MASTER

THERMOELECTRIC EFFECT IN A NONEQUILIBRIUM SUPERCONDUCTOR

CONF-770859--1

Charles M. Falco

Prepared for
International Conference on
Thermoelectric Effects in Metallic Conductors
East Lansing, MI
August 10-12, 1977

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

U of S - ANL - URGENT

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

**operated under contract W-31-109-Eng-38 for the
U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION**

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Energy Research and Development Administration, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie-Mellon University
Case Western Reserve University
The University of Chicago
University of Cincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
Iowa State University
The University of Iowa

Kansas State University
The University of Kansas
Loyola University
Marquette University
Michigan State University
The University of Michigan
University of Minnesota
University of Missouri
Northwestern University
University of Notre Dame

The Ohio State University
Ohio University
The Pennsylvania State University
Purdue University
Saint Louis University
Southern Illinois University
The University of Texas at Austin
Washington University
Wayne State University
The University of Wisconsin

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights. Mention of commercial products, their manufacturers, or their suppliers in this publication does not imply or connote approval or disapproval of the product by Argonne National Laboratory or the U. S. Energy Research and Development Administration.

Thermoelectric Effect in a Nonequilibrium Superconductor^{*}

Charles M. Falco

Argonne National Laboratory, Argonne, Illinois 60439

By acceptance of this article, the publisher or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering the article.

^{*}Work performed under the auspices of the U. S. Energy Research and Development Administration.

As Ginzburg¹ first noted, there exists in a superconductor the possibility of a simultaneous flow of a normal current of density $\vec{j}_n = L_T(-\vec{\nabla}T)$ and a supercurrent $\vec{j}_s = -\vec{j}_n$. Recently² calculations based on the two fluid model have predicted that this flow of normal current in a superconductor will give rise to a non-quantized contribution to the magnetic flux in a loop made up of two different superconductors. Experimental data³⁻⁵ indicate the existence of such a magnetic flux with a value of as much as five orders of magnitude⁵ larger than predicted by theory. However, more recent work⁶ has suggested that this magnetic flux may be due to the temperature dependence of the penetration depth. This discrepancy, coupled with the opportunity to study quasiparticle transport and relaxation processes in a nonequilibrium superconductor, prompted us to make measurements of the pair and quasiparticle electrochemical potentials in a superconductor held in a temperature gradient. It has been predicted⁷ that in nonequilibrium situations in which the electron and hole branches of the quasiparticle excitation spectrum are unequally populated, the quasiparticles in a superconductor may be described by a different electrochemical potential than that which describes the pairs. This paper reports initial results showing experimental evidence for a pair-quasiparticle electrochemical potential difference in a superconductor in a temperature gradient.

A normal metal tunnel junction and superconducting metal probe were placed in a nonequilibrium region of a thin film superconductor. It has been shown¹² that this allows a direct measurement of the quasiparticle and pair potentials to be made. A strip of 99.999% purity Sn in the form of a "T" (Fig. 1) of width ~ 2 mm, length ~ 2 cm and thickness $\sim 2000-4000$ Å was evaporated onto a 1 mm thick sapphire substrate and oxidized. A small rectangle of Cu (~ 2.5 mm $\times$ 0.6 mm $\times$ 1.5 μ m) was then evaporated in the center of the strip

to form the normal probe. Finally, a 3000 Å Pb film was deposited over the Cu to reduce the normal probe resistance. This was necessary in order to reduce the Johnson noise in the sample and thus enable very low voltage measurements to be made. The high thermal conductivity of the sapphire ensured that the temperature gradient in the vicinity of the junctions was constant to within 0.1%.

Additional leads attached to the sample enabled the resistance of the normal probe to be measured by applying a current between X and Z (Fig. 1) and measuring the voltage developed between X and Y. Typical junctions had a resistance of $1-4 \times 10^{-5} \Omega$ immediately below the T_c of Sn which, as shown in Fig. 2, increased approximately at the rate expected for a Normal-Superconductor tunnel junction. The voltage between X and Y was measured with a SQUID voltmeter in a feedback configuration. The resolution of this system was approximately 2×10^{-13} volts rms with a 1 sec averaging time. It was also possible to inject a current through the normal probe to verify that Josephson tunneling was not taking place through the Cu. Such tunneling would couple the pair electrochemical potentials in the Sn and Pb making the measurements described here impossible.

All measurements were conducted in a screened room with mu-metal and superconducting shields reducing the field in the sample vacuum chamber to less than 10^{-6} T. The temperatures of both ends of the sample were measured to within an uncertainty of less than 1 mK using calibrated Ge resistors. Any leaks in the vacuum chamber (which would reduce the temperature gradient along the sample) could be readily detected as a reduction of the thermal time constant of the system (approximately 15 minutes).

The voltage developed per unit temperature difference for one sample is shown in Fig. 3. All samples which showed no evidence of a superconducting short through the normal probe exhibited the same behavior shown in this

figure, except that the absolute magnitudes varied by as much as a factor of 8. This is not too surprising as we are measuring a quantity proportional to a thermal transport coefficient. This coefficient is extremely sensitive to impurities and can be expected to vary widely for thin film specimens. The data shown in Fig. 3 have the lowest magnitude of those measured. This thermally induced potential is linear in VT over at least a factor of ten change in the temperature gradient. Reversing the sign of VT does not reverse the sign of the observed voltage and leaves the magnitude unchanged to within 15-30% as shown in Fig. 4. This failure to reproduce the magnitude of V for opposite signs of VT is perhaps due to a small normal thermoelectric voltage contribution from the Cu. Such a conventional thermoelectric potential would change sign with VT and could cause the observed asymmetry.

This potential is reminiscent of that observed by Clarke⁸ in his branch mixing experiment. In that experiment an imbalance in the population of the electron and hole branches of the excitation spectrum created by tunnel injection led to a measurable potential difference between normal and superconducting probes. Similar effects have also been observed near superconductor/normal boundaries carrying a transport current⁹ and within Josephson weak links excited by rf radiation.¹⁰ In all of these experiments a flow of normal excitations is accompanied by a difference between the quasiparticle and pair electrochemical potentials. Tinkham has shown⁷ that such quasiparticle-pair electrochemical potential differences can only arise from an electron-hole branch imbalance. These results, together with the data presented here, is evidence that such a branch imbalance induced by a thermally generated quasiparticle current is the cause of the potential measured in the present experiment.

To first order, a branch imbalance should not arise in a superconductor in a thermal gradient since the increase in electron-like excitations and decrease in hole-like excitations on one side of the Fermi surface should be balanced by the opposite effect on the other side of the Fermi surface. However, there is not exact electron-hole symmetry since the two branches of the excitation spectrum have opposite curvature. This lack of symmetry, coupled with an energy dependent relaxation time,¹¹ will give rise to a branch imbalance.

If we assume that such a branch imbalance exists in our experiment, it is possible to extract information on the thermal transport coefficient for the quasiparticles from the data of Fig. 3. The quasiparticle current produced by the temperature gradients involved in this experiment should lead to a small asymmetry near the bottom of the electron and hole branches of the excitation spectrum. Another way a similar asymmetry could be produced is by injecting quasiparticles into a superconductor at very low voltages via a tunnel junction. Although to obtain detailed information will require a theory directly applicable to this experiment, the data of Fig. 3 can be interpreted using the theory of Tinkham⁷ for tunneling generation of an electron-hole imbalance in the appropriate limit of small injection voltages. In this limit the voltage is given by

$$V \leq \frac{If(\Delta)}{2e^2 N(0)\Omega g_{NS}^2} \tau_Q \quad (eV_{inj} \ll \Delta(T)) \quad (1)$$

where I is the injected quasiparticle current, $f(\Delta)$ is a Fermi factor, $N(0)$ is the one spin density of states at the Fermi surface, Ω is the volume sampled by the voltage probes, g_{NS} the normalized low-voltage conductance of the NS junction (Fig. 2) and τ_Q is the branch imbalance relaxation time.⁸ The equality sign in Eq. (1) is valid near T_c . Since there exist both theory¹¹

and experiments¹² for τ_Q in Sn, and since all of the other quantities in Eq. (1) are known or can be measured, it is possible to use Eq. (1) to extract a value for the transport coefficient L_T by assuming $I = L_T(-\nabla T)$. The results of such an analysis for three different samples are shown in Fig. 4.

Due to the small temperature gradients necessary and the concomitant small voltages developed, it is not possible at present to obtain information very near T_c ; at lower temperatures we find the data to fall off smoothly, apparently to zero. In absolute magnitude, $L_T = 2 - 16$ A/cm-K near T_c . Noting that in the normal state $L_T = \sigma S$ where σ is the electrical conductivity and S is the thermoelectric power, this transport coefficient corresponds to normal state thermoelectric powers between 3 and 24 $\mu\text{V/K}$. This is about what would be expected from measurements on the normal state thermoelectric power in Sn just above T_c .¹³

A theory for L_T has been developed by Gal'perin et al.¹⁴ This theory, which does not explicitly take into account the character of the electron and hole branches of the excitation spectrum, describes quasiparticle relaxation using the same mean free path appropriate to the normal state. The result of this theory with a one parameter fit to the data at T_c is shown as a solid line in Fig. 4. As can be seen, the fit with experiment is good. However, without a reliable theory for interpreting the experimentally measured voltages in terms of a transport coefficient, one cannot comment further on this agreement.

In summary, we have observed a difference between the quasiparticle and pair electrochemical potentials in thin film superconductors held in a temperature gradient. This potential diverges at low temperature and, within the resolution of our data, approaches a constant at T_c . It is possible to use our data to extract a value for the thermal transport coefficient L_T appropriate for the normal excitations in the superconductor. Unlike the experiments on

bi-metallic superconducting loops,³⁻⁵ this analysis leads to values for L_T near T_c which are in rough agreement with those in the normal state. We also find L_T to fall off to zero at low temperatures. However, in the absence of a satisfactory theory to interpret these observations, this agreement with normal state values must be regarded as very approximate. In particular, a satisfactory theory for thermoelectric effects in nonequilibrium superconductors must take into account the directional dependence of the distortion of the Fermi surface by a thermal gradient as well as the various relaxation mechanisms appropriate in the nonequilibrium state.

I would like to thank Drs. K. E. Gray, R. A. Sacks, and I. K. Schuller for numerous discussions and T. R. Werner for a critical reading of the manuscript.

REFERENCES

1. V. L. Ginzburg, J. Phys. USSR 8, 148 (1944).
2. J. C. Garland and D. J. Van Harlingen, Phys. Letters 47A, 423 (1974).
3. C. M. Pegrum, A. M. Guénault, and G. R. Pickett, Low Temperature Physics LT-14, edited by M. Krusius and M. Vuorio (North-Holland, Amsterdam, 1975), Vol. II, p. 513.
4. C. M. Falco, Solid State Commun. 19, 623 (1976).
5. D. J. Van Harlingen and J. C. Garland, to be published.
6. C. M. Pegrum and A. M. Guénault, Phys. Lett 59A, 393 (1976).
7. M. Tinkham, Phys. Rev. B 6, 1747 (1972).
8. J. Clarke, Phys. Rev. Letters 28, 1363 (1972).
9. M. L. Yu and J. E. Mercereau, Phys. Rev. B 12, 4909 (1975).
10. M. L. Yu and J. E. Mercereau, Phys. Rev. Letters 37, 1148 (1976).
11. S. B. Kaplan, C. C. Chi, D. N. Langenberg, J. J. Chang, S. Jafarey, and D. J. Scalapino, Phys. Rev. B 14, 4854 (1976) and Phys. Rev. B 15, 3567 (E) (1977).
12. J. Clarke and J. L. Paterson, J. Low Temp. Phys. 15, 491 (1974).
13. G. T. Pullan, Proc. Roy. Soc. London 217A, 280 (1953).
14. Yu. M. Gal'perin, V. L. Gurevich, and V. I. Kozub, Zh. Eksp. Teor. Fiz. 66, 1387 (1974) [Sov. Phys. - JETP 39, 680 (1974)].

FIGURE CAPTIONS

- Fig. 1 Sample configuration. The Sn film is deposited on a sapphire substrate and oxidized; followed by the Cu electrode and Pb strip. 0.08 mm diameter Nb wires connected to a SQUID voltmeter allow the potential difference between points X and Y to be measured.
- Fig. 2 Normalized low voltage conductance g_{NS} for four samples as a function of temperature compared with theory (solid line).
- Fig. 3 Potential difference between X and Y per unit temperature difference across the sample versus temperature for a 2510 Å Sn film.
- Fig. 4 Measured potential difference as a function of VT for a 2890 Å Sn film. $T/T_c = 0.90$.
- Fig. 5 Plot of the transport coefficient L_T normalized to its value at T_c versus temperature for three samples. The solid line is from a theory by Gal'perin et al.¹⁴ in which $L_T(T_c)$ is taken as the value in the normal state just above T_c .