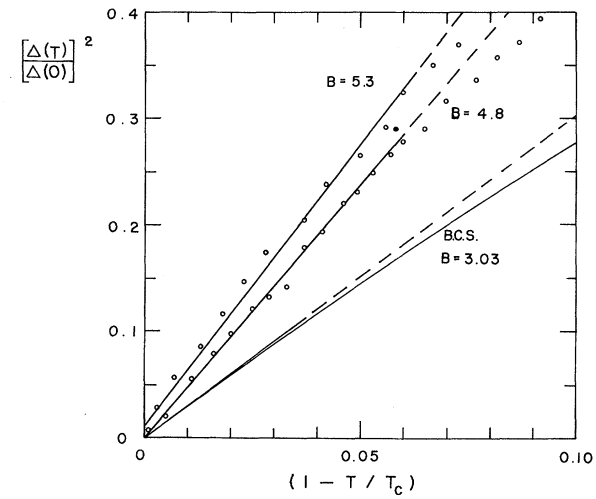

FIG. 4. Linear plot of the high-temperature variation of the energy gap in niobium from ultrasonic attenuation to obtain the parameter B. The data shown are for the highest and lowest values of B measured. — — — is tangent to the BCS curve, of slope 3.03.

ing of the quasi-particles proposed by Schrieffer and Wada.[13,14]

On the other hand, the anisotropy of the energy gap, which is so striking in Sn, and which is apparent in the low-temperature heat capacity of Pb,[15] is much less evident in the ultrasonic measurements on Nb and is not observed in the low-temperature heat capacity.[10] Probably niobium must be made much purer before its anisotropy can be extensively studied.

We are grateful to H. A. Boorse and R. W. Shaw for sending us their results prior to publication and to L. Falicov for a helpful discussion. We are indebted to the Department of Scientific and Industrial Research for a grant for equipment.

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Ultrasonic Attenuation in Superconducting Lead*

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INTRODUCTION AND EXPERIMENTAL

Early measurements of ultrasonic attenuation in single-crystal lead were reported by Bömmel[1] and Mason and Bömmel.[2] These results showed significant discrepancies which, together with the structure observed in the far-infrared transmission measurements on lead films,[3] resulted in the present investigation. Here the ultrasonic attenuation of lead has been measured in various crystallographic directions over the temperature range 2° to 20°K both in magnetic field and zero field in an attempt to determine the superconducting energy gap.

A standard ultrasonic pulse technique was used to measure the attenuation. The apparatus consisted basically of a modified Sperry attenuation comparator. Additional amplifiers, attenuator, and detection circuits were used to allow the amplitude of a particular echo to be continuously recorded as a function of temperature or magnetic field. The block diagram of our arrangement is essentially the same as that reported on by Bohm and Kamm.[4]

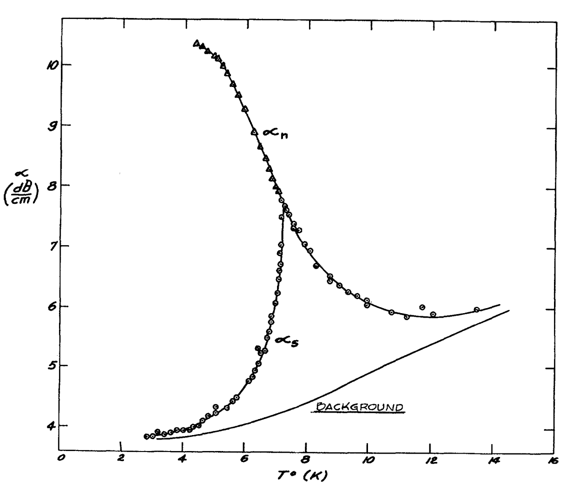

FIG. 1. Ultrasonic attenuation in lead for longitudinal waves propagating in the [100] direction at 50 Mc/sec.

DETERMINATION OF α_s/α_n

The normal-state attenuation was obtained by correcting data taken with 1000 G applied to the speci-

* This work was supported by the National Science Foundation and the National Aeronautics and Space Administration.
[1] H. E. Bömmel, Phys. Rev. **96**, 220 (1954).
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[3] D. M. Ginsberg and M. Tinkham, Phys. Rev. **118**, 990 (1960).
[4] G. N. Kamm and H. V. Bohm, Rev. Sci. Instr. **33**, 957 (1962).

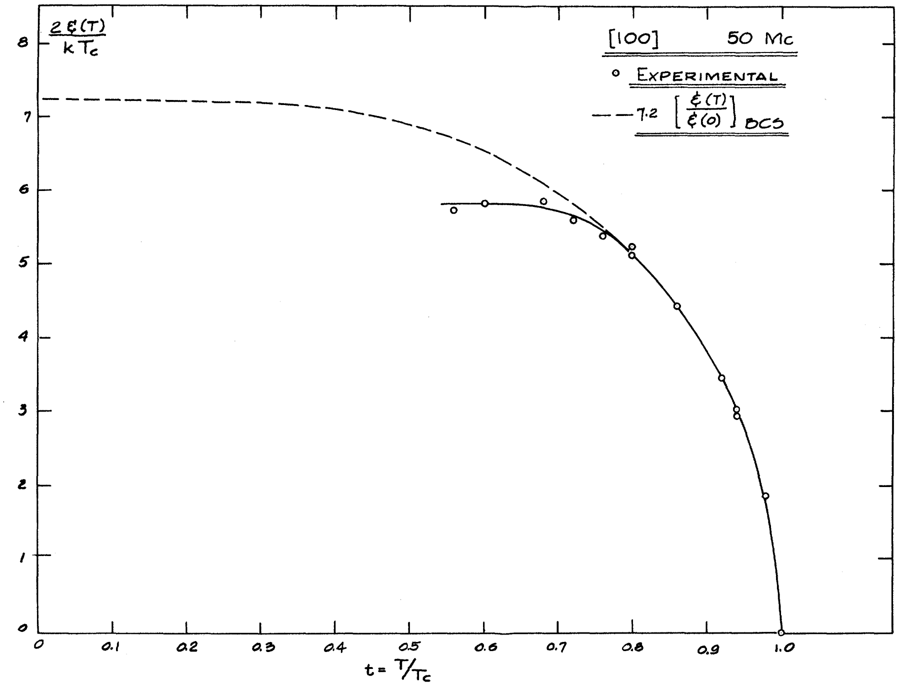

Fig. 2. Energy gap as a function of reduced temperature based upon data taken from Fig. 1. The dashed line represents the BCS energy gap normalized to $7.2kT_c$ at zero degrees.

men in accordance with attenuation vs field curves at constant temperature. It was found that, above 4.5°K at frequencies up to 50 Mc/sec, the dependence upon field has a simple resonance-free behavior, which allowed reliable corrections to zero field to be made. The background correction is more difficult and can be done with some confidence only where its variation in the superconducting region appears to be small.

Data for 50-Mc/sec longitudinal waves propagating in the [100] direction are shown in Fig. 1. Here interpolating to obtain a reasonable background

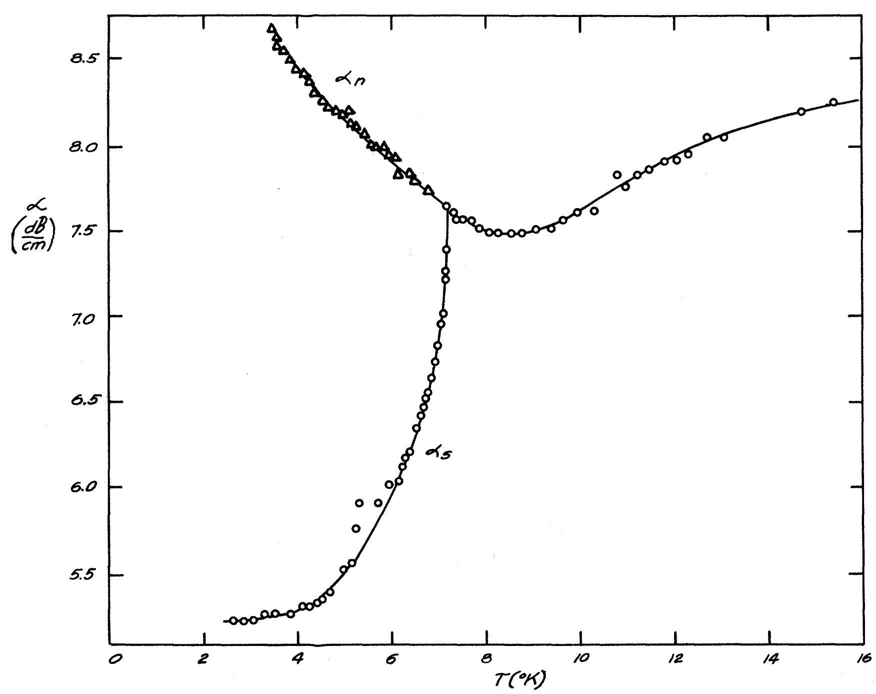

Fig. 3. Ultrasonic attenuation in lead for longitudinal waves propagating in the [111] direction at 30 Mc/sec.

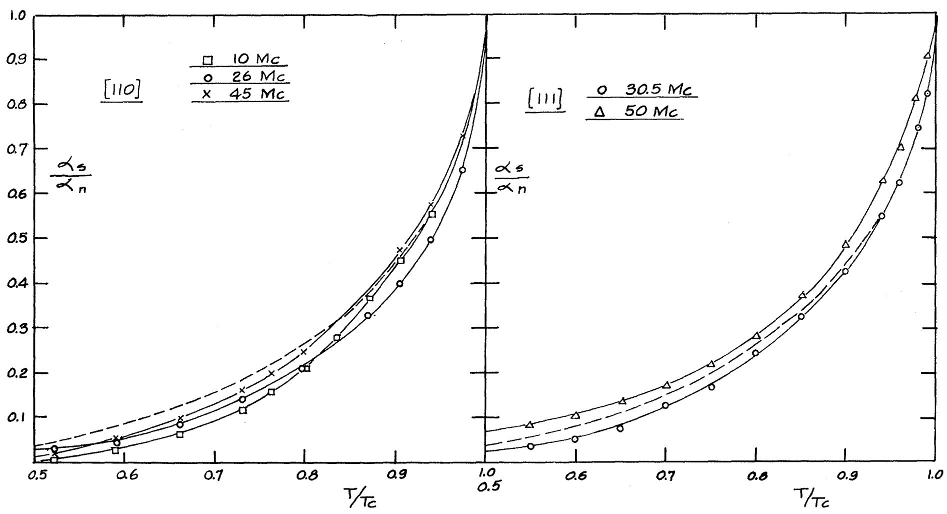

FIG. 4. α_s/α_n as a function of reduced temperature for various specimens at various frequencies assuming a constant background. The dashed curve is derived from the BCS expressions using a zero temperature energy gap of $4.2kT_c$.

curve presents the least difficulty. The curve in Fig. 2 shows the gap calculated on the assumption that α_s/α_n is equal to twice the Fermi function of half the energy gap. Because of the very rapid drop in α_s, the energy gap is probably not constant in the range where significant accuracy remains in the data so that a value of $\epsilon(0)$ is difficult to obtain. If one assumes the BCS variation of the gap, however, the best fit can be made at higher temperatures and yields approximately 7.2 kT_c for the full gap.

Figure 3 is representative of the data taken on the crystals of other orientations. Here the background is a very troublesome problem, of which the simplest solution may be to improve specimen preparation. One extreme in the choice of background which leads to a minimum gap is to simply take it as a constant. Figure 4 shows the α_s/α_n ratio resulting from such an analysis at various frequencies for longitudinal waves in the [110] and [111] cut crystals. Note that under such an assumption the resulting gap values are in reasonable agreement with values from other techniques. Any better approximation to the background would raise them.

PULSE-AMPLITUDE-DEPENDENT EFFECT

In the course of these measurements a dependence of the shape of the α_s curve upon the amplitude of initial ultrasonic pulse was observed. After various attempts to attribute it to the instrumentation had failed we investigated in more detail. The apparent attenuation vs temperature in the superconducting range has been plotted for various pulse amplitudes in Fig. 5. These curves were arbitrarily matched above T_c. Further testing has convinced us that the effect is not in the electronics. Several points should be made: (1) T_c reproduces to within 0.02°K during both warming and cooling runs indicating that the specimen temperature is being reliably measured. (2) Tests, to date, indicate that application of a magnetic field sufficient to drive the specimen normal eliminates the pulse-amplitude dependence. Thus the property appears to be a function of the superconducting state and not, for example, of the transducer or bond. (3) The effect occurs to essentially the same

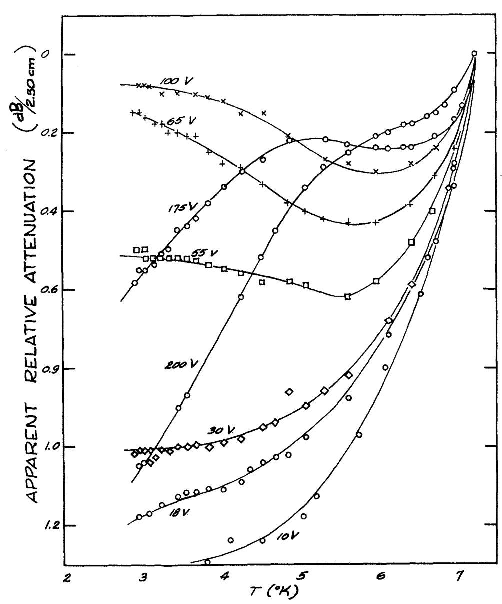

FIG. 5. The apparent attenuation in the superconducting state as a function of temperature for various voltages across transducer.

extent for shear waves and in other specimens. This, together with the lack of structure, indicates that this phenomenon is quite different from the defect associated properties observed by Claiborne and Einspruch.[5]

[5] L. T. Claiborne and N. G. Einspruch, Phys. Rev. Letters **10**, 49 (1963).

This effect naturally will influence our calculation of the energy gap. No correction for it has yet been made to any of the data above. Hence the error in the energy gap as calculated from these data may be the order of 25%. We prefer not to speculate on the source of this effect until further experimental tests have been made.

Discussion 40

J. P. Palmer, *General Dynamics:* I have a question for Dr. Dobbs. I understand the attenuation in the normal state to be around 400 dB per cm and this seems quite a bit higher than Dr. Love's value of 10 dB per cm for the lead. Also I understand that it is quite a bit higher than the attenuation noticed for say aluminum.

Dobbs: I'd like to point out that the normal attenuation in metals goes up as the frequency squared when the mean free path is small and as the frequency when the latter is large. Our frequency was 1280 megacycles compared with 10 megacycles used by Dr. Shaw.

J. D. Gavenda, *Institute for the Study of Metals:* I'd like to address a question to Dr. Dobbs. I wonder how you got the attenuation at absolute zero since these calculations are very sensitive to the extrapolated value of attenuation and the figure which you quote for the energy gap has an uncertainty listed of the order of 1%.

Dobbs: Well, the figures listed are for 288 megacycles where the attenuation is much less and there we used the standard method of reflection from the back face of the sample and only one transducer. In this case one can obtain a very accurate measure of the attenuation at very low temperatures. We see something like 25 to 30 echoes if we have a good sample and the low value of attenuation was therefore measured accurately. It is independent of temperature below about $2\frac{1}{2}°$ and we can go down to just over 1°. We therefore have a very accurate measure of α_s^0. The normal attenuation similarly is independent of temperature below about 3° and can be measured equally accurately. Hence, we get our values, for which the error quoted is a 4 or 5 run average. The reproducibility is better than that, but we're allowing for errors in the attenuator and the thermometer.

Gavenda: The extrapolated attenuation curves are extremely sensitive to this low temperature attenuation. If you vary the background attenuation which you've subtracted, you find that it shifts the curve up or down. Now with our measurements in tin [this is in the paper by R. W. Morse, T. Olsen, and J. D. Gavenda, Phys. Rev. Letters 3, 15 (1959)], we found that the only way we could extrapolate to zero was to vary the constant which we subtracted to achieve a reasonably straight line for the attenuation ratio curve at the lower temperatures. This leaves some uncertainty because the slope may not actually be constant. Now a very slight change in this quantity, since you're plotting a logarithmic quantity or I should say an exponential quantity, can make a tremendous difference in the energy gap and we could never reduce the errors due to this effect below several percent.

Dobbs: I'd like to point out that the transition temperature of niobium is 9.2°K compared to 3.7°K for tin and, therefore, if you go down to 1°, you go down to a very much smaller reduced temperature in niobium than in tin. Therefore, my original statement that the attenuation in the superconducting state is accurately measured without an extrapolation procedure is correct.

J. C. Swihart, *I.B M. Research Center:* I'd just like to say something in regard to the talk of Dr. Dobbs. First of all, my calculation was made using an approximation to the Bardeen–Pines–Fröhlich interaction. The Eliashberg interaction is a better one for the superconducting state and leads to more accurate results. Secondly, the large jump in the specific heat does not indicate that the energy gap function does not oscillate, rather it indicates that near zero energy the gap function first increases with energy as is found with the Eliashberg interaction. In fact the beautiful fit of the calculations of Schrieffer, Scalapino, and Wilkins to the measurements of Rowell indicates that the energy gap function does oscillate.

J. R. Leibowitz, *Westinghouse Research Laboratories:* A comment to Dr. Shaw. It has been noted that the procedure by which gaps are determined near T_c is rather dangerous; this, of course, is due to the fact that the BCS absorption curve near T_c is very insensitive to the $T = 0$ energy gap. In addition, it should be observed, if one assumes some kind of gap anisotropy, which one might well do in lead, that a "temperature selection" of energy gaps can occur, even at a fixed orientation. One manifestation of this is seen in the case of the electronic specific heats, and can, in principle, enter in identical fashion in the ultrasonic attenuation: the larger gap values can dominate at higher temperatures. Another, and perhaps more disconcerting effect which may be applicable here is that certain contributions from more than one gap may dominate the attenuation in a narrow temperature range at high reduced temperature, t. When one looks below t values of about 0.5, no such peculiar effect involving the different gaps enters. But in this high-temperature range (t between ≈ 0.6 to 0.8) a rather trivial phenomenon occurs in which sums of several gaps give apparent values which are nonphysical. And I think that one might argue that this determination of gaps of the order of $8kT_c$ at high reduced temperatures may be such a case.

Dobbs: I would just like to speculate on the peculiar results shown in Dr. Shaw's last slide. As we saw from his earlier slides, the background attenuation was very high near the transition temperature of lead and therefore because of the low Debye temperature of lead, a very large portion of the background is probably the phonon absorption as observed in insulators like germanium and quartz.

From a rough calculation I estimate that the 10-Mc/sec phonon absorption would cut off at something like 2°K. If this is so, it means in the range 2° to 7°K, where the attenuation in lead was measured, the mean free path of the phonons is only slightly greater than the sonic wavelength. The speculation is that the phenomenon of the change of attenuation with pulse amplitude might be similar to the phonon bottleneck found by de Klerk in quartz with much higher frequencies—the higher frequencies in quartz being associated with its much higher Debye temperature.

FLUX QUANTIZATION

CHAIRMAN: *W. M. Fairbank*

Long-Range Correlations in Superconductivity*

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It has long been recognized that in the superconducting state there is a range of order which extends over a distance in real space which is much greater than the depth of penetration of a magnetic field into the superconductor. This has been stressed by London[1] in his monograph on superconductivity in which he talks repeatedly of the concept of a "macroscopic quantum state" in which there is a long-range order of the momenta of the electrons, indeed, this forms the basis of his whole theory of superconductivity. Pippard[2] also showed in a very convincing manner from experimental measurements on the change of penetration depth with magnetic field that the range of order or "coherence length" as he defined it, was considerably greater than the penetration depth. Since that time, a great deal of data has been gathered to reinforce this concept of coherence and to show how it plays an important role in the detailed properties of superconductors.[3] While there is practically universal agreement over the need for such long-range order for an understanding of the superconducting state, the actual distance over which this order extends has not been determined either experimentally or theoretically at this time. This I believe is one of the outstanding problems of superconductivity and it is the one which I wish to discuss.

The problem can best be appreciated by considering the experiments on flux quantization carried out by Deaver and Fairbank[4] and Doll and Näbauer[5] two years ago. These experiments resulted from an observation by London[1] that an inevitable consequence of his idea of long-range order would be that the magnetic flux trapped in a cylindrical superconductor would be an integral multiple of a fundamental quantum of flux (hc/e) (4×10^{-7} G cm^2). Upon the successful completion of the experiments, it was found that such an effect did occur, but the magnitude of the flux quantum was found to be $hc/2e$ rather than hc/e. *After* this result was announced, it was recognized by many that this was apparently an *obvious* consequence of the Bardeen–Cooper–Schrieffer theory of superconductivity.[6] For in this theory, the electrons are correlated in pairs and the pairs with charge $2e$ would constitute the charge carriers. This would account for the factor of 2 between the measured value and London's prediction. The long-range order resulted from the assumption in the theory that all the pairs in the superconductor have the same center of mass momentum. The concept of

*This work was supported by the National Science Foundation and the Office of Naval Research.

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[2] A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

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