(3) With the exception of possibly small F'-bands formed after high intensity x-raying in NaCl and KBr, no bands appear to the infrared of the F-band after x-raying at 5°K.

(4) New bands appear to the ultraviolet of the F-band after x-raying at 5°K. On warming to 78°K, these bands bleach, resulting in a reduction of the number of F-centers and the growth of certain of the V-bands normally produced by x-rays at higher temperatures.

The possible future experiments at 5°K are so large that it is difficult to list them. Some suggestions are:

(1) An attempt should be made to obtain very high purity material to use at these temperatures.

(2) Curves showing the rate of growth of the bands with time of x-ray exposure should be very valuable. It would be particularly interesting to see if the past history of the crystal affects the growth-rate curves and what influence the x-ray intensities have.

(3) The optical and photoelectrical properties of the ultraviolet bands should be studied in detail.

(4) It will undoubtedly be necessary for a general understanding of the ultraviolet bands to measure the properties of these crystals between 5°K and 78°K. This will close the gap between Dorendorf's results and those given here.

The authors would like to state their appreciation to Mrs. B. Grisamore for help in taking and computing the data; to Dr. I. Mador for his cooperation in these experiments; to Dr. S. Zerfoss of the Naval Research Laboratory and Mr. B. Scribner of the National Bureau of Standards for analyzing the purity of the crystals; and to Professor F. Seitz for a helpful discussion of the results.

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The Thermal Resistivity of Superconductors*

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The thermal resistance of tin, indium, and an alloy of tin with 0.134 percent bismuth have been measured as a function of transverse magnetic field strength from zero to values greater than critical at temperatures below their respective superconducting transition temperatures. Measurements have been carried out on tin at several temperatures and with polycrystalline and single-crystal specimens. In all cases a distinct maximum is found in the intermediate state thermal resistance of the pure metals, while no such anomaly is observed in the alloy. The probable origin of this phenomenon is discussed.

I. INTRODUCTION

IN general, at all temperatures below the zero-field superconducting transition temperature, two values are found for the thermal resistivity of a superconductor, one when the specimen is electrically superconducting, and a different one, usually higher, when superconductivity is destroyed by the application of a magnetic field greater than the critical field. This is in qualitative agreement with the assumption that when a metal is in the superconducting state a certain fraction of the conduction electrons are in their lowest energy state and not available for heat transport.

Until recently, very little information was available on the thermal resistivity of superconductors in the intermediate state since most of the measurements had been made on thin cylindrical specimens with the magnetic field applied parallel to the geometrical axis of the cylinder, in which case there is no intermediate state. With the applied magnetic field normal to the axis of the cylinder, it would be reasonable to predice on the basis of the laminar structure of the intermediatt state[1–3] that the intermediate state thermal resistance (for $\frac{1}{2}H_c<H<H_c$ where H_c is the critical magnetic field) would vary linearly with magnetic field between the values characteristic of the superconducting and normal states, respectively, in analogy to the behavior of the electrical resistance.

Mendelssohn and Pontius[4] in 1937 did, indeed, find this intermediate state behavior for a lead-bismuth alloy (10 percent Bi) at about 5°K. However, in 1950, Mendelssohn and Olsen[5,6] made further measurements on niobium and a Pb-Bi alloy (0.1 percent Bi) and found a distinct maximum in the intermediate state resistance. More recently, a similar phenomenon has been reported in pure lead below about 4°K by Webber

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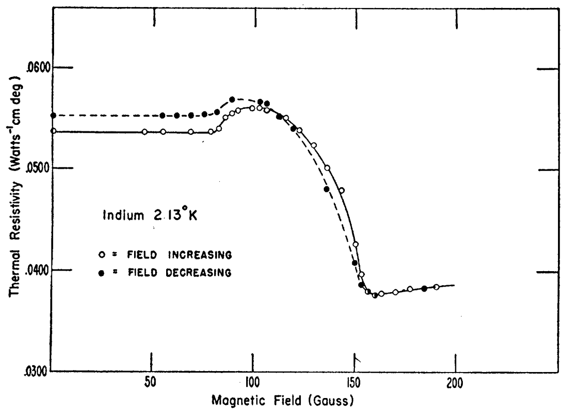

Fig. 1. The thermal resistivity of indium in a transverse magnetic field at 2.13°K.

and Spohr[7] and in tin and indium by the present authors.[8] In this paper we report in greater detail the results on tin and indium, as well as an alloy of tin and bismuth, and discuss the possible explanations of this anomalous behavior.

II. APPARATUS

The standard steady-state temperature gradient method was employed in the thermal resistance determinations. The specimen, a cylinder about 10 cm in length and 4 mm in diameter, was suspended from the top of a highly evacuated brass cavity. An electrical resistance heater, mounted on the lower end of the specimen, served as a heat source. The upper end of the specimen protruded through a sleeve in the top of the cavity into the surrounding helium bath which served as the heat sink. The thermometers used to determine the temperature gradient were two carbon composition resistors placed in thermal contact with the specimen at two points along its length. Rose alloy solder was used for all soldered connections to the specimen, its low melting point minimizing the danger of crystalline damage by overheating.

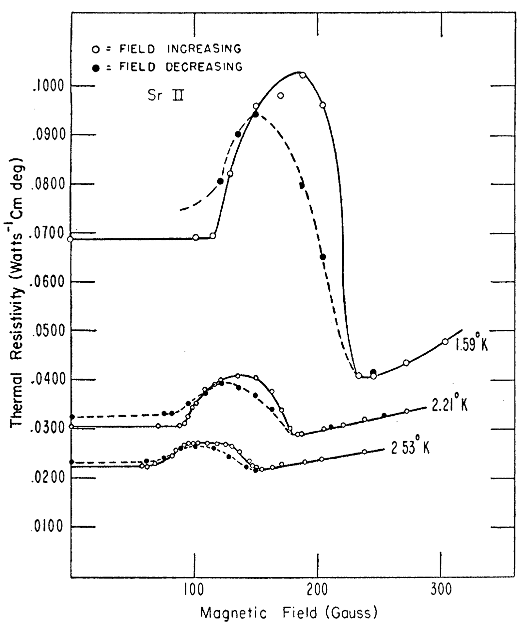

Fig. 2. The thermal resistivity of Sn II in a transverse magnetic field at various temperatures.

To permit evacuation of the specimen cavity, it was suspended in the helium bath by a stainless steel tube leading through the flask cap to vacuum gauges and an oil diffusion pump. A valve inserted between the pump and the gauges was closed when the cavity was immersed in helium to prevent back-diffusion of air through the pump. Baffles were placed in the pumping tube immediately above the specimen cavity to prevent room temperature radiation and "hot" gas molecules from impinging on the thermometers. To eliminate heat leakage to the specimen and thermometers by conduction down the electrical leads, these were led through the helium bath and into the specimen cavity via Stupakoff Kovar-glass insulators mounted in the bottom of the cavity. The calculated heat transfer from the specimen to the liquid helium bath through these leads (copper 0.003-inch diameter) was negligibly small compared to that through the specimen in every case.

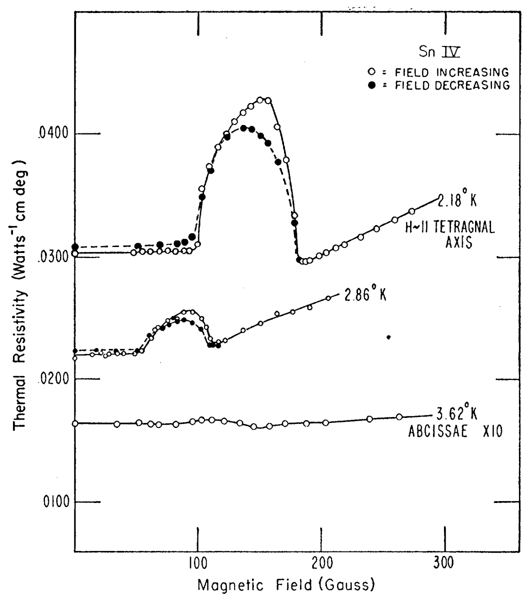

Fig. 3. The thermal resistivity of Sn IV in a transverse magnetic field at various temperatures. The angle between magnetic field and the tetragonal axis of the crystal was approximately 20°.

The thermometer resistances were measured with a bridge circuit, the power input to the resistors being maintained at less than 1 microwatt, and were calibrated against the vapor pressure of the helium bath using the vapor pressure tables of van Dijk and Shoen-

[7] R. T. Webber and D. A. Spohr, Phys. Rev. 84, 384 (1951).
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berg.[9] Interpolation between the calibrating temperatures was made by fitting the data to an empirical formula of the form suggested by Clement and Quinnell[10] for carbon composition resistors.

III. SPECIMENS AND RESULTS

A. Indium

A rod 2.8 mm in diameter was cast from Johnson Matthey spectroscopically standardized indium, J. M. Lab. No. 3249. The resulting specimen was a single crystal with a number of small surface pits which owing to its softness was somewhat strained in mounting in the apparatus. Consequently, although a ratio of electrical resistance at 0°C to resistance at 4.2°K of 5500 was found, indicating a rather good chemical and physical purity, the thermal resistance values shown in Fig. 1 are no doubt somewhat higher than for a perfect specimen of identical chemical purity.

A definite maximum in the thermal resistance is nevertheless plainly evident in the intermediate state.

B. Tin

Two specimens were prepared from Johnson-Matthey tin, J. M. Lab. No. 2356, with a stated purity of 99.996 percent. The specimen designated Sn II was 4.1 mm in diameter and consisted of several large crystals. The ratio of its electrical resistance at 0°C to that at 4.2°K was 8000. Sn IV was a single crystal, 4.3 mm in diameter, with an electrical resistance ratio of 11,200. In this specimen the tetragonal axis of the crystal lay at an angle of about 70° from the geometric axis.

Figures 2 and 3 show that a strong maximum exists in the intermediate-state thermal resistivity of tin. Although much less pronounced at higher temperatures, the maximum is present at temperatures as little as 0.1°K below the superconducting transition temperature. Sn IV exhibited no dependence of intermediate-state thermal resistance upon orientation of the magnetic field relative to the crystallographic axes in increasing fields, although some dependence upon orientation was observed in the hysteresis and in the magneto-thermal-resistance in fields greater than critical.

The intermediate-state electrical resistance of Sn IV as a function of applied magnetic field is shown in Fig. 4. The close approximation to linearity is in excellent agreement with theoretical predictions[1,3] and magnetization measurements[11] assuming that the fraction of normal resistance attained is equal to the fraction of the specimen converted to the normal state.

C. Tin+0.134 Percent Bismuth

A polycrystalline specimen, prepared of Johnson-Matthey materials and having a diameter of 5.0 mm

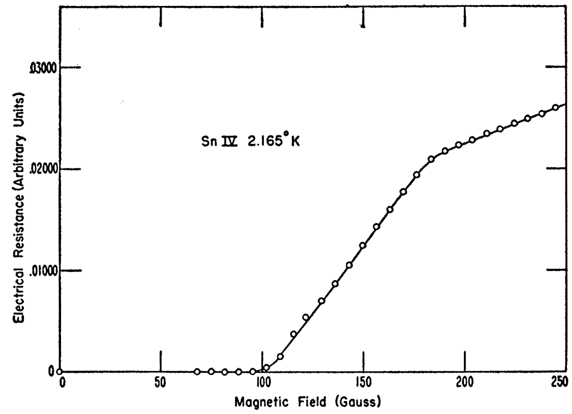

FIG. 4. The electrical resistivity of Sn IV as a function of transverse magnetic field at 2.165°K.

was also investigated. As shown in Fig. 5, this alloy has a much higher thermal resistance than pure tin. No evidence of a maximum in the intermediate state was found.

IV. DISCUSSION

Several hypotheses have been offered[7] to explain qualitatively the maximum observed in the intermediate-state thermal resistance. It is not yet possible to state unequivocally which, if any, of these suggestions is correct; however, two of them are open to serious criticism.

The first proposal, due to Mendelssohn and Olsen,[4] postulated a new mechanism of heat transport in the superconducting state in the form of a circulation current of normal and super-electrons, analogous to the heat transport in superfluid helium. The maximum in the intermediate-state resistance is then attributed to

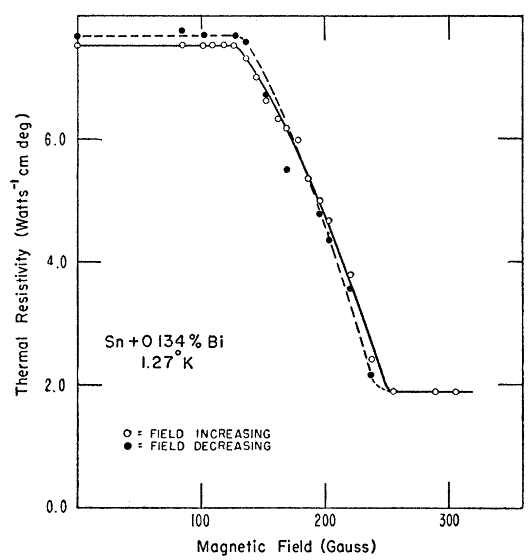

FIG. 5. The thermal resistivity of tin+0.134 percent bismuth in a transverse magnetic field at 1.59°K.

[9] H. van Dijk and D. Shoenberg, Nature 164, 151 (1949).

[10] J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. 23, 213 (1952).

[11] M. Desirant and D. Shoenberg, Proc Roy. Soc. (London) A194, 63 (1948).

the destruction of this circulation current by the transverse lamina of normal material present in the intermediate state. Since the existance of a circulation current requires, however, that the Meissner effect be incomplete in the specimen under consideration, this hypothesis is applicable only to alloys or "hard" superconductors, and would predict no anomalous thermal resistance in the soft superconductors here reported.

Furthermore, a calculation of the heat transport to be expected by such a circulation current, assuming very favorable conditions, namely a residual resistance comparable to that of a pure metal, a driving emf for the normal component equal to the thermal emf between the pure metals composing the alloy, and the entire cross section of the specimen available for the normal current flow, leads to a figure several orders of magnitude smaller than the observed anomalies.

A second hypothesis[7] is based on Hulm's[12] suggestion that the heat transport by the lattice is important in the superconducting state. It is proposed that as the specimen enters the intermediate state the scattering of lattice waves by electrons increases rapidly, thus reducing the heat transport by the lattice, while the heat transport by the electrons increases initially more slowly, thus leading to a maximum in the total resistance. This implies that the intermediate state is distinguished from the normal and superconducting states by having a normal electron density differing from either of these states. While such is undoubtedly the case on the average throughout the specimen, it is not true for any particular region. According to the present understanding of the intermediate state in a long, thin cylinder,[1,3] the structure consists of laminae, alternately normal and superconducting, perpendicular to the specimen axis. A heat current flowing parallel to the specimen axis, then, may be considered to flow through a group of thermal resistances in series, these having alternately the resistance of a normal and of a superconducting region, leading to the conclusion that the total thermal resistance is

$$\omega = \alpha\omega_n + (1-\alpha)\omega_s, \tag{1}$$

where ω_n and ω_s are the resistances in the normal and superconducting states, respectively, and α is the fraction of the specimen in the normal state. This clearly gives a linear dependence of ω upon α, and thus, also, according to the intermediate-state magnetization measurements of Desirant and Shoenberg,[11] upon the applied magnetic field.

If we are to accept this picture of the intermediate state, it appears that the anomalously high thermal resistance in the intermediate state must be associated with some new resistance mechanism not present in either the superconducting or the normal states. It seems reasonable to assume that the scattering of either electrons[7] or lattice waves[13] at the superconducting-normal region boundaries gives rise to this additional intermediate-state resistance. One would not expect this boundary scattering resistance to be significant in specimens where the phonon or electron mean free paths due to other scattering mechanisms are short compared to the distance between boundaries; hence it is not surprising that in our Sn-Bi alloy specimen the impurity scattering masks any such boundary scattering and the thermal resistance does, indeed, approximate Eq. (1).

The drastic reduction in the density of normal electrons in the superconducting state at temperatures appreciably below the transition temperature indicates that, since in this temperature region the conduction electrons are the chief scattering mechanism for phonons in a metal,[14] the heat transport by the lattice should be much greater in the superconducting than in the normal state. At sufficiently low temperatures, the thermal resistance in the superconducting state should then be similar to that of an insulating crystal. de Haas and Biermasz[15] have shown that insulating crystals may have in this temperature region thermal conductivities of several watts cm^{-1} deg^{-1}, so in superconducting metals it appears likely that a comparable lattice conductivity should be present in parallel with the residual electronic conductivity.

The measurements of de Haas and Biermasz indicate that a phonon mean free path of several millimeters is associated with such values of heat transport. Comparing this figure with the value of 0.1 mm found by Andrew[16] for the mean free path of an electron in tin at 4.2°K and the separation of about 0.1 mm of the normal-superconducting boundaries, it appears likely that the observed intermediate-state resistance maximum is due to scattering of phonons at the boundaries.

Clearly, however, it is premature to claim any explanation as final until more quantitative data is available. Further study of the dependence of the anomalous resistance upon specimen dimensions and impurity concentration would be particularly useful.

We are indebted to the other members of the Yale University low temperature group for assistance in acquiring this data, and particularly to Dr. G. B. Yntema, who generously loaned the apparatus used in the electrical resistance measurements.

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