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Far-Infrared Absorption in a Lead-Thallium Superconducting Alloy[*]

Abstract: Preliminary measurements have been made of the absorption of far-infrared radiation in the surface of a bulk superconducting alloy composed of lead with 10.0 atomic percent thallium at 1.4°K. The results indicate that the gap edge is quite distinct, in contrast to previous results of Richards and Tinkham on other alloys. The sharpness of the gap edge is thought to be characteristic of alloys which are homogeneous and have no trapped magnetic flux. Alloying narrows the observed gap width by about the same ratio as the critical temperature, and by an amount which is much smaller than that predicted by Suhl and Matthias from a simplified model. The subsidiary absorption maximum below the gap edge, which has been seen previously in pure lead, is also present in the alloy. This lends support to other evidence that it is not due to crystalline anisotropy.

Introduction

We have begun a series of experiments to investigate the electromagnetic properties of superconducting alloys in the far infrared region of the spectrum. These experiments are expected to yield information concerning the influence of electron concentration and mean free path on the subsidiary absorption below the gap edge in lead,[1] the width of the gap, and the detailed shape of the absorption edge. This report on our first investigation of this sort concerns an alloy consisting of the 10.0 atomic percent thallium in lead.

The experiment is performed by measuring the difference between the power reflected by the sample in the superconducting state and that reflected when the sample at the same temperature is forced into the normal state by a magnetic field. This type of experiment was first performed on pure metals with far-infrared radiation by Richards and Tinkham.[1] They also investigated two alloys, one consisting of 1% bismuth in lead and the other consisting of 50% tin in lead. Their results indicated that the gap edge is badly smeared out in an alloy, so that the rise in absorption occurs gradually over a wide frequency range. They suggested that a homogeneous alloy might have a sharp gap edge. Our experiment shows this is the case, at least for our alloy. This result would seem to lend support to the idea of long-range order in a superconductor.[2,3] Our samples are produced in a way designed to avoid variations in composition as much as possible. We have also been careful to perform the experiment in a manner which avoids the effects of trapped magnetic flux, which was present in large amounts in the earlier experiments.[1] Flux trapping is usually quite severe in alloys, although there is evidence that this is not the case for extremely homogeneous samples of small size and favorable geometry.[4]

Experimental method

- *Sample preparation*

The sample consists of a hollow cone, 4 in. long and with a 1 in. diameter at its truncated end, with a wall thickness of 3/32 in. It was produced in the following way. The alloy constituents were weighed and sealed in an evacuated pyrex tube. The tube was then heated to melt all of the metal, agitated vigorously to mix the ingredients, and cooled rather quickly in a blast of compressed air. The alloy ingot was then removed and placed in one chamber of a demountable iron mold, the interior of which had been previously coated with a thin layer of graphite[5] to facilitate removal of the specimen. The mold was placed in a vacuum, heated to a temperature slightly above the alloy's melting

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point, agitated, and then inverted, so that the molten metal ran through a tube into a chamber in the same mold which gave it the desired shape. Nitrogen was then admitted into the vacuum, and the mold was quickly removed and quenched in distilled water. (A chart recorder monitored the voltage of a thermocouple attached to the mold to assure that the alloy did not solidify before the quenching operation.) After removing the sample from the mold, we etched its surface in hydrochloric acid to remove any surface contamination. The sample surface was then bright, and the etch pattern disclosed large crystals of the order of 1 cm in size. Four wire samples, each 1/16 in. in diameter, were made and quenched in the same mold with the conical sample. These can be used conveniently to measure resistivity and critical temperature.

Rapid quenching through the solidification range of temperature for the alloy prevents the large-scale segregation of the components. This rapid quenching was promoted in our work by two factors: the small heat capacity of the mold, which had a mass of only 615 gm, and the narrowness of the temperature region over which the alloy solidifies.[6] We attempted to remove any remaining inhomogeneities by annealing the conical sample and the wires in an evacuated pyrex tube at 300°C for four months.

A chemical analysis[7] of part of the metal cast and annealed with the sample showed 10.6 atomic percent thallium. The analysis was stated to be accurate to within 0.1 atomic percent. The indicated percentage of thallium was larger by 0.6 atomic percent than the amount indicated by the weights of the ingredients. The reason for this discrepancy is not clear.

A 99.99% pure lead sample was produced in the same way and annealed in a separate pyrex tube.

Method of making the measurements

The measuring techniques are essentially the same as those of Richards and Tinkham,[1] except that we avoid the effects of trapped magnetic flux. The conical sample is at a temperature of 1.4°K and forms the walls of a nonresonant cavity, into which the radiation is conducted. A bolometer in the cavity measures the energy density. A shutter in the cavity is operated from the top of the dewar so that the bolometer measures first the radiation reflected after many bounces from the cavity surface, and then the radiation reflected by a brass surface, with the superconducting metal completely hidden from the radiation and the bolometer. In this way variations in source intensity and/or bolometer sensitivity are monitored by a reference signal. This process is repeated at each desired wavelength as many times as necessary to decrease random scatter in the averaged results. A magnet is then turned on to force the metal into the normal state, and the measurements are made again. We call P_S and P_N the power incident on the bolometer while the cavity is superconducting and normal, respectively, divided by the reference signal.

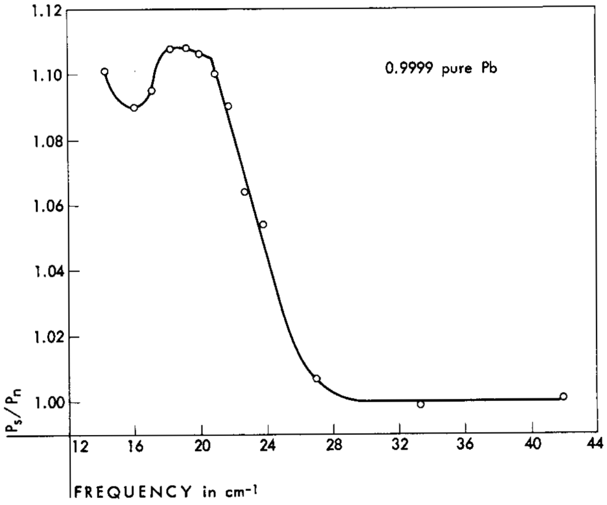

Figure 1 **Absorption curve for pure lead.** *All of the points have been arbitrarily raised by 0.015, as described in the text.*

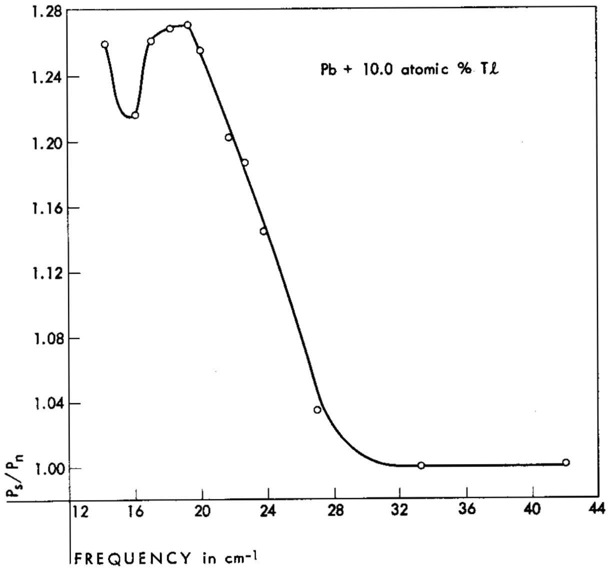

Figure 2 **Absorption curve for an alloy of 10.0 atomic percent thallium in lead.** *All of the points have been arbitrarily raised by 0.032, as described in the text.*

Experimental results

The frequency dependence of P_S/P_N for pure lead and for the alloy is shown in Fig. 1 and Fig. 2. The data actually indicated that the P_S/P_N approaches 0.985 at high frequencies for pure lead and 0.968 for the alloy. These are slightly different from the expected value of 1.000. The reason for this small discrepancy is not known and may be an instrumental error. Pending further investigation, we have arbitrarily raised all of the points for the pure lead by 0.015 and all of those for the alloy by 0.032. The band of frequencies used in obtaining each reading has a half-width of 3% at half-maximum. The accuracy of the readings is best judged by the scatter of the data in the wavelength regions where P_S/P_N varies slowly with frequency.

The maximum size of P_S/P_N is greater for the alloy than for the pure lead, since the normal-state surface resistance is greater for the alloy than for the pure metal. In each of the Figures one can easily see the gap edge. One can also see a subsidiary absorption below the edge, which has been observed previously in pure lead and mercury.[1]

A wire sample which was cast and annealed with the conical alloy sample was found to have an electrical resistance which decreased by a factor of 9.33 when the wire was cooled from 300°K to 1.6°K. This result will be useful in our discussion of the significance of the infrared data.

Comparison of results with other experiments and with theory

• *Gap width*

Our results indicate that the gap width is less in the alloy than in the pure lead by 6.7 ± 2%. This should be compared with the decrease in critical temperature caused by alloying. We have not yet measured this, but data obtained previously[8] on the lead-thallium alloy system indicate that the critical temperature is about 6.3% less for our alloy than for pure lead. Thus, the gap width is approximately proportional to the critical temperature. Our value for the size of the gap in pure lead, $4.14 \pm 0.1\ kT_c$, is roughly the theoretical value of $3.52\,kT_c$.[3] Richards and Tinkham[1] found a gap width of $4.1 \pm 0.2\ kT_c$, in agreement with our value.

A theoretical calculation has been made by Suhl and Matthias[9] to determine the decrease in gap width which results when a superconductor is alloyed with an impurity. The calculation is based on the BCS theory,[3] together with some admittedly drastic simplifying assumptions concerning the band structure of the metal and the nature of the electron-impurity scattering. The results of this calculation indicate that for our alloy, which has a residual resistance ratio of 9.33, the gap width ought to be less than that of pure lead by a factor of about eleven. This is in clear disagreement with our results. The discrepancy is in the expected direction.[9]

• *Sharpness of gap edge*

The sudden onset of absorption which has been observed in the alloy sample indicates that a considerable amount of electron scattering does not necessarily smear out the gap edge. This is in accord with some work[10] on alloys, which shows that the specific heat depends exponentially on reciprocal temperature. It is also in agreement with far-infrared work[11] on thin films in which very rapid electron scattering occurs.

A relaxation time, τ, to describe the impurity scattering, can be estimated from our measured residual resistance ratio, using Matthiessen's rule[12] and Chambers' value[13] for $\sigma/v_0\tau$ in lead, where σ is the conductivity of lead and v_0 is the Fermi velocity, which we take as roughly 10^8 cm/sec. The value of τ calculated in this way indicates that $\hbar/\tau$ is approximately seven times the gap width. Under these conditions, our alloy fits Anderson's description[14] of a "dirty" superconductor. His theoretical treatment indicates that the gap edge in the alloy might be even more distinct than in the pure metal, since the rapid electron scattering tends to diminish the effects of crystalline anisotropy.

• *Structure in the gap*

The appearance of an initial dip in the P_S/P_N curve below the gap edge is shown by our measurements to be definitely associated with the superconducting state, and to be present in the alloy as well as in the pure metal. This structure, observed previously in lead and mercury,[1] has not yet received any satisfactory theoretical explanation. Our work indicates that it is not sensitive to electron mean free path or concentration.

Conclusions

It has been shown that a homogeneous sample of 10 atomic percent thallium in lead has a sharp gap edge. It also has a gap width which is related to that in pure lead by about the same ratio as the critical temperatures of the two materials. The decrease in gap width is much less than that predicted by a simplified theoretical treatment. The structure on the gap edge which has been observed in pure lead is also present in the alloy, and therefore seems insensitive to changes in electron concentration and mean free path.

References and footnotes

1. P. L. Richards and M. Tinkham, *Phys. Rev.* **119,** 575 (1960).
2. A. B. Pippard, *Proc. Roy. Soc. (London)* **A216,** 547 (1953).
3. J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108,** 1175 (1957).
4. E. A. Lynton and B. Serin, *Phys. Rev.* **112,** 70 (1958).
5. Dag Dispersion No. 154, Acheson Colloids Co., Port Huron, Michigan.
6. M. Hanson, *Constitution of Binary Alloys*, McGraw-Hill Co., Inc., New York, 1958, p. 1115.
7. Performed by Lucius Pitkin, Inc., New York.
8. W. Meissner, W. Franz, and H. Westerhoff, *Ann. Physik* **13,** 967 (1932).
9. H. Suhl and B. Matthias, *Phys. Rev.* **114,** 977 (1959).
10. R. R. Hake, in *Proceedings of the VIIth International Conference on Low Temperature Physics*, Ed. G. M. Graham and A. C. Hollis Hallett, 1961, University of Toronto Press, Toronto, pp. 359–361.
11. D. M. Ginsberg and M. Tinkham, *Phys. Rev.* **118,** 990 (1960).
12. C. Kittel, *Solid State Physics*, John Wiley and Sons, New York, 1956, p. 305.
13. R. G. Chambers, *Proc. Roy. Soc. (London)* **A215,** 481 (1952).
14. P. W. Anderson, *J. Phys. Chem. Solids* **11,** 26 (1959).

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