14 erg/h. The upper uncalibrated resistance thermometer served, via electronic regulation of the dilution refrigerator, to keep that point on the sample at a constant temperature in the presence or absence of an applied heat flux. By nulling the magnetic field of the earth, it was shown that the thermal conductivity was independent of fields of order 1 G or less.

The data are presented in Fig. 1. Two other samples of intermediate resistivity ratio were also measured, and their conductivities fall between the curves for samples A and D of Fig. 1. At the highest temperature ($\gtrsim 4$ K), the thermal transport is dominated by normal-state electrons. With decreasing temperature and the condensation of electrons into the superconducting ground state, the electronic scattering of phonons decreases and the lattice conductivity increases and eventually dominates the thermal transport. At still lower temperatures ($\lesssim 1.5$ K), the lattice conductivity is limited by phonon scattering from sample boundaries and crystalline imperfections.¹⁷ The solid line in Fig. 1 is the calculated T^3 phonon conductance assuming a diam of 0.32 cm, a Debye $\Theta = 277$ K,^{2,18} and diffuse reflection at the sample boundaries. It will be noted that only below ~ 0.1 K does the thermal conductivity due to phonons approach a value limited by the size of the specimen.¹⁹

Hence, we do not find in Fig. 1 any evidence for an enhanced or anomalously large thermal conductance near 0.5 K, but rather a depression below what would be expected for a perfect crystal.²⁰ A phonon mean free path much shorter than the sample dimensions is observed in almost all superconductors in which the lattice conduction has been measured.²¹ It has been demonstrated in Ref. 17, as well as in our own unpublished data on strained samples, that the excess phonon scattering in Nb is primarily associated with physical strain, although a quantitative description of the scattering mechanism is not available. In other words, if the sample is either strained or annealed, the magnitude of the defect or internal scattering changes but not the temperature dependence.

The limitations placed on the two-band theory by the present measurements may be stated in the following manner. If it is assumed that the normal-state electrons associated with each of the two gaps contribute the same thermal conductance per electron, we deduce from any excess or nonlattice conductivity near 0.8 K in curve A of Fig. 1 an *upper*

limit of 10^{-3} for N_s/N_d . On the other hand, if it is assumed that the normal electrons associated with either gap exhibit the same cross section, per electron, to the scattering of phonons, we deduce an upper limit of roughly 10^{-3} for N_s/N_d from excess phonon scattering near 0.8 K which may not be associated with defects in the crystal lattice. In obtaining these ratios, it has been assumed that Δ_s is independent of temperature near 1 K.¹³ A BCS or temperature-dependent behavior of Δ would reduce the ratios slightly. Also if the comparison is made at lower temperatures, that is if one assumes $\Delta_s/\Delta_d < 10^{-1}$, one obtains an even smaller upper limit on N_s/N_d .

The two bands should not, of course, have identical properties. In particular one might expect an "s-band" normal-state electron to make a relatively larger contribution to thermal transport for $T/T_c \ll 1$, where $T_c = 9.3$ K, since it has a much smaller ef-

fective mass and since scattering into "d" states has been diminished. Hence, the upper limit of $N_s/N_d \approx 10^{-3}$ found above may be reduced even more relative to the value of $\sim 10^{-1}$ deduced from previous data on a crystal of similar purity.¹⁴ There is an obvious need for a detailed theory of thermal conductivity consistent with the two-band model, provided that a second gap does, in fact, exist.

In summary, we find no evidence in the thermal conductivity of single-crystal superconducting Nb for thermal transport by electrons associated with a second energy gap, nor do we see evidence for the scattering of phonons by such electrons.

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¹H. Suhl, B. T. Matthias, and L. R. Walker, *Phys. Rev. Letters* **3**, 552 (1959). See also, J. W. Garland, Jr., *ibid.* **11**, 111 (1963).

²L. Yun Lung Shen, N. M. Senozan, and N. E. Phillips, *Phys. Rev. Letters* **14**, 1025 (1965).

³C. C. Sung and L. Yun Lung Shen, *Phys. Letters* **19**, 101 (1965).

⁴T. Soda and Y. Wada, *Progr. Theoret. Phys. (Kyoto)* **36**, 1111 (1966).

⁵R. H. Burkel and W. S. Chow, *Phys. Rev. B* **3**, 779 (1971).

⁶V. Radhakrishnan, *Nuovo Cimento* **48B**, 111 (1967).

⁷V. K. Wong and C. C. Sung, *Phys. Rev. Letters* **19**, 1236 (1967).

⁸C. C. Sung, *Phys. Rev.* **187**, 548 (1969).

⁹V. Radhakrishnan, *Phys. Status Solidi* **20**, 783 (1967); see also, I. M. Tang, *Phys. Letters* **32A**, 185 (1970).

¹⁰V. Radhakrishnan, *Phys. Status Solidi* **18**, 113 (1966).

¹¹J. W. Hafstrom, R. M. Rose, and M. L. A. MacVicar, *Phys. Letters* **30A**, 379 (1969).

¹²M. L. A. MacVicar, *Phys. Rev. B* **2**, 97 (1970).

¹³J. W. Hafstrom and M. L. A. MacVicar *Phys. Rev. B* **2**, 4511 (1970).

¹⁴Ratios of N_s/N_d deduced from previous data depend on sample purity and range up to $\sim 10^{-1}$ for crystals having a resistivity ratio R_{300K}/R_{4K} of ~ 2000 , which is

similar to sample A of the present work. See, for example, I. M. Tang, *Phys. Rev. B* **2**, 2581 (1970).

¹⁵J. R. Carlson and C. B. Satterthwaite, *Phys. Rev. Letters* **24**, 461 (1970).

¹⁶I. M. Tang, *Phys. Letters* **31A**, 480 (1970).

¹⁷P. M. Rowell, *Proc. Roy. Soc. (London)* **A254**, 542 (1960).

¹⁸G. A. Alers and D. L. Waldorf, *Phys. Rev. Letters* **6**, 677 (1961).

¹⁹The failure of these samples to exhibit a T^3 phonon conductivity for $T < 2$ K is not due to some error in measurement. Dielectric crystals of similar net conductance were measured using the same technique, and the conductivities were found to be proportional to T^3 and to have the correct magnitude.

²⁰This is counter to the interpretation given in Ref. 15, although the data of Ref. 15 are correct and reproducible. The T^3 regime of Fig. 1 in Ref. 15 is primarily due to the scattering of phonons by lattice defects, the T^3 dependence being coincidental. The relative increase in conductivity below 0.5 K in Fig. 1 of Ref. 15 is similar to that of the present work, but of greater magnitude because of a longer phonon mean free path resulting from specular reflection from the nonabraded sample surfaces.

²¹An exception is Sn; see, for example, N. V. Zavaritskii, *Zh. Eksperim. i Teor. Fiz.* **33**, 1085 (1957) [*Sov. Phys. JETP* **6**, 837 (1958)].