

**EVIDENCE FOR ANISOTROPY OF THE SUPERCONDUCTING ENERGY GAP  
FROM ULTRASONIC ATTENUATION\***

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The Bardeen, Cooper, and Schrieffer theory of superconductivity has shown remarkably good agreement with most experiments considering that a single isotropic energy gap has been used.<sup>1</sup> However, there are disagreements, particularly with respect to specific heats, as was emphasized by Boorse in a recent Letter.<sup>2</sup> A likely explanation of such discrepancies is that the energy gap in most superconductors is appreciably anisotropic.<sup>3</sup> Thus the specific heat variation with  $T$  would be determined near the transition temperature ( $T_c$ ) by some average value of the gap, while at low temperatures the smaller values would dominate.

In order to demonstrate whether or not the energy gap depends upon the electron's position on the Fermi surface, an experiment must select electrons from a fairly limited region of the surface. Such is the case with the ultrasonic attenuation. If the electronic mean free path ( $l$ ) is large compared to the wavelength ( $\lambda$ ), then a sound wave having vector  $\vec{q}$  scatters electrons from state  $\vec{k}$  to  $\vec{k}'$ , where  $\vec{k}' = \vec{k} \pm \vec{q}$ . In addition, a phonon is absorbed or emitted; i.e.,  $E(\vec{k}') = E(\vec{k}) \pm \hbar\omega$ , where  $\omega$  is the angular frequency of the sound wave. These conditions of momentum and energy conservation are satisfied only by a particular group (or groups) of electrons on the energy surface. Since  $\hbar\omega$  is small, then  $\Delta E = (\Delta\vec{k}) \cdot (\nabla_{\vec{k}} E)$ , or  $\hbar\omega = \vec{q} \cdot (\nabla_{\vec{k}} E)$ , where  $\nabla_{\vec{k}}$  is the gradient operator in  $k$  space. Since the electronic group velocity is  $\vec{v}_0 = \hbar^{-1} \nabla_{\vec{k}} E$ , the required electrons are those for which  $v_0 \cos\theta = v_s$ , where  $v_s$  is the velocity of sound and  $\theta$  is the angle between  $\vec{q}$  and  $\vec{v}_0$ . Thus the scattered electrons are ones which drift in the direction of the wave with the speed of sound and so remain in a constant phase of the wave. For a spherical energy surface these electrons lie on a ring perpendicular to the direction of the sound propagation, and since  $v_0 \gg v_s$ , this ring of electrons is nearly an equatorial one.<sup>4</sup>

As has been shown previously,<sup>5</sup> the temperature dependence of the longitudinal wave attenuation in superconductors is determined in the Bardeen-Cooper-Schrieffer theory by the energy-gap temperature variation. By this theory the ratio of the superconducting attenuation coefficient

( $\alpha_s$ ) to that in the normal state ( $\alpha_n$ , a constant) is given by

$$\alpha_s/\alpha_n = 2(e^{\epsilon/kT} + 1)^{-1}, \quad (1)$$

where  $2\epsilon$  is the temperature-dependent energy gap. Thus measurements of  $\alpha_s/\alpha_n$  as a function of  $T$  for waves in various directions in a single crystal, by selecting different groups of electrons, should show up any significant anisotropy of  $\epsilon$ .

We have made measurements of longitudinal wave attenuation at frequencies up to 80 Mc/sec in oriented single crystals of tin at temperatures down to 1.00°K. From these observations it appears that  $2\epsilon_0$ , the energy gap as  $T \rightarrow 0$ , varies at least between  $3.2kT_c$  and  $4.3kT_c$ . The samples were oriented such that propagation was along [001], [100], and [110]. Figure 1 shows the measurements along two of these directions and displays the extreme behaviors. Observations

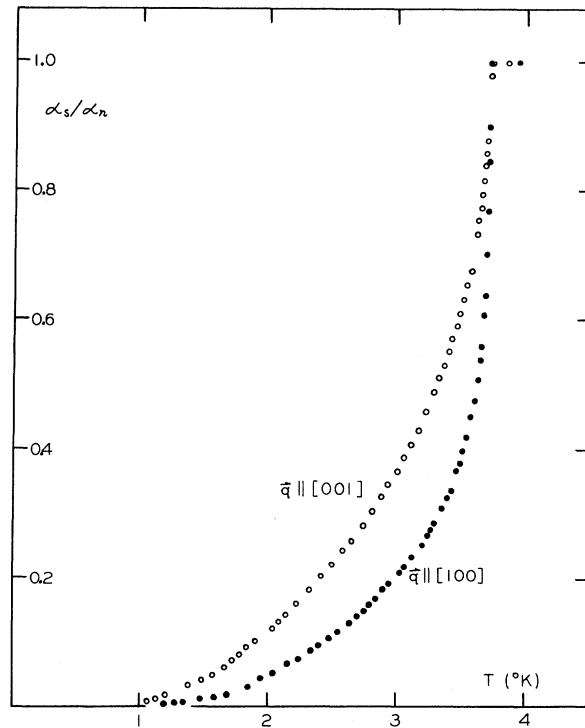


FIG. 1. Normalized longitudinal wave attenuation in tin. Propagation along [001] is at 72 Mc/sec; that along [100] is at 42 Mc/sec.

reported earlier by Bohm and one of us,<sup>5</sup> which were made on a different [001] crystal with different equipment, agree closely with the [001] measurements shown here. It should be noted that in all the measurements made, the condition  $\lambda \gg l$  was amply satisfied ( $ql$  is estimated to be 20 or more).

The energy gap anisotropy is most effectively demonstrated if  $\log(\alpha_s/\alpha_n)$  is plotted versus  $T_c/T$  since this curve should approach a straight line for large  $T_c/T$ , the slope being determined by  $\epsilon_0$ . In order to do this, however, an extrapolation of  $\alpha_s$  to  $T=0$  must be made in order to find  $\alpha_n$  and to eliminate attenuations of nonelectronic origin. This was done by choosing that extrapolation which gave the best straight-line limit when  $\log(\alpha_s)$  is plotted vs  $T_c/T$ . The measurements for the three orientations when plotted in this way are shown in Fig. 2. The estimates of  $2\epsilon_0$ , determined by the straight-line portions of the curves, are as follows: [001],  $(3.2 \pm 0.1)kT_c$ ; [100],  $(4.3 \pm 0.2)kT_c$ ; and [110],  $(3.8 \pm 0.1)kT_c$ .

Naturally, the attenuation in any one direction

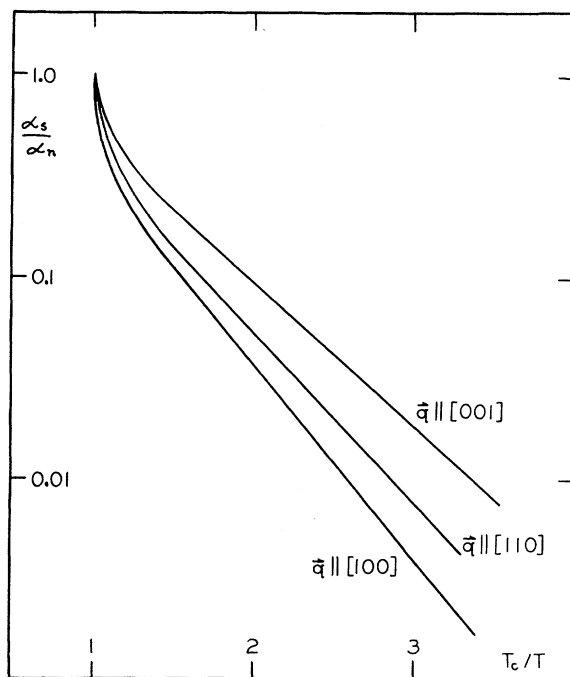


FIG. 2. Plots of  $\log(\alpha_s/\alpha_n)$  vs  $T_c/T$  for longitudinal waves along different crystalline axes in tin. Propagation along [110] is at 76 Mc/sec. Measurements for the other directions are those shown in Fig. 1.

would not necessarily reflect a single value for  $2\epsilon_0$  since the scattering involves an average around a ring of the Fermi surface (or perhaps more than one in tin). Thus the values for  $2\epsilon_0$  given above probably represent only approximate values for dominant parts of the surface. However, the large qualitative differences observed seem most reasonably explained by energy gap variations of at least the magnitude indicated above. Such differences cannot be explained by variations among the samples since the same sample was used for measurements along [001] and [110]. Furthermore, measurements in one crystalline direction at different frequencies and on different samples gave very similar results.

It should be noted that Eq. (1) does not give a very good fit to the experimental points shown in Fig. 1 when the single energy gaps quoted above are used. In particular, the experimental decrease just below  $T_c$  is steeper than indicated by these energy gaps. This suggests that in each direction of propagation there are some electrons involved which have an energy gap higher than the value estimated by the slope of Fig. 2. Thus one obtains a good fit to the experimental curve for [001], for example, by assuming that 80% of the electrons have  $3.2kT_c$  and 20% have  $4.3kT_c$  for  $2\epsilon_0$ .

Similar measurements are being made with shear waves. Because of the introduction of a plane of polarization, these should be more selective in choosing electrons on the Fermi surface than are longitudinal waves.

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<sup>1</sup>Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957).

<sup>2</sup>H. A. Boorse, Phys. Rev. Letters **2**, 391 (1959).

<sup>3</sup>This possibility, which has been suggested by a number of persons, was discussed at the International Conference on the Electronic Properties of Metals at Low Temperatures, Geneva, New York, August 25-29, 1958 (unpublished).

<sup>4</sup>It is probable that the group velocity of a given group of electrons becomes modified in the superconducting state [see Bardeen, Rickayzen, and Tewordt, Phys. Rev. **113**, 982 (1959)]. This effect, however, does not alter the argument that propagation in different directions involves different electrons.

<sup>5</sup>R. W. Morse and H. V. Bohm, Phys. Rev. **108**, 1094 (1957).