Transmission of Far-Infrared Radiation through Thin Films of Superconducting Amorphous Bismuth and Gallium and Beta-Phase Gallium*†

RICHARD E. HARRIS‡ AND D. M. GINSBERG
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801
(Received 17 July 1969)

The ratio T_s/T_n of the far-infrared radiation transmitted through a thin film in the superconducting state to that transmitted through it in the normal state has been measured at 1.1°K for thin-film samples of amorphous bismuth and gallium and samples of partially annealed (β-phase) gallium. The transition temperature T_c of each film was also measured. The sample thicknesses were approximately in the range 50–200 Å. Numerical calculations based on the strong-coupling theory of superconductivity and on tunneling data produced theoretical values of T_s/T_n which were in reasonably good agreement with the experimental results. The only adjustable parameter was the energy-gap width $2\Delta_0$. The quantities T_c and $2\Delta_0$ decrease with increasing film resistance. The shift in T_c has been previously observed by Naugle and Glover in amorphous bismuth and gallium. The abrupt resistance change in these materials at about 19°K, which is characteristic of thicker amorphous films, appeared instead as a more gradual change in resistance beginning at higher temperatures.

I. INTRODUCTION

SINCE the first far-infrared measurements on superconductors were performed by Glover and Tinkham,[1] a number of other far-infrared investigations have been made on superconducting metals[2–9] and alloys.[10,11] The agreement between experiment and theory has generally become closer as radiation detectors and optical systems have been improved and as the theory has been developed. Several reviews include descriptions of these developments.[12–14]

The theory of Mattis and Bardeen[15] deals with superconductors in which there is weak coupling between the conduction electrons and the phonons. This theory is easily applied to materials for which the coherence length of the pure unstrained superconductor is large compared with the electromagnetic penetration depth or the electron mean free path in the sample being studied (the Pippard limit or the extreme local limit, respectively). The agreement between experiment and this theory is satisfactory.[16] Calculations by Miller[17] and by Ginsberg,[18] based on the theory of Mattis and Bardeen, have been made for weak-coupling superconductors which are in neither of these limits. Finally, Nam[19] has extended the theory to strong-coupling superconductors[20] in the Pippard limit or the extreme local limit.

Nam's calculations of the frequency-dependent superconducting conductivity $\sigma_s=\sigma_1-i\sigma_2$ of lead, a strong-coupling superconductor, have been found by Palmer and Tinkham to fit the values determined by their measurements of far-infrared transmission and absorption by lead films.[7] The purpose of this work is to test the theory further by investigating three other strong-coupling superconductors, amorphous bismuth and gallium and partially annealed (β-phase) gallium.[21] We have used Nam's theory to calculate the ratio of σ_s to the normal-state conductivity σ_n of these materials from the complex gap parameter functions which have been determined in tunneling experiments by Chen, Chen, Leslie, and Smith[22] (amorphous bismuth and

* Research supported in part by the National Science Foundation and in part by the Advanced Research Projects Agency under Grant No. SD-131.
† Based in part on the Ph.D. thesis of R. E. Harris, University of Illinois, 1969 (unpublished).
‡ Present address: United Aircraft Research Laboratories, East Hartford, Conn. 06108.

1 R. E. Glover and M. Tinkham, Phys. Rev. **108**, 243 (1957).
2 D. M. Ginsberg and M. Tinkham, Phys. Rev. **118**, 990 (1960).
3 P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).
4 J. D. Leslie *et al.*, Phys. Rev. **134**, A309 (1964).
5 S. L. Norman and D. H. Douglass, Jr., Phys. Rev. Letters **17**, 875 (1966); **18**, 339 (1967).
6 H. D. Drew and A. J. Sievers, Phys. Rev. Letters **19**, 697 (1967).
7 L. H. Palmer and M. Tinkham, Phys. Rev. **165**, 588 (1968); L. H. Palmer, Ph.D. thesis, University of California at Berkeley, 1966 (unpublished).
8 S. L. Norman, Phys. Rev. **167**, 393 (1968).
9 W. S. Martin and M. Tinkham, Phys. Rev. **167**, 421 (1968).
10 J. D. Leslie and D. M. Ginsberg, Phys. Rev. **133**, A362 (1964).
11 R. L. Cappelletti, D. M. Ginsberg, and J. K. Hulm, Phys. Rev. **158**, 340 (1967); G. J. Dick and F. Reif, *ibid.* **181**, 774 (1969).
12 M. Tinkham, *Superconductivity* (Gordon and Breach, Science Publishers, Inc., New York, 1965).
13 M. Tinkham, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland Publishing Co., Amsterdam, 1966).
14 D. M. Ginsberg and L. C. Hebel, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, Inc., New York, 1969), Chap. 4.
15 D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958).

16 The far-infrared transmission data in Ref. 2 for tin and indium films agree within 7 and 5%, respectively, with the theoretical values if the frequency scale is adjusted by a constant factor. This agreement should be considered satisfactory, especially because of possible effects stemming from differential contraction between the films and their substrates, and because of the somewhat primitive far-infrared techniques to which one was limited at that time.
17 P. B. Miller, Phys. Rev. **118**, 928 (1960).
18 D. M. Ginsberg, Phys. Rev. **151**, 241 (1966).
19 S. B. Nam, Phys. Rev. **156**, 487 (1967). This paper contains the result of an incorrect numerical calculation of the imaginary part of the conductivity for lead. The error was corrected by Nam and the correct result supplied by private communication.
20 D. J. Scalapino, Ref. 14, Vol. 1, p. 449.
21 W. Buckel, Z. Physik **138**, 136 (1954).
22 J. T. Chen, T. T. Chen, J. D. Leslie, and H. J. T. Smith, Phys. Letters **25A**, 679 (1967); Phys. Rev. Letters **22**, 526 (1969); (private communication). The numerical values of the complex gap parameter are to be published.

gallium) and by Wühl, Jackson, and Briscoe[23] (amorphous and β-phase gallium). From the conductivity ratio σ_s/σ_n, we have calculated the ratio T_s/T_n of the transmissivity of films composed of these materials in the superconducting state to that in the normal state in the spectral region where the photon energy $\hbar\omega$ is comparable to the energy-gap width $2\Delta_0$. We compare the theoretical values of T_s/T_n to values which we have determined experimentally. Our samples should be accurately described by Nam's theory, since they are close to the extreme local limit.

II. EXPERIMENTAL TECHNIQUES

A. General Description

The basic methods used in this experiment were developed from those of Ginsberg and Tinkham.[2] The cryostat, which has been used previously in this laboratory,[24] was modified for the present experiment. It had one nitrogen tank and two helium tanks. It permitted us to produce a sample film of the desired thickness and measure its far-infrared properties without exposing the sample to air or warming it above 5°K, unless we wished to measure its transition temperature or to anneal it at some higher temperature. The sample was surrounded by a 4.2°K heat shield during the measurements. The radiation was allowed to pass alternately through the substrate supporting the film and through an identical dummy substrate without a film, so the beam intensity could be monitored for each far-infrared frequency. The film could be forced into the normal state by means of a dc current passing through the film, so the ratio T_s/T_n could be determined. Many systematic errors cancel out in this ratio. Furthermore, it is directly related to the ratio σ_s/σ_n of the superconducting to normal conductivity, which is the theoretical quantity predicted by the theory. One finds

$$T_s/T_n=(B+1)^2/|B+\sigma_s/\sigma_n|^2, \qquad (1)$$

where $B=(n+1)R/Z_0$, n is the refractive index of the substrate (2.10 in this experiment), R is the resistance which the film would have if it were square, and Z_0 is the impedance of free space (377 Ω).

B. Far-Infrared Techniques

The far-infrared radiation was generated, chopped at 39 Hz, and filtered in the same grating monochromator which has been previously used in this laboratory.[11] The radiation filters which we used to remove harmonic frequencies of the desired fundamental far-infrared frequency are listed elsewhere.[25] The bandwidth of the far-infrared radiation in the beam varied between 3.0 and 4.5% half-width at half-maximum.

The radiation was led into the cryostat through a monel light pipe with 0.5 in. diam and 0.008 in. wall thickness.[26] This light pipe was thermally grounded to the cryostat's 77°K heat shield. For thermal isolation, there was a gap at the low-temperature end of the light pipe which separated it from a wedge-shaped, sooted, crystal-quartz radiation filter with a thickness varying from 0.080 to 0.086 in. to average over multiple internal reflections. The z axis of the quartz was perpendicular to one of the filter's large surfaces. This quartz filter was thermally grounded to the 1.1°K tank of liquid helium.

For one of the samples (Bi-1) a potassium bromide filter was also placed in the light pipe and was held at about 77°K. The thickness of this wedge-shaped filter varied from 0.232 to 0.240 in. It enabled us to test for radiation impurity in the spectral range from 15 to 30 cm^{-1}, but made it impossible to obtain accurate data at higher frequencies. A comparison of our results for sample Bi-1 with those for our other amorphous bismuth samples indicates that the radiation filtering was adequate for all of our samples. However, we will describe below in Sec. II E evidence that the radiation was not perfectly pure.

After passing through the sample and the sample substrate or through the dummy substrate, the radiation was focused by a brass cone onto the bolometer detector. Multiple reflections from the back of the substrate were decreased by pieces of radiation-absorbing foam material,[27] $\frac{1}{8}$ in. thick, which were placed in the region between the light pipe and the substrate, in a $\frac{3}{8}$-in. gap between the substrate holder and the brass cone, and around the inside of the brass radiation shield which contained the bolometer. Four coats of black paint[28] also covered the entire inner surface of the 4.2°K heat shield and the inside of the bolometer's radiation shield. Measurements showed that the paint and especially the foam material were very good radiation absorbers.[25]

The bolometer detector was a single crystal of gallium arsenide doped with $1\text{–}2\times10^{17}$ atoms/cm^3 of zinc.[29] The bolometer's dimensions were 1 mm×1 cm ×0.08 mm thick. The electrical leads to the bolometer were 0.127-mm-diam copper. The length of each of these leads between the bolometer and the 1.1°K heat sink was 1.3 cm. The thermal conductance between the bolometer and the heat sink was about 7×10^{-6} W/°K at the operating temperature, and the thermal time

[23] H. Wühl, J. E. Jackson, and C. V. Briscoe, Phys. Rev. Letters **20**, 1496 (1968); (private communication). The numerical values of the complex gap parameter are to be published.

[24] J. S. Shier and D. M. Ginsberg, Phys. Rev. **147**, 384 (1966).

[25] R. E. Harris, Ph.D. thesis, University of Illinois, 1969 (unpublished).

[26] R. E. Harris, R. L. Cappelletti, and D. M. Ginsberg, Appl. Opt. **5**, 1083 (1966).

[27] Eccosorb LS-22 foam sheet, $\frac{1}{8}$ in. thick, available from Emerson and Cuming, Inc., Canton, Mass.

[28] Nextel Brand Velvet Coating (Black), available from 3M Reflective Products Division, 2501 Hudson Road, St. Paul, Minn. 55119.

[29] Obtained from Monsanto Corp., 800 N. Lindbergh Blvd., St. Louis, Mo.

constant was about 2 msec. In preparing to attach the leads to the bolometer, copper was evaporated onto each end of the gallium arsenide crystal, which was then heated to 400°C in a vacuum for several hours. This is similar to the procedure recommended by Wheeler and Hill.[30] The copper leads were then soldered to the evaporated copper with indium in a hydrogen atmosphere.

A number of germanium bolometers were also tried. These were doped with antimony or gallium.[31] Ohmic contacts were easily made, and these detectors had about the same sensitivity as the gallium arsenide device. However, they all produced at least twice as much noise as the gallium arsenide bolometer.

The bolometer signal was measured and displayed by means of a lock-in amplifier and chart recorder.

C. Sample Production

The substrate for each sample was an optically polished crystal-quartz plate. To average over multiple internal reflections in the plate, its thickness varied from 0.070 to 0.090 in. The z axis of the quartz was perpendicular to one of the plate's large faces. Four gold electrodes, previously evaporated onto the sample substrate, enabled us to measure the film resistance with a four-terminal method. The sample material for each film was evaporated from a molybdenum boat which was located outside the 77°K heat shield, and which was displaced sideways from the film's center by 6° so the boat would not interfere with the light pipe. The distance between the boat and the substrate was 3.5 in. The purity of the starting materials was 99.999% for bismuth and 99.99% for gallium. Each film evaporation took approximately 15 sec. Before the evaporation began, the material in the boat was cleaned up by evaporating some of the metal onto a shutter in the 77°K heat shield which was opened only during the evaporation.

During the condensation of each sample on its substrate, the helium bath cooling it was pumped down to 1.2°K. The bismuth films were found to be in the normal state during the evaporations, but the gallium films were superconducting. Therefore, the surface of the substrate must have been below about 8°K during the film formation.

D. Other Procedures

Temperatures were measured by a calibrated germanium resistance thermometer. Temperature control during the measurement of a sample's transition temperature was provided by a carbon resistance thermometer and an electronically controlled heater. Short term regulation of 1 m°K near 7°K was achieved. Measuring currents below 120 nA were used in ac resistance measurements to determine the transition temperatures of the samples.

For normal-state far-infrared transmission measurements, the sample film was driven normal by a dc current. Joule heating set in as the film became normal. To avoid annealing the sample, the current was automatically reduced by a factor between 3 and 5 as the film's resistance increased to its normal-state value. After a film had been driven into the normal state for the first time, its transition temperature was found to have decreased by not more than 10 m°K.

The Joule heating which has just been described changed the bolometer's temperature by about 0.3°K, and altered its sensitivity. Also, the bolometer's temperature was a little lower (and its sensitivity higher) when the sample was in the far-infrared beam than when the dummy substrate was in the beam, because of unchopped radiation coming through the light pipe. Means were devised to correct for these effects by periodically determining the bolometer's resistance during the far-infrared measurements.[2,25] The correction to T_s/T_n amounted to about 5%. This correction was refined by making some transmission measurements with the film in the superconducting state and with the effect of the Joule heating in the film simulated by a heater.

The normal-state transmissivity of each film was found to be independent of far-infrared frequency. Therefore, normal-state data were obtained for only about one-third as many frequencies as superconducting data. These normal-state data are presented elsewhere.[25] For each sample, the value of T_n at each far-infrared frequency was taken as the average of all the values determined at the various frequencies.

Although film-thickness measurements were not required to analyze our data, we made such measurements for most of our samples. After the far-infrared measurements on a sample were completed, it was warmed up to room temperature and transferred to a vacuum coater in which a reflective layer of silver was evaporated onto it.[32] The film thickness was then determined by multiple interferometry.[33,34]

E. Uncertainties

Discrepancies in repeated measurements of T_s/T_n indicated random errors averaging about 1.5%. The measured transmission curves which are presented below contain discontinuities, up to about 5% in size, at the far-infrared frequencies at which the main

[30] R. G. Wheeler and J. C. Hill, J. Opt. Soc. Am. **56**, 657 (1966).

[31] The resistivity of these samples had been previously measured. See E. A. Davis and W. Dale Compton, Phys. Rev. **140**, A2183 (1965).

[32] Warming the samples before application of the reflective coating may have produced small errors in the measured film thicknesses. See A. v. Bassewitz and G. v. Minnigerode, Z. Physik **181**, 368 (1964).

[33] S. Tolansky, *Multiple-Beam Interferometry of Surfaces and Films* (Oxford University Press, New York, 1948), p. 147.

[34] H. E. Bennett and J. M. Bennett, Phys. Thin Films **4**, 1 (1967).

grating in the monochromator was changed. These discontinuities could be "explained" by assuming that the grating used at the frequency below the bump allowed more low-frequency radiation contamination to pass than the grating used at the frequency above the bump. We were not able to remove this apparent contamination by covering various surfaces in the monochromator with the previously mentioned lossy foam material. Similar discontinuities are seen in the data of other experimenters.[7]

III. CALCULATION OF THEORETICAL CURVES

We can calculate the theoretically predicted transmission ratio from Eq. (1) if we know σ_s/σ_n. To show the effect of strong electron-phonon coupling, we have done this both from the expressions of Mattis and Bardeen[15] for a weak-coupling BCS-model superconductor[35] and from the expressions of Nam[19] for a strong-coupling superconductor. The relevant equations are Eqs. (3.9) and (3.10) of the former paper and Eqs. (1.5)–(1.7) of the latter. [Since $\exp(-\Delta_0/kT)\ll 1$, we have been able to use Nam's expressions in the zero-temperature limit with no appreciable error.]

Both the weak-coupling theory and the strong-coupling theory predict that in the zero-temperature limit $\sigma_1/\sigma_n=0$ when $\hbar\omega<2\Delta_0$. Equation (1) shows that T_s/T_n increases with photon energy in that region, because σ_2/σ_n decreases. The transmission ratio is increasing because less energy is being reflected from the superconducting film. At the gap edge, where $\hbar\omega=2\Delta_0$, a discontinuous change is expected in the slope of the transmission curve because energy absorption is setting in. However, T_s/T_n is expected to continue to increase above the gap edge if the film resistance is small enough, because of the further decrease in σ_2/σ_n. The transmission curve must go through a maximum at or slightly above the gap edge and must decrease toward unity at sufficiently high frequencies.

Since the peak in the transmission curve does not necessarily occur at the gap edge, and since the expected

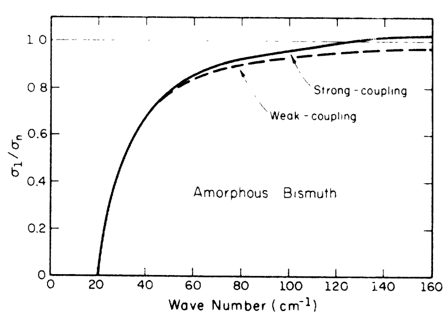

FIG. 1. Ratio of the real part σ_1 of the superconducting conductivity to the normal conductivity σ_n as a function of the frequency, calculated for amorphous bismuth by Nam's strong-coupling theory from the tunneling results of Chen *et al.* (Ref. 22).

[35] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

discontinuity in slope is too small to be seen in the experimental data, a precise value for the energy-gap width $2\Delta_0$ can be determined only by fitting theoretical curves to the data.

In the weak-coupling BCS theory, the energy-gap parameter Δ is a real constant, independent of quasi-particle energy E. In the strong-coupling theory, Δ is a complex energy-dependent function $\Delta(E)=\Delta_1(E)+i\Delta_2(E)$. Nam's equations express σ_s/σ_n as an integral of a function which involves the gap function $\Delta(E)$. In evaluating Nam's expressions, we have used the values of $\Delta(E)$ which have been determined in tunneling experiments on amorphous bismuth[22] and gallium[22,23] and preliminary tunneling experiments on β-phase gallium.[23]

The values of the gap function which are determined by tunneling experiments extend only down approximately to the energy Δ_0. To calculate σ_2/σ_n we needed to know $\Delta(E)$ down to zero energy. To find $\Delta(E)$ in the range $E=0$ to Δ_0 we used two properties of the gap function. First, $\Delta_2(E)=0$ in that energy range. Second, $\Delta_1(E)$ is the Kramers-Kronig transform[36,37] of $\Delta_2(E)$. Therefore, $\Delta_2(E)$ was known down to $E=0$ and $\Delta_1(E)$ could be computed from $\Delta_2(E)$ by evaluating an integral.[38] The region of integration extended to the maximum energy for which $\Delta_2(E)$ was known; the remaining part of the integral was treated as a constant. This constant was determined by requiring that $\Delta_1(E)$ for $E<\Delta_0$ join smoothly to $\Delta_1(E)$ for $E>\Delta_0$.

Our calculations[38] of σ_s/σ_n from the theory of Mattis and Bardeen yielded results which agreed well with those of Miller[17] except for several small errors which Waldram has also noted.[39] Two checks verified our computer program for finding the strong-coupling values of σ_s/σ_n. One of these was a calculation with a real constant gap parameter, which again yielded the Mattis-Bardeen results, as expected. The other check was a calculation of σ_s/σ_n for lead from tunneling data of McMillan and Rowell.[40] The results agreed within 0.1% with those which Shaw and Swihart[41] computed from the same data, using a different method.

The calculated conductivity ratios for amorphous bismuth are given in Figs. 1 and 2. (Similar curves are available for amorphous gallium[25] and β-phase gallium.[42]) It is seen that strong-coupling corrections have only a small percentage effect on σ_1/σ_n, particularly near the gap edge, but have a sizeable percentage effect

[36] L. P. Kadanoff (private communication).

[37] C. Kittel, *Elementary Statistical Physics* (John Wiley & Sons, Inc., New York, 1958), p. 210.

[38] The computer programs for the weak- and the strong-coupling calculations are described and listed in R. E. Harris, University of Illinois Technical Report No. 180, 1969 (unpublished).

[39] J. R. Waldram, Advan. Phys. **13**, 1 (1964).

[40] W. L. McMillan and J. M. Rowell, Phys. Rev. Letters **14**, 108 (1965).

[41] W. Shaw and J. C. Swihart, Phys. Rev. Letters **20**, 1000 (1968).

[42] The numerical values of σ_s/σ_n for β-phase gallium are available from the present authors.

TABLE I. Sample characteristics.

Film	T_c(°K)	$2\Delta_0$(cm^{-1})	$2\Delta_0/kT_c$	$R(\Omega/\square)$ ($\pm 0.5\%$)	t(Å) (± 20 Å)	$\rho(\mu\Omega$ cm)	$T_{\text{transformation}}$(°K)
Bi-1	5.82±0.03	$18.75_{-0.3}^{+0.8}$	$4.63_{-0.10}^{+0.22}$	87.5	143	125±18	
Bi-2	5.68±0.03	$18.63_{-0.3}^{+0.5}$	$4.72_{-0.10}^{+0.15}$	132.7	112	149±27	26±3
Bi-3	5.35±0.03	17.7 ±0.6	4.76±0.19	246			
Bi-4	5.97±0.03			51.8			21±2
Bi-5	5.87±0.03			90.1	200	180±18	>29
Bi-6	6.11±0.03			1.3±0.1			19±2
Ga-1	8.05±0.07	24.33±1.1	4.35±0.24	51	210	107±11	48–82
Ga-2	7.87±0.07				48		38±5
Ga-3	7.09±0.07						>31
Ga-4	8.45±0.07			0.18±0.01			19±2
Ga-1 (77°K)	7.74±0.07	20.8 ±1.0	3.87±0.22	29.9	210	63±6	200±15
Ga-1 (200°K)	6.55±0.07	17.95±0.7	3.94±0.20	24.0	210	50±5	
Ga-2 (77°K)	6.31±0.07				48		110–240
Ga-4 (20°K)	6.26±0.07			0.6±0.1			

on σ_2/σ_n. This effect on σ_2/σ_n is largely due to the part of σ_2 which is the Kramers-Kronig transform[37] of the δ function in σ_1 occurring at zero frequency.[12] This part of σ_2 is proportional to $1/\omega$, and has a magnitude which is determined by the integral of σ_1 according to the sum rule.[43,44] Shaw and Swihart[41] have noted that about 99% of the strong-coupling correction to σ_2/σ_n for $\hbar\omega < 2\Delta_0$ in lead is due to the altered magnitude of this $1/\omega$ term. This is also true for β gallium; it is true for amorphous bismuth and amorphous gallium for $\hbar\omega < 5\Delta_0$.

In order to achieve a satisfactory fit between the experimentally determined transmission curves and those which we have calculated from the strong-coupling theory, we have had to scale the frequencies downward for amorphous bismuth and gallium and upwards for β-phase gallium. That is, the frequency scale of the theoretical σ_1/σ_n and σ_2/σ_n curves has been multiplied by a constant factor. Thus, we have one adjustable parameter for each sample. This method of fitting cannot be rigorously defended, but is required by the differences in Δ_0 which are found for different samples of the same material. (For one sample, Ga-1 annealed at 200°K, two adjustable parameters were required because our data were incomplete, as described below in Sec. IV D.)

IV. RESULTS

A. Film Parameters

The samples which we have investigated are characterized in Table I. For each sample which was annealed above 9°K before measurements were made of its transition temperature or electromagnetic properties, the annealing temperature is shown in parentheses next to the film number in the first column of the Table. The transition temperature of each film was taken as that temperature for which the film's electrical resistance was one-half of its normal-state value. The value $2\Delta_0$ of the energy-gap width was determined by scaling the frequency to fit the far-infrared transmission curve to the curve calculated by strong-coupling theory from tunneling data results, as described above in Sec. III. The dc resistance in ohms per square, shown in the fifth column of the Table, was obtained by multiplying the measured resistance of a sample (at about 0.2°K above its transition temperature) by the ratio of its width to its length, to obtain the resistance which the sample would have had if it had been square. Each film thickness t was found by optical techniques, as described above in Sec. II D, and was used to calculate the resistivity ρ listed in the seventh column. The transformation temperature presented in the last column indicates the temperature at which each film's crystal structure began to change as it was warmed up. This transformation was signaled by a steeper irreversible change in the film's electrical resistance.[21] The resistances of some of the samples (Bi-5 and Ga-3) were

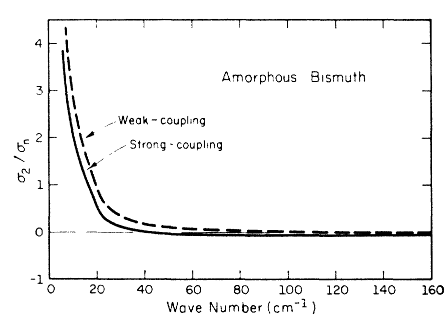

FIG. 2. Ratio of the imaginary part σ_2 of the superconducting conductivity to the normal conductivity σ_n as a function of the frequency, calculated for amorphous bismuth by Nam's strong-coupling theory from the data of Chen *et al.* (Ref. 22).

[43] R. A. Ferrell and R. E. Glover, Phys. Rev. **109**, 1398 (1958).
[44] M. Tinkham and R. A. Ferrell, Phys. Rev. Letters **2**, 331 (1959).

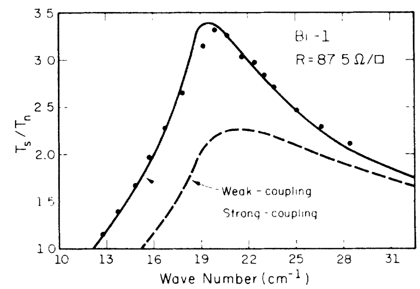

FIG. 3. Experimental points and theoretical curves for the transmission ratio as a function of photon wave number for amorphous bismuth sample Bi-1.

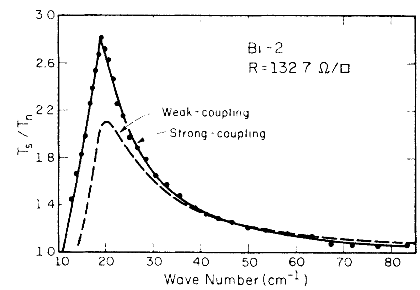

FIG. 4. Experimental points and theoretical curves for the transmission ratio as a function of photon wave number for amorphous bismuth sample Bi-2.

not monitored all the way up to this structural change, so that only lower limits could be placed on their transformation temperatures. Other films (Ga-1 and annealed Ga-2) underwent the structural change while the resistance was not being monitored, so that the transformation temperature was known only to lie somewhere in a rather broad range of temperatures.

Error bars are not shown in the plots of the far-infrared transmission curves, but uncertainties in the measured values are discussed above in Sec. II E. We present plots of the far-infrared data for all samples on which we made reliable transmission measurements, and for which the normal-state resistance was accurately determined.

TABLE II. Comparison with results of other experiments.

Ref.	T_c(°K)	$2\Delta_0$(meV)	$2\Delta_0/kT_c$
Amorphous bismuth			
Reif and Woolf[a]		2.15	
Zavaritski[b]	6	2.370	4.6
Minnigerode and Rothenberg[c]	5.93 ± 0.12	2.33	4.56 ± 0.09
Chen *et al.*[d]	6.11 ± 0.03	2.42 ± 0.02	4.59 ± 0.06
This work[e]	6.11 ± 0.03	2.19 ± 0.08 to $2.32_{-0.04}^{+0.10}$	$4.63_{-0.10}^{+0.22}$ to 4.76 ± 0.19
Amorphous gallium			
Minnigerode and Rothenberg[c]	8.47 ± 0.17	3.29–3.30	4.50 ± 0.08 to 4.52 ± 0.08
Wühl, Jackson, and Briscoe[f]	8.4 ± 0.1	3.26 ± 0.06	4.5 ± 0.1
Chen *et al.*[d]	8.56 ± 0.02	3.32 ± 0.02	4.51 ± 0.04
This work[e]	8.45 ± 0.07	3.02 ± 0.1	4.35 ± 0.24
β-phase gallium			
Minnigerode and Rothenberg[c]	6.21 ± 0.12	2.11–2.15	3.95 ± 0.08 to 4.02 ± 0.08
Wühl, Jackson, and Briscoe[f]	6.2 ± 0.1	2.12 ± 0.04	3.97 ± 0.10
This work[e]	6.26 ± 0.07	2.58 ± 0.13 to 2.23 ± 0.09	3.87 ± 0.22 to 3.94 ± 0.20

[a] F. Reif and M. A. Woolf, Phys. Rev. Letters **9**, 315 (1962).
[b] N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **5**, 434 (1967) [English transl.: Soviet Phys.—JETP Letters **5**, 352 (1967)].
[c] G. v. Minnigerode and J. Rothenberg, Z. Physik **213**, 397 (1968).
[d] Reference 22.
[e] The values of T_c are for thick films and should be directly comparable with the values obtained from other experiments. The values of $2\Delta_0$ and $2\Delta_0/kT_c$ are for the thin films studied. Uncertainties shown are estimated maximum values.
[f] Reference 23.

In Table II, we list our measured values of T_c and $2\Delta_0$ together with the values of those quantities obtained from other experiments in which $2\Delta_0$ was measured. All of the values of $2\Delta_0$ other than ours were obtained from tunneling experiments. In addition, the Table includes the reduced energy-gap width $2\Delta_0/kT_c$.

B. Amorphous Bismuth

The far-infrared transmission curves for three samples of amorphous bismuth are shown in Figs. 3–5. In each case the curve calculated from the weak-coupling theory is a poor fit to the data, as might have been expected, whereas that calculated from the strong-coupling theory and the tunneling data of Chen *et al.*[22] is a reasonably good fit to the data.

The values listed in Table I show that T_c and $2\Delta_0$ decrease with increasing film resistance. This is also shown in Fig. 6 and will be discussed in Sec. V.

As indicated in Table I, the thin bismuth films crystallized at temperatures above the transformation temperature for thick films, which is about 19°K. The transformations in these thin films also occurred over a broader temperature range.

C. Amorphous Gallium

The far-infrared transmission data for an amorphous gallium film are plotted in Fig. 7. Again the weak-coupling theory predicts a curve which fits the data

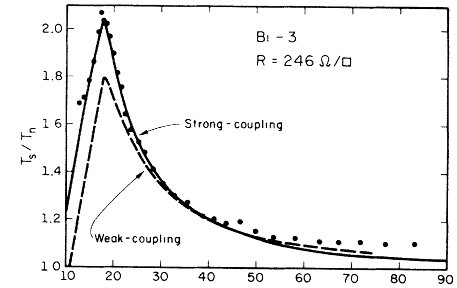

FIG. 5. Experimental points and theoretical curves for the transmission ratio as a function of photon wave number for amorphous bismuth sample Bi-3.

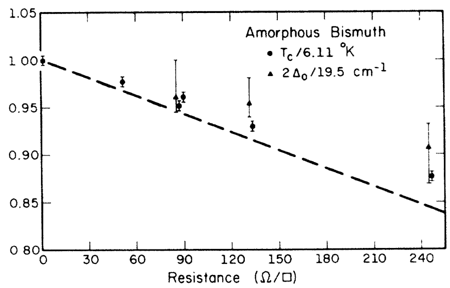

FIG. 6. Dependence of T_c and $2\Delta_0$ on dc resistance for amorphous bismuth films, normalized to the values found for a thick film by Chen *et al.* (Ref. 22). The dashed line is discussed in Sec. V.

poorly. The strong-coupling theory has been used with tunneling data obtained by Chen *et al.*[22] to calculate a curve which is in fair agreement with the data, as shown, although the agreement is not as good as for amorphous bismuth. A similar strong-coupling curve was calculated from tunneling data obtained by Wühl, Jackson, and Briscoe.[23,45] This curve is in slightly better agreement with the data than the curve shown in Fig. 7; the peak of the curve is lower than that of the indicated strong-coupling curve by 1.7%.

The values for T_c presented in Table I indicate that for amorphous gallium, as for amorphous bismuth, T_c decreases with increasing film resistance.

D. Partially Annealed Gallium

Figures 8 and 9 show the far-infrared transmission data which were obtained for gallium film Ga-1 after it was annealed at 77 and at 200°K, respectively. The data shown in Fig. 9 were analyzed differently from those of the other samples. For technical reasons we did not obtain a reliable value of T_n for this film. We therefore fitted the data to the strong-coupling curve in the region between 40 and 90 cm^{-1} by adjusting T_n.

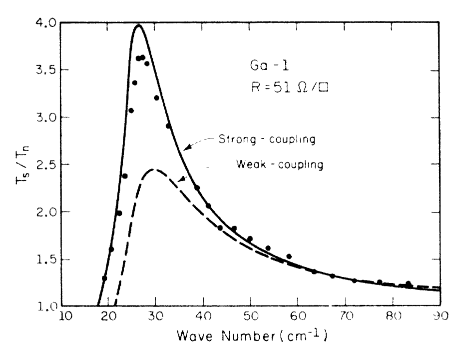

FIG. 7. Experimental points and theoretical curves for the transmission ratio as a function of photon wave number for amorphous gallium sample GA-1.

[45] A preliminary calculation of the gap parameter for amorphous gallium by the authors of Ref. 23 produced a transmission curve which was in quite good agreement with the experimental data, as is shown in Ref. 25.

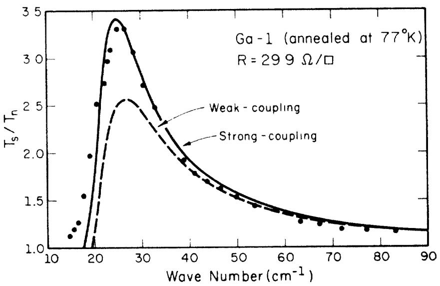

FIG. 8. Experimental points and theoretical curves for the transmission ratio as a function of photon wave number for gallium sample Ga-1 annealed at 77°K.

Thus, for this film alone, there were two adjustable parameters, T_n and $2\Delta_0$, rather than one.

Although thick amorphous gallium films[21] crystallize and transform to the β phase at about 15°K, the numbers listed in Table I show that the thinner gallium films transformed at higher temperatures. Furthermore, the transformation was spread out over a range of temperatures. A 12-h annealing of sample Ga-1 at 77°K lowered the superconducting transition temperature from 8.05 to 7.74°K. This was assumed to indicate a partial transformation to the β phase, in which gallium has a transition temperature at 6.2–6.3°K. When sample Ga-1 was warmed up from 77 toward 200°K, its electrical resistance decreased with increasing temperature, indicating further crystallization. Only at (200±15)°K did the resistance begin to increase with increasing temperature, indicating that the structural transformation may have been complete. After this annealing, the superconducting transition temperature was 6.55°K, almost as low as that for thick films of β-phase gallium.

In calculating theoretical far-infrared transmission curves from the strong-coupling theory for sample Ga-1 annealed at 77 and at 200°K, we have used preliminary calculations of $\Delta(E)$ from the tunneling results obtained by Wühl, Jackson, and Briscoe for β-phase gallium.[23] This was not well justified for the

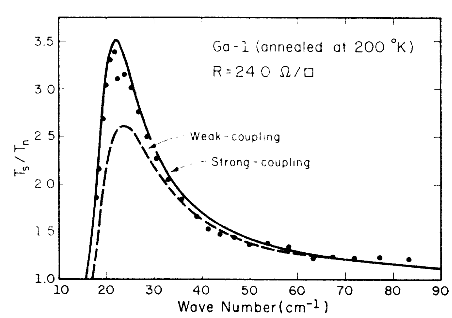

FIG. 9. Experimental points and theoretical curves for the transmission ratio as a function of photon wave number for gallium sample Ga-1 annealed at 200°K. For this sample only, the normal-state transmission T_n was treated as an adjustable parameter, because it was not measured experimentally. See Sec. IV D.

sample annealed at 77°K, since the transformation to the β phase was obviously incomplete. For the sample annealed at 200°K, the transformation may have been almost complete, so it was less arbitrary to use β-phase tunneling data. Had we compared the experimental points with transmission curves calculated from σ_s/σ_n for amorphous gallium, very poor agreement would have resulted.

Again the curves for T_s/T_n calculated from the strong-coupling theory are in reasonably good agreement with the experimental data, whereas the weak-coupling theory yielded curves which are in rather poor agreement with the data.

V. CONCLUSIONS AND DISCUSSION

From these results we may draw three main conclusions: (a) The far-infrared transmission curves could be interpreted rather well by means of theory, provided strong-coupling effects were taken into account, together with a simple scaling of the energies; (b) the superconducting transition temperature and the energy-gap width decreased as the film thickness decreased; (c) within our estimated maximum uncertainties the reduced energy-gap width $2\Delta_0/kT_c$ for each of our samples agrees with the results of other measurements on much thicker films; (d) the transformation from the amorphous phase to the crystalline phase occurred at higher temperatures and over a broader temperature range than for thick films of amorphous bismuth or gallium.

The agreement between our far-infrared data and the curves which were calculated by using the strong-coupling theory and the results of tunneling measurements is probably as good as would have been expected, in view of the slight differences between the properties of different samples.

Our values of T_c for thick samples of amorphous bismuth and gallium and annealed gallium are in good agreement with those of other investigators. A decrease in T_c with increasing film resistance (decreasing thickness) has also been observed by Naugle and Glover.[46] For both amorphous bismuth and gallium, they found the shift in T_c to be approximately proportional to the film resistance for films thicker than 150 Å. This relation is indicated for amorphous bismuth by the dashed line in Fig. 6. The transition temperatures of our thin films were shifted less than indicated by this linear relation, in agreement with observations of Naugle and Glover for films thinner than 150 Å.

Naugle and Glover[46] suggested that this effect may be due to a proximity effect, a boundary condition on the order parameter, or thermodynamic fluctuations near the superconducting transition. Although fluctuations may affect the transition temperature, we have observed a decrease in Δ_0 which is nearly proportional to that in T_c, and Δ_0 was determined at a temperature far from the superconducting transition where fluctuations are significant.

Gamble and Shimshick[47] and Garland, Bennemann, and Mueller[48] have pointed out that at the surface of a film or a crystal the reduction in symmetry at the lattice sites shifts part of the phonon spectrum to lower frequencies. This would be expected to increase the electron-phonon coupling and produce a T_c which is higher than that for thick samples, the opposite of the effect observed for amorphous superconductors. Ginzburg[49] has also discussed the importance of surfaces in determining the transition temperature.

The effect of film thickness on the transformation of amorphous bismuth or gallium to the crystalline state has also been observed by Sander.[50] He studied this effect by measuring the heat of transformation for thin bismuth films, and he showed that a layer of bismuth deposited over an incompletely crystallized thin bismuth film apparently assisted in subsequently annealing the thin underlying film.

ACKNOWLEDGMENTS

We thank J. D. Leslie, H. Wühl, J. E. Jackson, and C. V. Briscoe for supplying us with their calculated energy-gap functions prior to publication. In addition, we thank J. C. Swihart for sending us the calculated energy-gap function and complex conductivity for lead which we used to verify the correct operation of our computer program. Our germanium bolometers were made from material supplied by W. D. Compton. One of us (REH) is grateful to the National Aeronautics and Space Administration for fellowship support during part of this work.

[46] D. G. Naugle and R. E. Glover, Phys. Letters **28A**, 611 (1969).

[47] F. R. Gamble and E. J. Shimshick, Phys. Letters **28A**, 25 (1968).

[48] J. W. Garland, K. H. Bennemann, and F. M. Mueller, Phys. Rev. Letters **21**, 1315 (1968).

[49] V. L. Ginzburg, Phys. Letters **13**, 101 (1964).

[50] W. Sander, Z. Physik **147**, 361 (1957).