Ultrasonic Studies of the Superconductivity of Doped Tin. II

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Recent ultrasonic-attenuation studies have led to conflicting interpretations concerning the reduced anisotropy of the superconducting energy gap characteristic of impure Sn. Perz and Dobbs have concluded that the reduced anisotropy is only due to an averaging of the electron–sound-wave interaction over the Fermi surface, while we have concluded that under the specified conditions the reduced anisotropy is indeed a real measure of the superconducting properties. The two conclusions are discussed here in detail, and additional ultrasonic data are presented. Finally, comparison is made with recent thermal-conductivity measurements in impure Sn.

IN a recent paper Perz and Dobbs[1] have reported the observation of a dependence on $q\bar{l}$ of the anisotropy of the superconducting energy gap as measured by ultrasonic attenuation, where $\mathbf{q}$ is the propagation vector of the sound wave and $\bar{l}$ is the "average" electron mean free path as determined from resistivity-ratio measurements. This result is in conflict with (1) the observations of Thomas[2] for $q\bar{l}$ values as low as ~ 0.25, and (2) the observation by the authors[3,4] of no frequency dependence of the anisotropy for $q\bar{l}$ values as low as 0.5. The authors[3,4] found a reduced anisotropy of the superconducting energy gap in impure Sn; it was ascertained that the anisotropy was a function of the transition temperature and not a function of $q\bar{l}$. Consequently, the reduced anisotropy was interpreted as a real change in the superconducting properties of the doped Sn system. The resolution of these differing results and interpretations are important to the application of the ultrasonic technique in the elucidation of the properties of real superconductors. This paper is intended as a comment on Ref. 4 in the light of the questions raised by Perz and Dobbs and also in consideration of recent thermal-conductivity measurements.[5]

The BCS[6] theory predicts that for an isotropic superconductor the ratio of the compressional wave attenuation in the superconducting state to that in the normal state is given by $\alpha_s/\alpha_n = 2f(\Delta)$, where f is the Fermi function and $\Delta(T)$ the temperature-dependent superconducting energy gap. This result has been shown by Tsuneto[7] to be independent of sound frequency and electron mean free path for impurity-limited scattering. Morse[8] and Leibowitz[9] have assumed that the above form is correct for anisotropic superconductors, but that for a given crystal direction the value of the limiting energy gap $\Delta(0)$ can assume a value different from the BCS value of $1.76\ k_BT_c$, where T_c is the transition temperature. The $\Delta(0)$ for a given crystallographic direction was obtained in early studies by measuring the slope of a plot of $\ln(\alpha_s/\alpha_n)$ versus T_c/T over the low-temperature range, for which $f(\Delta) \sim \exp[-\Delta(0)/k_BT]$ and $\Delta(T) \sim \Delta(0)$. In more recent studies the authors[3,4] have taken into account the temperature dependence of the energy gap and have used nonlinear least-squares fitting techniques to analyze the data rather than graphical extrapolation techniques.

The "selectivity" of the interaction between the conduction electrons and a sound field can be discussed in terms of the product ql for the free-electron model, where l is an isotropic electron mean free path. It was shown by Pippard[10] that for $ql \ll 1$, the interaction is averaged over the entire Fermi surface, but that for $ql \gg 1$, conservation of energy and momentum restricts the interaction to carriers having a velocity component in the direction of $\mathbf{q}$ equal to the sound velocity. For intermediate values of ql, Leibowitz[9] discussed the selectivity in terms of the angle for which the amplitude of the perturbation of the electron distribution due to the sound field is reduced to half-maximum, and showed that the interaction is weighted toward the electrons near the equator for $ql \gtrsim 1$. In the case of a multizoned, real superconductor, the attenuation in both the normal and superconducting states is complicated considerably. The complications of a real superconductor have been discussed at length by Kadanoff and Pippard.[11] Attempts to use more sophisticated models to analyze data for Sn have been presented by the authors.[4]

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It is well established that small amounts of impurity added to a pure superconductor tend to reduce the transition temperature (cf. Lynton *et al.*[12]). The reduction is approximately linear in $\bar{l}^{-1}$, and according to the current theories of dirty superconductivity due to Anderson,[13] Tsuneto,[14] and Markowitz and Kadanoff,[15] the decrease in transition temperature is simultaneous with a smearing out of the energy-gap anisotropy. The energy gap should be approximately isotropic when $\Delta(0)<\hbar\tau^{-1}$, where τ is an isotropic relaxation time for the electrons. In an attempt to verify the removal of gap anisotropy with doping, the authors made measurements in single crystals of doped Sn. The first results for In-doped Sn were given in Ref. 3. A decrease in the anisotropy of the limiting energy gap measured in the [110] and [001] directions at low temperatures was observed for solute concentrations of ~0.1 at. %. Even though no $q\bar{l}$ variation in gap was found for any given sample, a great deal of care was taken to avoid a decrease in $q\bar{l}$ upon going to the more impure samples. After the similarity to the results of Thomas was noted, the point was not discussed in detail in Ref. 4.

In Table I, data from Ref. 3 are presented along with $q\bar{l}$ values for the cited experiments. The values of $\bar{l}$ are obtained by use of the formula of Doidge,[16] as was done in Ref. 1. A lack of any $q\bar{l}$ dependence for the anisotropy can be seen by comparing the data for pure Sn and the most dilute alloy. It can also be seen that in the range of concentration for which the anisotropy changed, the value of $q\bar{l}$ was actually increased by a factor of almost 2 upon going to the most heavily doped sample. These results are illustrated in Fig. 1 and demonstrate that the decrease in anisotropy with increasing $q\bar{l}$ is counter to the change predicted by consideration of an ultrasonic averaging process. The additional data used by the authors in Ref. 4 were taken at similar $q\bar{l}$ values. Thus it was concluded that the averaging was associated with the change in $\bar{l}$ in accordance with the notions of Anderson.[13] These results are also in agreement with the infrared-absorption data of Richards[17] for similar impurity concentrations.

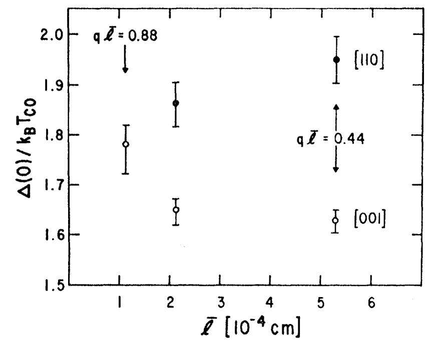

FIG. 1. Measured values of the limiting energy gap as a function of $\bar{l}$. The two extreme values of $q\bar{l}$ are indicated.

TABLE I. Comparison of $q\bar{l}$ values and measured energy gaps for In-doped Sn used by Claiborne and Einspruch.[a] R is the resistivity ratio, $\bar{l}$ is the electron mean free path determined from R, ν is the frequency of ultrasonic wave, q is the propagation vector, $\Delta(0)$ is the limiting energy gap, and T_{c0} is the transition temperature of pure Sn.

Direction of propagation	R	$\bar{l}$ (10^{-4} cm)	ν (MHz)	$q\bar{l}$	$\Delta(0)$ (k_BT_{c0})
[001]	$>10^4$	10^2	50	>10	1.63±0.02
	500	5.3	50	0.44	1.63±0.02
	196	2.1	150	0.52	1.65±0.02
	108	1.1	460	0.88	1.78±0.04
[110]	$>10^4$	10^2	50	>10	1.97±0.04
	500	5.3	50	0.45	1.95±0.04
	196	2.1	130	0.46	1.86±0.04

[a] Reference 3.

Gueths *et al.*[5] have estimated the superconducting energy gap for impure Sn from thermal-conductivity measurements. The dependence of the [001] gap upon resistivity ratio in Cd-doped Sn is in precise agreement with the ultrasonic data.[4] The internal consistency between these results and the infrared-absorption data confirms that the change in anisotropy is indeed associated with the actual superconducting properties. There is some scatter between the thermal-conductivity data and ultrasonic data for the [110] direction; however, reduced anisotropy is indicated for the same values of resistivity ratio. As was mentioned by the authors in Ref. 4, the [110] direction involves more complicated averaging for the ultrasonic wave than the [001]. Hence it is not surprising that there may be some minor variations in the actual gap values for this direction compared with results obtained with other measurement techniques.

The Anderson criterion for going from the weak-scattering case is that $\hbar\tau^{-1}$ is comparable to the energy gap $\Delta(0)$. Using standard definitions, BCS,[6] and the average value for $\bar{l}$ in the most heavily doped sample mentioned in Ref. 3, $\Delta(0)\tau/\hbar=1.5$. Thus it is not at all incredible that some decrease in gap should be observed for this range of impurity concentrations. Order-of-magnitude arguments for either the Anderson criterion or for the ultrasonic averaging should be used with extreme caution; however, and as will be discussed below, there are other more proper questions which should be considered.

Perz and Dobbs[1] point out quite correctly the dangers inherent in extrapolating the data at low temperatures to find a value of the limiting attenuation α_0; this point was discussed as well by the authors.[4] In order to avoid such extrapolation, Perz and Dobbs[1] extended their measurements to 0.8°K, at which point the

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attenuation was temperature-independent within the sensitivity of their apparatus. Their data were analyzed using this value as α_0. The measurements by Morse *et al.*,[8] Leibowitz,[9] and Thomas,[2] as well as by the authors,[4] have been made to $\sim$1.1°K. The authors used a nonlinear least-squares fitting technique in which α_0 was left as a parameter. Both techniques explicitly assume that the BCS temperature dependence for the attenuation is correct. No other subjective elements are introduced in the authors' analysis, *since the data points from $\sim$1.5 to 1.1°K are all weighted equally*.

There are some dangers in using a measured value of α_0 which must be pointed out. First, if the measured value of α_0 is assumed to be absolute and the attenuation in the superconducting state is measured relative to it, then *the value of α_0 is given a statistical weight far in excess of its experimental certainty*. The proper method for processing this datum is to weigh it equally with all the other low-temperature data points. Of necessity, such treatment will require some analytical fitting technique in which the "true" α_0 is left as a fitting parameter. In most cases this parameter would have to be known with far more accuracy than is experimentally possible in order to determine a meaningful value for the limiting energy gap. In addition to experimental uncertainties there are at least two physical effects which can also result in uncertainties in the data at low temperatures. The first of these effects is the possible amplitude-dependent attenuation such as that found in Pb by Love,[18] which would manifest itself first at the lowest temperatures. Neither Perz and Dobbs[1] nor the authors observed any amplitude dependence at temperatures above 1.1° K, but the possibility should always be considered. The second possible physical effect to be considered is the domination of low-temperature attenuation by a minimum in the energy gap which is localized in k space, as discussed by Kadanoff and Pippard.[11] Because of the limited amount of phase space available for quasiparticle scattering, the relaxation times involved for such regions would be much longer than under normal circumstances. The addition of impurities can reduce the relative contribution to the attenuation by the carriers associated with the average gap in the zone without appreciable effect on the contribution due to carriers associated with the minimum gap. Thus, in impure samples the low-temperature data can be more strongly influenced by such a localized minimum of the gap than would be the case for pure material. These considerations are pertinent to any studies of impure superconductors.

To develop a realistic model for discussion of the averaging processes associated with Sn, one cannot simply add energy-gap anisotropy to a single-zone, free-electron picture; other anisotropic properties must be considered as well. Extensive tunneling measurements by Zavaritskii[19,20] in single-crystal Sn have yielded a workable picture for the multizone material. The energy gaps appear to be relatively isotropic within a zone but vary from zone to zone. Both Perz and Dobbs[1] and the present authors[4] have invoked this picture in explaining data for pure Sn. The only calculation of attenuation relevant to this more complex situation is that by Pippard[10] for a normal two-band metal. It is clear from his calculations that both inter- and intraband relaxation must be considered. As mentioned in Ref. 4, ionized impurity scattering depends strongly on v_F, the Fermi velocity, and will vary from zone to zone. For dilute alloys and high frequencies, it is likely that the relevant ql for some zones will correspond to $ql \gg 1$ and be independent of scattering mechanisms; while for other zones, scattering may strongly influence the attenuation. For such a case, doping can cause an explicit change in the relative contributions to the attenuation as well as a reduction of any gap anisotropy within a given zone.

In conclusion, the data on the reduced anisotropy in doped Sn reported by the authors[3,4] are more consistent with the averaging associated with dirty superconductors than with the "$q\bar{l}$" effect reported by Perz and Dobbs.[1] This conclusion is supported by thermal-conductivity measurements. For studies of the details of the "washout" the above discussion is important; however, for simple comparisons between the isotropic and anisotropic attenuation the discussion of the averaging process becomes somewhat academic.

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