K. Mendelssohn*

Experimental Work on Superconductivity

Abstract: The high thermal conductivity in the superconductive state at low reduced critical temperatures has been used for the detection of metal imperfections, including those caused by radiation damage. A statistically disordered single crystal of Ta with 30% Nb has also been investigated. Work is described on specific heats, ultrasonic attenuation and on the behaviour of thin superconductive films. An experiment for observing quantization of persistent currents is described.

Thermal conductivity experiment

- *Measurements on pure metals*

Much of the work on superconductivity at the Clarendon Laboratory, Oxford, is concerned with determinations of the thermal conductivity. Some years ago it was discovered that K_s, the heat conductivity in the superconductive state of a pure tantalum single crystal, begins to rise with falling temperature at about $0.3T_c$.[1] Further experiments and extension of the work to niobium and vanadium[2] revealed a maximum in K_s at about $0.2T_c$, which can be attributed to an increase in the lattice conductivity K_{gs} due to the falling off of scatter of phonons by free electrons. It was further shown that cold work of the specimens would reduce this maximum because the phonons were now scattered at the dislocations in the metal which had been introduced by the strain.[3] The heat conductivity in the normal state K_n, on the other hand, is entirely due to conduction electrons and while these are scattered by point imperfections, such as impurities, K_n remains largely unaffected by strain. Separate determination of K_s and K_n thus serves as a useful metallurgical method for the individual observation of point imperfections and large-scale lattice faults in the same specimen.[4] This method has recently been used by us for the assessment of damage induced by neutron irradiation.[5] These measurements have yielded the result that neutron irradiation, besides producing a large number of point imperfections, also causes an appreciable amount of large-scale faults. It appears likely that while the former is due to vacancies in the lattice, the latter is the effect of migration of interstitials which form

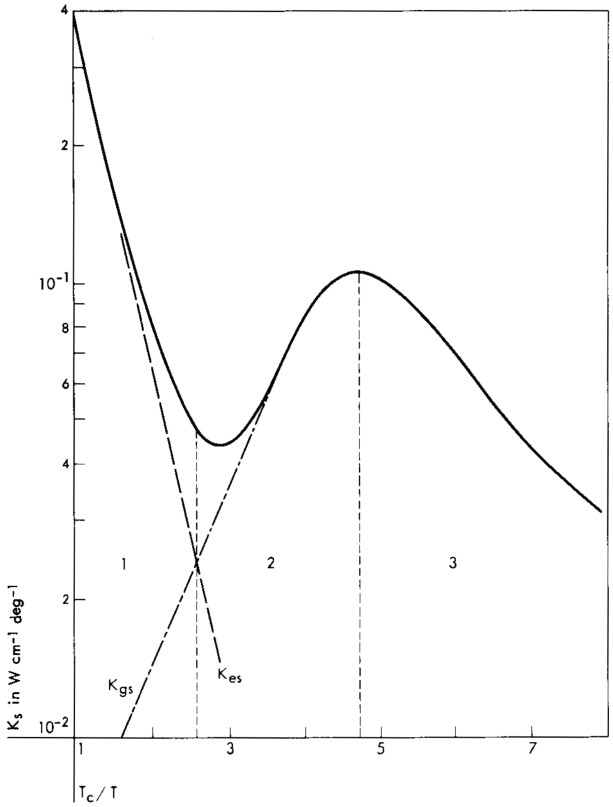


Figure 1 **Typical result for K_s vs T_c/T for tantalum single crystal.** *In first region, conduction is due to free electrons; in second, phonon conduction is dominant; in third, boundary scatter is dominant.*

---

* Oxford University, Oxford, England.

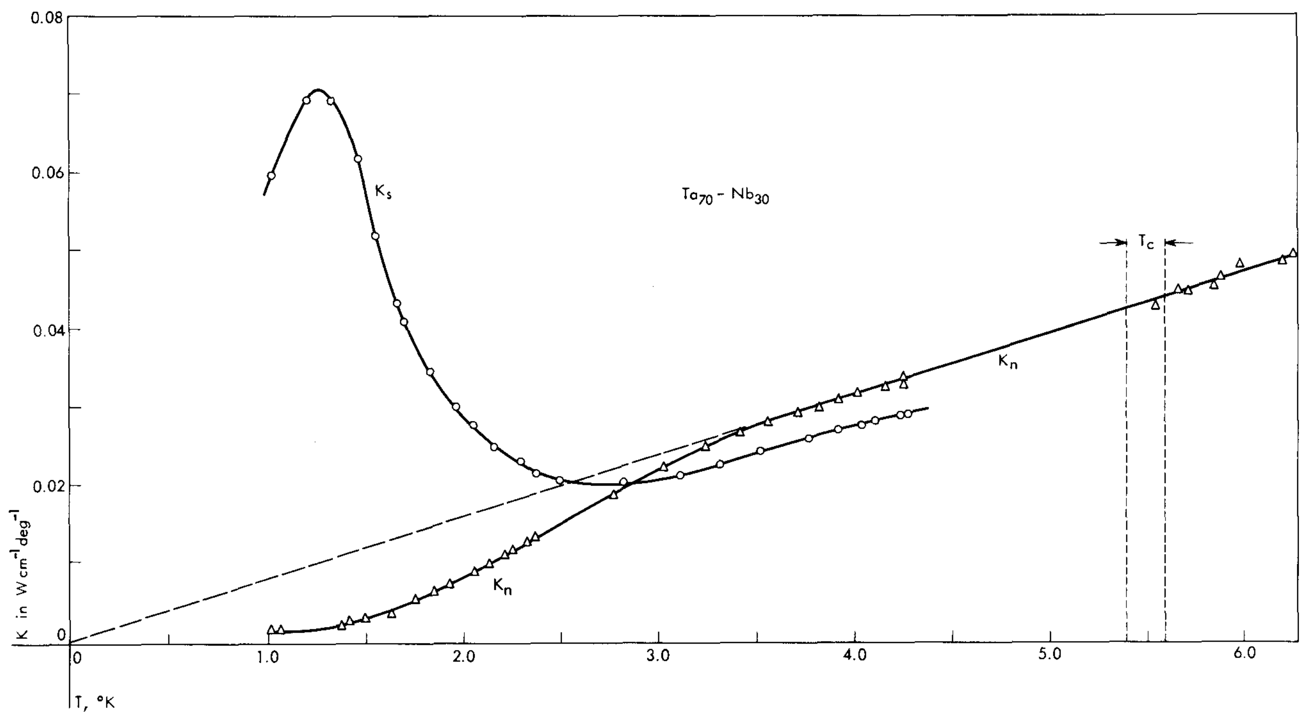


Figure 2 **Temperature dependence of heat conductivity in 70 Ta-30 Nb alloy.**

small dislocation loops or jogs on existing dislocation lines.

The work on pure, undisturbed single crystals of tantalum and niobium has now been extended to temperatures of the order of 0.2°K, which has given us a good survey of K_s over a wide range of T/T_c. A typical result (on a tantalum single crystal) is shown in Fig. 1, where K_s is plotted against T_c/T. Near T_c the curve follows the theoretical function for K_{es}, the electronic term of the heat conductivity, as derived from the BCS theory. This is followed by a minimum at $\sim T_c/3$ and a maximum at $\sim T_c/5$, which is due to phonon conduction. The whole curve can be conveniently divided into three sections. In the first one conduction is entirely due to the free electrons, and their gradual disappearance from the thermal distribution results in a fall of K_s with decreasing temperature. In the second section phonon conduction becomes the dominant process, and K_s rises with falling temperature as the number of free electrons decreases in states where they can scatter phonons. Finally, in the third section this phonon conduction falls again as boundary scatter becomes dominant. The behaviour of the thermal conductivity of a pure superconductor at very low temperature is thus analogous to that of a dielectric crystal, as may indeed be expected for an energy spectrum showing a gap.

According to the BCS theory K_{gs}/K_{gn} is almost proportional to $e^{\varepsilon_0/kT}$ at low reduced temperatures and this permits an evaluation of the energy gap. We obtain[6] for tantalum $\varepsilon_0 = (1.75 \pm 0.1)kT_c$ and for niobium $\varepsilon_0 = (1.9 \pm 0.1)kT_c$.

- *Measurements on alloys*

Recently Calverley and Rose-Innes[7] have succeeded in making single crystals of tantalum-niobium mixtures over the whole range of concentrations. These specimens, which do not "freeze in" any appreciable amount of magnetic flux, have allowed us to extend our measurements of the thermal conduction of solid solutions—which up to now had been limited to the narrow range of the tin-indium system.[8] The results obtained by A. Rice on a specimen with 70% Ta are shown in Fig. 2. The fairly narrow transition range for this sample is at 5.5°K. Near T_c, K_s is smaller than K_n but a little below 3°K, K_s and K_n become equal, with K_s rising to a very pronounced maximum at about 1.2°K. This maximum is of the same order of magnitude as those in pure tantalum and niobium single crystals and is clearly due to the same cause, i.e. enhanced phonon conduction. This shows that the sample is remarkably free of large-scale crystal imperfections. Taken together, with the fact that these crystals do not freeze-in flux, the result leads to an interesting elucidation of the "sponge model" for superconductive alloys proposed many years ago.[9] In this model the freezing in of flux was attributed to regions of high critical field, forming the mesh of the sponge, which are caused by inhomogeneities of the metal. The present experiments show indeed that the absence of inhomogeneities of structure, as evidenced by the heat conductivity measurements, leads to an absence of magnetic inhomogeneity.

A curious and disturbing feature of the results is the low value of K_n at low temperatures. While above

3.5°K, K_n is linear in T, it begins to drop anomalously below this temperature and at 1°K has only a fraction of the value to be expected. Since it is difficult to think of any reason why K_n should deviate from the linear form, its behaviour suggests that superconductivity was not completely suppressed during the measurement. However, a plot of the thermal conductivity as function of the magnetic field at various temperatures, shown in Fig. 3, yields a levelling off above 4 koe. The only explanation which we can offer at this stage is that, with rising field, the thermal conductivity still rises imperceptibly between 4 koe and 6 koe, and that fine superconductive filaments will continue to exist in this specimen up to very high fields. Further measurements, extending to much higher fields, are required to settle this point. In this connection it would be interesting to investigate also the dependence of the thermal conductivity on the magnetic field in Nb_3Sn and in lead-bismuth alloys.

Specific heat measurements

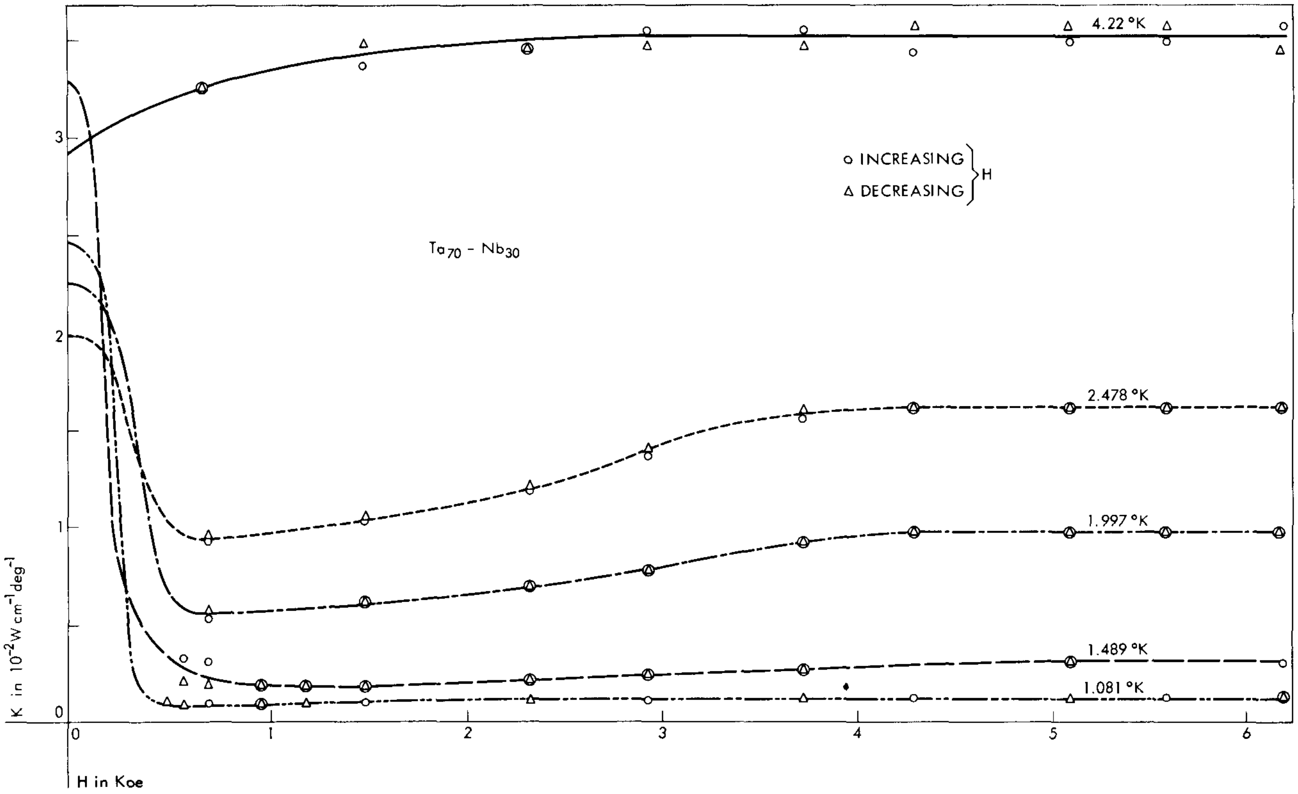
In conjunction with the work on obtaining cooling by the adiabatic magnetization of superconductors,[10] Dr. M. Yaqub has measured the specific heat of normal and superconductive pure tin and tin with 1% and 2% of indium down to temperatures below 1°K.[11] The normal specific heat of the 2% alloy showed a number of small peaks in the range between 0.6°K and 1.2°K which indicate that the field of 500 oersteds in which the experiment was carried out was not wholly sufficient to suppress all traces of superconductivity. There evidently remained some meshes of a "sponge" of high critical value which were successively broken as the temperature was gradually raised. In each case the material within the mesh then became normal and the small peaks are thus direct evidence for the existence of the sponge.

Another feature of these measurements is the difference in the superconductive specific heat between the pure metal and the two alloys, respectively. Whereas in the latter case all the values fell with good accuracy on a curve for the electronic specific heat $C_{es}/\gamma T_c = 9.17 \exp(-1.5T_c/T)$, the measured points for pure tin could not be expressed by such a simple relation but were found, with varying temperature, to oscillate about this value. The consistency of the data for the two alloys suggests that, as would be expected in any case, the irregularities in the case of pure tin are unlikely to be due to the subtracted lattice specific heat. A possible explanation is the effect of anisotropy of the energy gap in tin which would show up in the pure metal but which should disappear in the alloys owing to the shortening of the correlation length.

Ultrasonic attenuation

Another aid to the investigation of the effect of structure on the superconductive behaviour of metals is the observation of attenuation of sound in the ultrasonic range. This work, using monochromatic phonons, is yielding a good deal of information which supplements the experiments on thermal conduction. The phonons used so far (~5 Mc/sec) by us are far removed from

Figure 3 **Heat conductivity as function of magnetic field for several temperatures.**



the wavelengths of thermal phonons, but it is hoped that recent improvements in the technique of very high sound frequencies will permit observations which make this correlation much closer.

Thin superconductive film

The prospect of superconductive switching elements has renewed interest in the behaviour of thin superconductive films. One of the problems we have investigated is that of the relation between the direction of the magnetic field and its critical value. Tin films deposited on a mica base, 2000 and 3500 A thick, were used with the measuring current running in the plane of the film and always perpendicular to the direction of the field. It was found that the critical field had a minimum in the direction perpendicular to the film plane and a maximum parallel to it. If the angle between the field direction and the plane of the film was $90 - \alpha$, it was noticed that the measured transition curves for a given field could be made to coincide if they were plotted against $H \cos \alpha$.[12] The value of α varied between 0 and 75 degrees and it is clear that the relationship must break down for large angles. While a simple cosine law of this kind seems eminently reasonable, it is by no means clear what is the mechanism in the intermediate state which gives rise to it.

Another part of the film work concerns the limiting thickness down to which a metal film will retain its superconductive property. In particular, there are theoretical reasons to believe that superconductive films laid down on a nonsuperconductive metal base may not exhibit zero resistance if their thickness is decreased below a certain value. In these experiments, which have been carried out in collaboration with Professor M. Blackman and his research group at the Imperial College, the persistent current in ring-shaped films has been measured. Films of 3000, 2000 and 1000 A thickness were laid down simultaneously for each thickness on a silver and a mica substrate. The first experiments were carried out on tin and it was indeed observed that while the thinnest films on mica still showed a persistent current, those on silver were not superconductive. However, even for films which were cooled down within a few minutes of their deposition, there was a suspicion of alloy formation, and the work has now been changed to the use of lead films in which alloying is less likely. Here the results have yielded persistent currents, even for the thinnest films on silver, although it must be stated that the value of the current on silver is much smaller than on mica. However, only further experiments on still thinner films will settle the question whether superconductivity can, in fact, be suppressed by contact with a normal metal.

An experiment on flux quantization

Finally, I should like to mention an experiment on a basic problem of superconductivity which is at present in progress. If, as appears likely, the lowest energy states of a superconductor involve collectively the whole of the electron fluid, macroscopic currents must be quantized. We have shown earlier that even at finite temperature the entropy of a persistent current is zero,[13] and we have suggested that the existence of persistent currents can only be understood under the assumption of quantization coupled with zero fluctuation.[14] Quantization of magnetism has been suggested by Dirac,[15] who pointed out that quantum mechanics requires the dimension of the quantum to be of the order of hc/e, that means about 5×10^{-7} gauss cm^2. Orders of magnitude of a millionth part of the earth's magnetic field are not easy to detect, and although a number of methods involving a very small ring carrying the persistent current suggest themselves, we have been unable to think of an elegant short cut which is not open to grave objections. On the other hand, this is the kind of experiment where one would like to see an accurate and unambiguous result.

One of the most serious difficulties is the possible presence of flux frozen into the metal of the ring. Here one can only feel reasonably certain if the cross section of the metal is small in comparison with the area inside the ring containing a single quantum. Since for other reasons thin metal films have to be avoided, the cross section of a reliable ring will have to be at least 1 mm^2, which requires the measurement of field strengths of 10^{-5} oersted. Our experiment is being carried out in collaboration with Dr. P. Vigoureux of the National Physical Laboratory. It simply consists of a small generator made up of two coils between which the ring rotates on a shaft perpendicular to its axis. Since measurements indicate that in our arrangement we can compensate external fields to 10^{-7} oersted over the whole volume of the experiment, we should be able to detect flux changes of about one percent of the quantum.

References

1. K. Mendelssohn, *Can. J. Phys.*, **34**, 1315 (1956).
2. A. Calverley, K. Mendelssohn and P. M. Rowell, *Cryogenics*, **2**, 26 (1961).
3. P. M. Rowell, *Proc. Roy. Soc.*, **A254**, 542 (1960).
4. K. Mendelssohn, *Physica*, **24**, Supplement, 53 (1958); H. Montgomery, *Proc. Roy. Soc.*, **A244**, 85 (1958).
5. K. D. Chaudhuri, K. Mendelssohn and M. W. Thompson, *Cryogenics*, **1**, 47 (1960).
6. A. Connolly and K. Mendelssohn, to be published.
7. A. Calverley and A. C. Rose-Innes, *Proc. Roy. Soc.*, **A255**, 267 (1960).
8. C. A. Shiffman, *Proc. Phys. Soc.*, **71**, 597, 1958; K. Mendelssohn and C. A. Shiffman, *Proc. Roy. Soc.*, **A255**, 199 (1960).
9. K. Mendelssohn, *Proc. Roy. Soc.*, **A152**, 34 (1935).
10. M. Yaqub, *Cryogenics*, **1**, 101 (1960).
11. M. Yaqub, *Cryogenics*, **1**, 166 (1961).
12. J. M. Corsan, *Cryogenics*, **1**, 180 (1961).
13. J. G. Daunt and K. Mendelssohn, *Proc. Roy. Soc.*, **A185**, 225 (1946).
14. K. Mendelssohn, *Cryophysics*, Interscience, New York, 1960, p. 114.
15. P. A. M. Dirac, *Proc. Roy. Soc.*, **A133**, 60 (1931); *Phys. Rev.*, **74**, 817 (1948); see also F. London, *Superfluids*, Wiley, New York, 1950, vol. 1, p. 152.

Received September 1, 1961