fore, presume that there is an antiferromagnetic exchange interaction between electrons in this f band. Under these assumptions we find that it is energetically favorable for some of the electrons in the Fermi sea to be promoted into the f band, and aligned in suitably ordered states. If we make a BCS ansatz for the wave function, including finite occupancy of the states in this f band, we find that this antiferromagnetic interaction in the f band can indeed assist superconductivity and the transition temperature can be much higher than one expects from the electron–phonon interaction alone. A typical assumption that we make of this band (which we treat as a completely degenerate single level) is that the height above the Fermi surface is less than the Debye temperature. Because of the assumption of a completely sharp level in the f band the BCS integral equation simplifies to an algebraic equation, and one can calculate the effect of the energy gap for the f band rather simply. It differs from the energy gap of the s band. One has to bring in an interband pairing interaction to produce an energy gap in the s band. Superconductivity will be enhanced in this case by the fact that the whole of the condensed f band is within the available distance of the Fermi surface. A firm prediction which one is able to make is that these elements should show no isotope effect if our model is applicable. I don't believe there are any available data on this point; unfortunately Lanthanum has only one stable isotope, but I hope some measurements can be made in Uranium. The second firm prediction is that the law of corresponding states should not hold; in particular, whereas the BCS value for $H_c^2/\gamma T_c$ is 5.9, we would predict a value somewhat larger. In fact, for all the superconductors for which data are available, with the exception of Lanthanum, the BCS value seems correct to within about 25%. For Lanthanum the data seem to indicate a value of 14 instead of 5.9. The third prediction (this is a less certain one) is that since there are two energy gaps for the s and f bands, one might hope to see in a tunneling experiment an f-band gap which might be rather bigger than the s-band gap (possibly even by a factor of 3 or 4). Whether this really is observable is a bit hard to say because of the large effective mass of f electrons.

ULTRASONICS

CHAIRMAN: *R. W. Morse*

Anisotropy of the Energy Gap in Niobium from Ultrasonic Measurements

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In its original formulation, the theory of Bardeen, Cooper, and Schrieffer[1] was based on a model superconductor, which had a spherical Fermi surface, an isotropic energy gap ($\Delta_k = \Delta$), and a simple, weak electron–electron interaction $-V$. This model led to a law of corresponding states for superconductors, in which the energy gap at 0°K, $\Delta(0) = 1.76\, kT_c$. At higher temperatures the BCS energy gap $\Delta(T)$ is given by the equation[2]

$$\frac{\Delta(T)}{\Delta(0)} = \tanh\left[\frac{T_c}{T}\cdot\frac{\Delta(T)}{\Delta(0)}\right]. \qquad (1)$$

The theory has been remarkably successful for most superconductors, in which the "weak coupling" approximation [$N(0)V \ll 1$ or $T_c \ll \theta_D$] is valid, although it is well known that their Fermi surfaces are far from spherical. For a few "strongly coupled" superconducting elements, such as niobium and lead, it is less successful and it is therefore possible, by studying the way in which they deviate from the law of corresponding states, to investigate the electron–electron interaction responsible for superconductivity in detail. We have used the ultrasonic method[3] to measure the energy gap in niobium as a function of temperature, and of orientation, in single crystals of resistivity ratio $R_{300}/R_4 = 300$.

* Associated Electrical Industries Fellow in Physics.
† Shell Scholar.
[1] J. Bardeen, L. N. Cooper, and J. R. Schreiffer, Phys. Rev. **108**, 1175 (1957).
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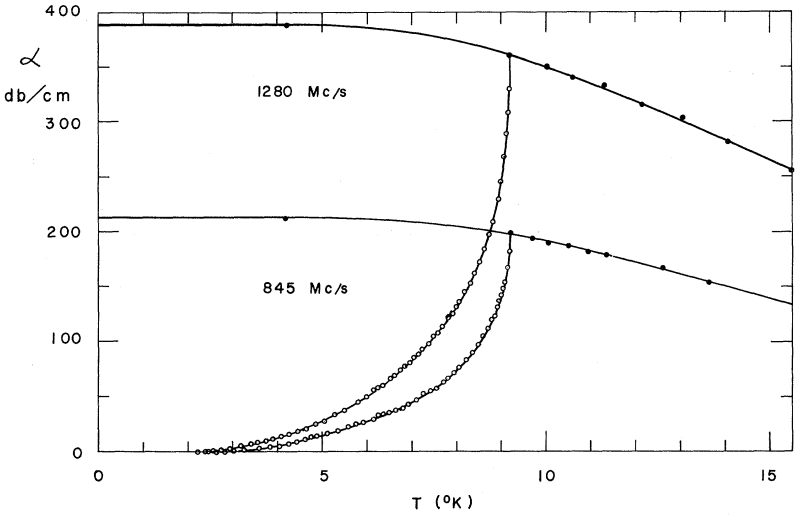

FIG. 1. Attenuation of compressional waves in the [111] direction of normal (●) and superconducting (○) niobium at 845 and 1280 Mc/sec. The transition temperature is 9.20°K.

Our preliminary data[4] at 250–370 Mc/sec showed that the reduced energy gap

$$A = 2\Delta(0)/kT_c$$

was greater than the BCS value for propagation in the [100] direction,[5] while the measurements of Levy, Kagiwada, and Rudnick[6] showed that $A = 3.5$ for shear waves with wave vector along the [110] direction. We have now made an extensive investigation of the attenuation of compressional waves in each pure mode of direction over the frequency range 288–1280 Mc/sec. Some of the data obtained for the [111] direction are shown in Fig. 1, where it can be seen that the attenuation in both the normal and superconducting states (α_n and α_s) become independent of the temperature below 2.5°K.

The reduced energy gap A is computed from a least-squares fit to the low-temperature data,[4] as illustrated in Fig. 2, where $1/[\ln(2\alpha_n/\alpha_s - 1)]$ is plotted against T/T_c for the 1280-Mc/sec curve of Fig. 1. The value of A measured is an average gap over a region of the Fermi surface nearly normal to $\mathbf{q}$ and should show any anisotropy[7] if $\mathbf{q}l_e \gg 1$, where $\mathbf{q}$ is the acoustic wave vector and l_e is the electron mean free path for impurity scattering. We have found that at 288 Mc/sec, where $\mathbf{q}l_e \simeq 1$ in our samples, the energy gaps A are for propagation parallel to each axis:

$$3.77 \pm 0.03, [100]; 3.74 \pm 0.04, [111];$$
$$3.68 \pm 0.04, [110].$$

Such "isotropy" is to be expected when $\mathbf{q}l_e \simeq 1$, but not at higher frequencies. At 1280 Mc/sec there is some anisotropy (Fig. 3), although the range of values (3.4–3.6) is much less than that found in tin

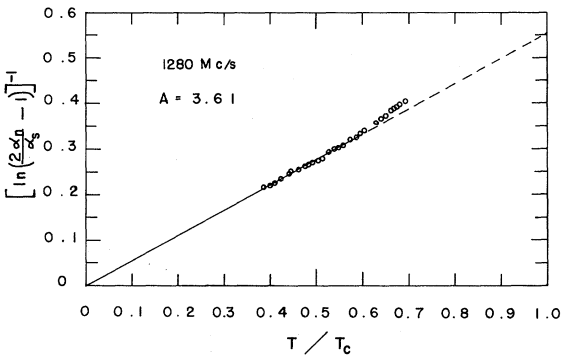

FIG. 2. Linear plot of the low temperature variation of the ultrasonic attenuation in niobium to obtain the reduced energy gap A, using the 1280Mc/sec data shown in Fig. 1.

by Morse, Olsen, and Gavenda.[7] This is in accord with the recent calculations of Garland,[8] who finds that the anisotropy of the energy gap in the transition metals will be smeared out by the $s - d$ scattering, unless the metal is extremely pure ($R_{300}/R_4 \sim 10^4$).

The mean value of the energy gap A measured at 288 Mc/sec is 3.75 ± 0.05, which is in good agreement with the values 3.84 ± 0.06 obtained by

[4] E. R. Dobbs and J. M. Perz, in *Proceedings of the Eighth International Conference on Low Temperature Physics* (to be published).

[5] The preliminary value $A = 3.96$ reported in Ref. 4 was later found to contain a calibration error. The corrected value for the [100] direction at 300 Mc/sec is $A = 3.77$.

[6] M. Levy, R. Kagiwada, and I. Rudnick, in *Proceedings of the Eighth International Conference on Low Temperature Physics* (to be published).

[7] R. W. Morse, T. Olsen, and J. D. Gavenda, Phys. Rev. Letters **3**, 15 (1959); Erratum **3**, 193 (1959).

[8] J. W. Garland, Phys. Rev. Letters **11**, 111 (1963).

tunneling,[9] and 3.85 estimated from the low-temperature heat capacity.[10] It is noticeable, however, that the value of A measured in the [100] direction decreases at higher frequencies. If this is anisotropy, it agrees with the anisotropic energy-gap model of Pokrovskii,[11] in which the effective energy gap

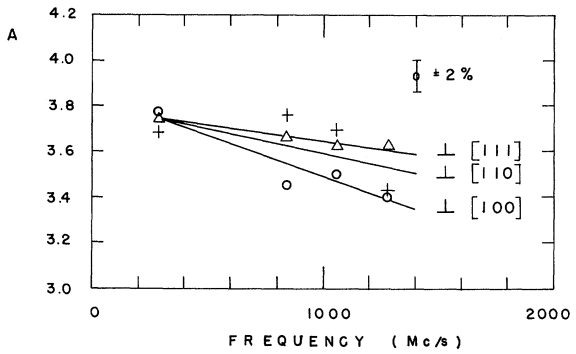

FIG. 3. Variation of the reduced energy gap A with frequency and orientation in niobium crystals. The anisotropy shown is small compared with the range of 3.1 to 3.8 found in tin. Propagation along [100] = O; [110] = +; [111] = Δ.

measured by the ultrasonic attenuation is the minimum gap.

At higher temperatures, the energy gap found from inverting the expression[1]

$$\frac{\alpha_s}{\alpha_n} = \frac{2}{\exp\left[\Delta(T)/kT\right] + 1}$$

shows a more rapid decrease with temperature[4] than can be accounted for by the BCS theory. Near T_c the function [Eq. (1)] is approximately

$$\left[\frac{\Delta(T)}{\Delta(0)}\right]^2 = B\left(1 - \frac{T}{T_c}\right),$$

where the constant $B \simeq 3.0$. We have found much higher values of B, in the range 4.8–5.3, from our measurements on niobium, as shown in Fig. 4. It is difficult to measure B accurately, since the linear plot is only valid within 0.5°K of T_c, but a reasonable estimate for B would be 5.0 ± 0.2.

Since the temperature variation of the energy gap in niobium has not been measured near T_c by any other method, it is of interest to compare our value with the "jump" in the heat capacity,[12]

$$C \equiv \frac{C_{es} - \gamma T_c}{\gamma T_c} = \frac{3A^2BF}{4\pi^2},$$

where C_{es} and γT_c are the electronic heat capacities in the superconducting and normal states at T_c, and where F is an integral over the energy gap function $\Delta(\epsilon,T)$, which for the BCS model is simply $\frac{1}{2}$. Using the recent value[10] of $C = 1.97 \pm 0.06$, and our value of B, we find that $F = 0.36$. This is considerably less than the BCS value, but close to that (0.40) obtained by Swihart[12] for an oscillating energy gap function, which he derived from a simplified Bardeen–Pines interaction.

The deviations from the BCS model shown by niobium are compared with theory, and with those found for tin and lead, in Table I. It is seen that the empirical values of A, B, and F show increasing deviations from their BCS values, as T_c/θ_D increases. The rise in A and fall in F may be accounted for by better models of the interaction $V_{kk'}$, such as those proposed by Swihart[12] and Garland.[8] But the BCS theory gives $B \simeq 3$ for all such interactions. Evidently the high B values for Sn, Nb, and Pb require a further refinement of the theory, such as the damp-

TABLE I. Parameters in the BCS Law of Corresponding States, evaluated for different electron–electron interactions and compared with experimental values for three superconductors with increasing coupling strength. $A = 2\Delta(0)/kT_c$ is the reduced energy gap; $B = [\Delta(T)/\Delta(0)]^2/(1 - T/T_c)$ shows the temperature dependence near T_c; $F = (4\pi^2C)/(3A^2B)$, where $C = (C_{es} - \gamma T_c)/(\gamma T_c)$, is an integral over the energy gap function $\Delta(\epsilon,T)$.

Interaction	T_c/θ_D	A	B	F	Source
Weak BCS model	<0.01	3.52	3.03	0.500	*a*
Strong BCS model	∞	4.00	3.00	0.500	*b*
Swihart model	0.21	4.01	3.18	0.405	*c*

	T_c	θ_D	T_c/θ_D	C	A	B	F
Sn	3.722	195[d]	0.019	1.54[d]	3.5[e]	3.5[e,f]	0.47
Nb	9.20	255[g]	0.036	1.97[g]	3.8	5.0	0.36
Pb	7.175	107[h]	0.067	2.66[i,j]	4.3[e]	8.0[k]	0.24

[a] B. Mühlschlegel, Z. Physik **155**, 313 (1959).
[b] See Ref. 2.
[c] See Ref. 12.
[d] W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).
[e] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).
[f] See Ref. 3.
[g] See Ref. 10.
[h] See Ref. 15.
[i] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958).
[j] C. A. Shiffman, J. F. Cochran, and M. Garber, Bull. Am. Phys. Soc. **8**, 307 (1963).
[k] R. E. Love and R. W. Shaw, Bull. Am. Phys. Soc. **8**, 420 (1963) and private communication.

[9] P. Townsend and J. Sutton, Phys. Rev. **128**, 591 (1962).
[10] H. A. Boorse and H. A. Leupold (private communication).
[11] V. L. Pokrovskii, Zh. Eksperim. i Teor. Fiz. **40**, 641 (1961) [English transl.: Soviet Phys.—JETP **13**, 447 (1961)].
[12] J. C. Swihart, IBM J. Res. Develop. **6**, 14 (1962).

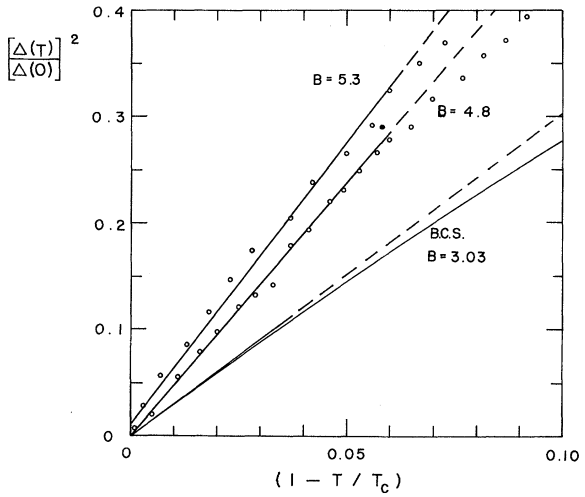

FIG. 4. Linear plot of the high-temperature variation of the energy gap in niobium from ultrasonic attenuation to obtain the parameter B. The data shown are for the highest and lowest values of B measured. — — — is tangent to the BCS curve, of slope 3.03.

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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[15] P. H. Keesom and B. J. C. van der Hoeven, Phys. Letters **3**, 360 (1963).

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

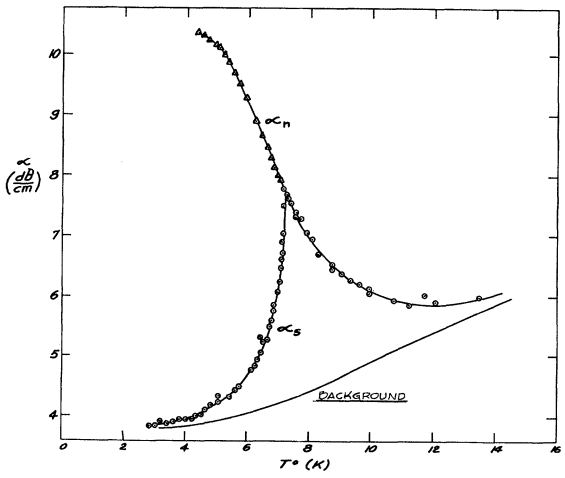

FIG. 1. Ultrasonic attenuation in lead for longitudinal waves propagating in the [100] direction at 50 Mc/sec.

diagram of our arrangement is essentially the same as that reported on by Bohm and Kamm.[4]

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.
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[2] W. P. Mason and H. E. Bömmel, J. Acoust. Soc. Am. **28**, 930 (1956).
[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).