esting to us.

J. A. HULBERT, *Royal Radar Establishment:* I just want to make a remark in connection with Dr. Lynton's remarks on the puzzle about the Shapoval and the Gor'kov theories and their relative ranges of validity. We have measured some niobium–zirconium wires and looked at the upper part of the transition where the last part of the normal resistance had just returned. In these circumstances, we observe a positive curvature in the relation between the critical field and the temperature, down to temperatures of half the critical temperature. The amount of curvature is a function of the value of kappa. The interesting thing about these results is when we work out the thermodynamic critical field using Shapoval's relations we obtain results which are very close to those obtained by direct measurement (Blaugher and Hulm, for example) on the 25% zirconium alloy. The values of kappa obtained near T_c and from the zero-temperature extrapolation using the Shapoval theory again are extremely close, within 10%. It appears from these results that the curvature changes from positive to negative at a kappa of about 20. Similar results on lead–bismuth (eutectic alloy) which have a kappa value lower than 20 fit into the general picture. It appears that the critical field defined by the restoration of full normal resistance is not inconsistent with both Gorkov and Shapoval theories in their stated ranges of validity.

WERTHAMER: I've re-examined Shapoval's derivation and find that although he seems, in principle, to proceed along correct lines, there's a serious algebraic error at a rather crucial stage in the calculation. In a preliminary attempt to repeat the calculation with the error corrected, I find that the mean free path drops out of the final expressions. This is well-known to be true in the limit of vanishing magnetic field, but is contradicted by Shapoval's formulas. It appears that Gor'kov's result holds independent of the mean free path.

Mean Free Paths in the Normal and the Superconducting State

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Until now, no direct measurements of the mean free path of the excited electrons in a superconductor have been made. The purpose of this investigation is to determine experimentally the mean free path of indium in the superconducting state by size effect measurements of the thermal conductivity, and to compare it with the mean free path of the electrons in the normal state. Our results indicate that in the limit of the precision of such size effect measurements these two mean free paths are equal.[1]

If the mean free path is comparable to the dimensions of the specimen, there will be an additional scattering of the electrons at the boundaries. This gives an additional term in the resistivity. If one assumes that the thermal conductivity is proportional to the mean free path l, and that all electrons are scattered diffusely at the surface of the specimens, one has for the thermal resistance $W(d)$ of a cylindrical wire of diameter d according to a qualitative argument due to Nordheim[2]

$$W(d) = W_\infty(1 + l/d) .$$

W_∞ represents the thermal resistance of an infinitely thick specimen. This formula agrees very well with Dingle's[3] exact solution. Now it is possible to determine the mean free path for the thermal conductivity by measuring the thermal resistance of wires with several thicknesses and by fitting the experimental data either to Nordheim's formula or to Dingle's table, using W_∞ and l as parameters.[4] This can be done both in the normal and in the superconducting state. In this manner, the mean free paths in the two states are determined. The measurements have been carried out on indium of remarkably high purity, where, in the temperature range investigated, the heat conductivity due to phonons can entirely be neglected compared with the conductivity due to electrons. The specimens were extruded very carefully through nozzles made from sapphire, and self-annealed at room temperature for several weeks. Superconductivity was quenched with a longitudinal magnetic field, and the resultant magnetoresistance of several percent was corrected either by Kohler's rule or by using a quadratic extrapolation.

In Fig. 1, the measured thermal resistance W in the normal and in the superconducting state is plotted as a function of the temperature T for several wires of different thicknesses. The ratio W_n/W_s is independent of the thickness and in good agreement

[1] For preliminary results of this investigation, see P. Wyder, Phys. Letters **5**, 301 (1963).

[2] L. Nordheim, Acta Sci. et Ind. No. 131, Paris (1934).

[3] R. B. Dingle, Proc. Roy. Soc. (London) **A201**, 545 (1950).

[4] J. L. Olsen and P. Wyder, Helv. Phys. Acta **32**, 311 (1959).

with Jones' and Toxen's[5] results. Fitting these data to Nordheim's formula, one gets the mean free path in the normal and the superconducting state. This is plotted in Fig. 2 as a function of the reduced temperature T/T_c. In the limit of the precision of these size effect measurements, the two mean free paths

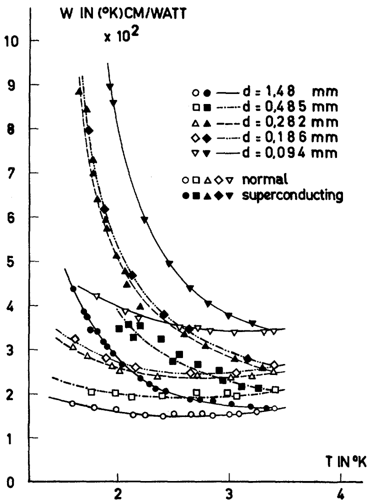

FIG. 1. Thermal resistance in the normal and in the superconducting state of indium wires of several thicknesses as a function of the temperature.

are equal. It is worth noting that for the indium investigated, at $T = 3°K$ about 50% of the thermal resistance is due to inelastic electron–phonon collisions.[4] This means that the mean free paths are equal not only in the elastic impurity scattering region, but also at higher temperatures; this confirms one of our assumptions recently made[6] to explain the maximum in the thermal resistance in the intermediate state.

Measurements of this kind have a certain interest, since for many investigations of transport phenomena of superconductors one uses the assumption that the mean free paths of the electrons in the normal and in the superconducting state are the same. This assumption, which as far as we know has never been directly proved, is made in the determination of the energy gap in the superconducting state through ultrasonic attenuation,[7] in certain tunneling investigations,[8] and also in the discussion of measurements of thermal conductivity, especially with respect to measurements in the intermediate state where electron scattering at interphase boundaries makes a sizable contribution to the thermal resistance,[6] and also to the thermal conductivity of superconductor-normal metal sandwiches.[9] However, this assumption is in disagreement with the old Heisenberg theory,[10] which represents the experimental data on the temperature dependence of thermal conductivity[11] quite well. In this theory, the mean free path of the "normal" electrons in a superconducting metal—in the sense of a two-fluid-model—is dependent on the order parameter of the superconducting state. This would mean that the mean free paths in the normal and in the superconducting state are not the same.

More recently, Kadanoff and Martin[12] have found that the experimental data of Guenault[13] on tin, in the temperature region where the electrons are mainly scattered by phonons, can be fitted approximately by a theory in which it is assumed that the relaxation time for electron–phonon interaction is the same in the normal and superconducting state. Because of the differences in the energy spectra of the two states, this theory would also lead to different mean free paths. However, their assumption does not agree with the detailed calculations based on the Boltzmann equation.[14]

If electrons are only scattered elastically, i.e. by impurities, a relaxation time τ can easily be calculated. Bardeen, Rickayzen, and Tewordt[14] have shown that in this case one has

$$\tau_s = |(E_k/\epsilon_k)|\tau_n ,$$

where s and n refer to the superconducting and to the normal state, ϵ_k is the Bloch energy for an electron with wave vector **k** in the normal metal, and E_k represents the Bardeen–Cooper–Schrieffer energy of an excitation in the superconducting state, given by

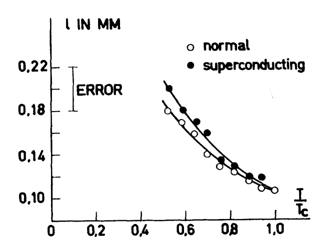

FIG. 2. Mean free path in the normal and in the superconducting state as a function of the reduced temperature. The estimated error in the determination of the mean free paths is indicated.

$$E_k = (\Delta^2 + \epsilon_k^2)^{\frac{1}{2}}$$

and Δ is the BCS-energy-gap.

[5] R. E. Jones and A. M. Toxen, Phys. Rev. **120**, 1167 (1960).
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[14] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959).

The group velocity v of the excitations is given by

$$v_s = (1/\hbar)\partial E/\partial k = (\epsilon_k/E_k)\cdot v_n \,.$$

For the mean free paths, one then has

$$l = v\tau = l_s = l_n \,.$$

Thus, if only elastic scattering is present, the two mean free paths must be equal. When inelastic phonon-scattering is present, a relaxation time cannot be defined unambiguously, and this simple discussion no longer applies.

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Reduction of the Lattice Thermal Conductivity of Superconductors due to Point Defects

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In the theory of the lattice thermal conductivity of solids the thermal resistivity can be regarded, as a first approximation, to be additively composed of the resistivity of the various scattering processes present. However, this approximation becomes progressively poorer, the more these scattering processes differ from each other in frequency dependence. In particular, in the lattice thermal conductivity of alloys, the scattering of phonons by electrons and by point defects (solute atoms) varies as the first and fourth power of frequency, respectively, and the additive resistance approximation underestimates the resistance. Furthermore, the effect of point defects is appreciable at somewhat lower temperatures than one would have expected from the additive resistance rule.

Hulm,[1] in his systematic analysis of the thermal conductivity of superconductors, makes use of the additive resistance approximation for the lattice thermal conductivity κ_g. Thus, he obtained the following relation for the normal state

$$1/\kappa_{gn} = W_e + W_p \,, \tag{1}$$

and for the superconducting state

$$1/\kappa_{gs} = (W_e/h) + W_p \,, \tag{2}$$

where W_e is the lattice thermal resistance due to phonon–electron scattering, W_p that due to all other scattering processes, and h, a function of T/T_c, is the reciprocal of the reduction of the phonon–electron scattering.

If W_p arises mainly from point defects, the additive resistance approximation is a poor one, and if one uses Eqs. (1) and (2) to determine the h function from observed values of κ_{gn} and κ_{gs}, this function should depend on the amount of point–defect scattering. Sladek[2] found, indeed, for a series of In–Tl alloys that the experimentally obtained h function varied with solute content.

Point defect scattering can have a pronounced effect on κ_{gs} even at low temperatures where W_p is negligible compared to W_e, because in the superconducting state W_e is reduced by $1/h$. Furthermore, this sensitivity will be increased if one discards the additive resistivity approximation [Eqs. (1) and (2)], but considers the effect of both scattering mechanisms on each phonon frequency separately.

A further complication arises when one considers that, in the treatment of the lattice thermal conductivity of superconductors[3] in terms of the BCS theory, this reduction of W_e arises from a reduction in the phonon scattering cross section, which is not by the same factor $1/h$ for all phonons, but which is significant only for phonons of energy $\hbar\omega$ less than the gap energy $2\Delta(T)$. The reason is that phonons with $\hbar\omega < 2\Delta(T)$ cannot decay into pairs of quasi-parti-

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[1] J. K. Hulm, Proc. Roy. Soc. (London) **A203**, 74 (1950).

[2] R. Sladek, Phys. Rev. **97**, 902 (1955).

[3] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959), referred to hereafter as BRT.