Energy Gap and Thermal Conductivity of Pure and Impure Superconducting Tin*

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A theory is presented for the energy gap and the thermal conductivity in pure and impure tin. The central features are taken from the papers of Markowitz and Kadanoff and of Hohenberg, and include anisotropy in the pure material which is systematically eliminated by increased doping. First the usual theory of thermal conductivity is generalized to allow for gap anisotropy. Next an anisotropic gap function for pure tin is constructed using experimental results of other investigators. Synthesizing these two stages yields a prediction for the thermal conductivity of pure superconducting tin as a function of orientation and temperature. This prediction is in fair agreement with the data of Guénault. Turning to the impure metal, we find that the gap depends upon four quantities: energy ω, angle Ω, mean free path l, and temperature T. Simplifications are introduced whereby the complicated dependences are separated into simpler factors. Stress is laid upon the distinction between anisotropy in the gap edge and the effect of anisotropy on quantities such as the average gap and T_c. The gap edge is rendered isotropic by impurities well before the effect is felt by the other quantities. In fact it is the gap edge which is vital to thermal conductivity, since it is there that the carriers reside. Predictions for thermal conductivity in impure tin are compared with data of Pearson *et al.* and found to show good qualitative agreement. In particular, a reduction in the ratio of superconducting to normal thermal conductivity for certain sample directions is explained by the elimination of gap-edge anisotropy. However, this effect occurs at a much smaller impurity concentration than that predicted theoretically. This discrepancy and related matters are fully discussed.

I. INTRODUCTION

THIS paper will attempt to correlate our understanding of energy-gap anisotropy in a superconductor with the behavior of thermal conductivity. It is well known that in a pure material the gap anisotropy has a small influence on most properties that do not single out a particular portion of the Fermi surface. These include most of the properties discussed by BCS as well as transport properties, where essentially all the carriers contribute to a comparable extent. However, when dealing with the latter, if one computes ratios of the superconducting to normal-state values, then anisotropy present in the normal state largely cancels out, and one is left only with the gap anisotropy, which, though small, is then very apparent.

If one considers the change in certain properties with small additions of impurities, one often finds that the main effect is a result of the washing out of anisotropy. This is the case if, once again, one considers superconducting-to-normal ratios, since any influence of reduced mean free path on the normal-state parameters then cancels out and one is left with the effect of reduced mean free path on gap anisotropy. This effect is generally also small but very apparent.

Until now treatments of anisotropy in pure and impure materials have relied upon gross features such as the mean-squared anisotropy around the entire Fermi surface. No sustained attempt has been made at a detailed comparison of gap anisotropy and anisotropy in other properties. However, there is now available sufficient data on gap anisotropy and on the anisotropy of thermal conductivity in the same material, namely tin, to make a detailed comparison possible. The data on gap anisotropy are summarized by Douglass and Falicov[1] and are also supported by the conclusions of Markowitz and Kadanoff (MK).[2] The thermal conductivity data were reported by Guénault[3] for pure tin and by Pearson *et al.*[4] for pure and impure tin.

A second motivation for this work follows from a result of Pearson *et al.* In the low-impurity region, $K_g^n \ll K_e^n$ and also $K_g^s \ll K_e^s$. (The notation is conventional. See Pearson *et al.*) Using these facts, Pearson finds that $K_e^s(T)/K_e^n(T)$ *decreases* with small amounts of impurity. This result is surprising according to one's first line of reasoning. This is to note that Anderson's theorem[5] implies that any impurity-induced alteration in a property which depends only on the energy gap is due to washing out of anisotropy. But the washing out process has been shown (by MK and Hohenberg[6]) to cause a decrease in the ability of electrons to make full use of the (anisotropic) pairing potential, and this in turn always diminishes the effective gap. Now $K_e^s(T)/K_e^n(T)$ is simply a gap-dependent integral, except for ultrapure samples. (This will appear below.) On this basis we would expect $K_e^s(T)/K_e^n(T)$ to *increase* (i.e., to draw closer to unity) with small

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[1] D. H. Douglass, Jr., and L. M. Falicov, in *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1964), Vol. IV, p. 97.

[2] D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963), referred to as MK.

[3] A. M. Guénault, Proc. Roy. Soc. (London) **A262**, 420 (1961).

[4] G. J. Pearson, C. W. Ulbrich, J. E. Gueths, M. A. Mitchell, and C. A. Reynolds, preceding paper, Phys. Rev. **154**, 329 (1967).

[5] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).

[6] P. Hohenberg, Zh. Eksperim. i Teor. Fiz. **45**, 1208 (1963) [English transl.: Soviet Phys.—JETP **18**, 834 (1964)].

amounts of impurity. Thus we appear to have an anomalous experimental result to explain.

We shall now call attention to a rather unexpected feature of the current theory of a doped anisotropic superconductor. This feature is central to the present work. A prediction of MK is that, as far as critical temperature is concerned, anisotropy is substantially eliminated from the system when $\xi_0/l\approx 3$; ξ_0 is the coherence length, l is the mean free path. Hohenberg[6] uses a model similar to that of MK to investigate, among other things, the washing out of gap anisotropy at $T=0$. The prediction is that anisotropy is substantially eliminated when $\xi_0/l\approx\frac{1}{4}$. This prediction was implied, but not stated, in that paper. It is not widely appreciated that this difference in predicted behavior exists, namely, that anisotropy in the gap at $T=0$ disappears at a mean free path a dozen times larger (impurity concentration a dozen times smaller) than it does at $T=T_c$. The present paper concurs with the others and provides an explanation for this difference in a later section.

In the succeeding sections of this paper, we set up and solve a specific model of thermal conductivity in the presence of gap anisotropy. There are three central ingredients in the model, treated in turn: an anisotropic generalization of a pre-existing isotropic theory, that of Kadanoff and Martin[7] for thermal conductivity in the superconducting state; a model of the gap anisotropy specific to tin, adapted from Douglass and Falicov; and a model of the impurity-induced reduction in anisotropy based on the work of MK and Hohenberg. Finally, we perform a machine computation to obtain the anisotropic thermal conductivity of the pure material, and also the effect of impurities upon the anisotropy of thermal conductivity.

It turns out that we can go some distance in the explanations and correlations called for by this introduction. In particular, the effect observed by Pearson is attributed to the elimination of anisotropy of the thermal conductivity ratio by impurities, which results in a decrease in this ratio for his sample orientation. However, the magnitude of the effect is greater than predicted, and it occurs at a lower impurity concentration.

II. ANISOTROPIC THERMAL CONDUCTIVITY

The effect of an anisotropic gap on the thermal conductivity can be displayed by a straightforward extension of the theory of Kadanoff and Martin.[7] This is most easily done using the Boltzmann-equation approach of Tewordt.[8] One weak point in this type of approach is that it treats excitations as quasiparticles, whereas we know from the more general Green's-function analysis that the excitations are more complex than the quasiparticle picture. Nevertheless, it is hoped that any errors brought about by this weakness will cancel out in the difference between the doped and undoped cases.

For transport in an anisotropic medium the current and the temperature gradient (or field, in the electrical problem) lie in different directions. The angle ξ between these directions will be small for small anisotropy. A factor of $(\cos\xi)^{-1}$ will appear in any expression for conductivity, but one may use $\cos\xi\approx 1-\frac{1}{2}\xi^2$. Anticipating that the eventual correction term to the ratio K_e^s/K_e^n will be $\frac{1}{2}(\xi_s^2-\xi_n^2)$ (where this quantity is temperature-dependent), we shall now call attention to the smallness of this quantity.

Simple tensor relations determine ξ in any case where one knows $K_{\parallel}$ and $K_{\perp}$, the relevant conductivities parallel and perpendicular to the c axis. The result is

$$\xi\approx\tfrac{1}{2}(K_{\perp}/K_{\parallel}-1)\sin 2\theta. \tag{II.1}$$

This is a maximum at $\theta=45°$, and it is zero at $\theta=0°, 90°$. From values of K tabulated by Guénault and Pearson, we find that $K_{\perp}/K_{\parallel}$ differs from one typically by 20% for the purities of interest in the present paper. Thus the correction term to K_e^s/K_e^n is less than 1% and in fact is exactly zero for the angles of greatest interest to us. For this reason, ξ is later neglected.

Returning to Tewordt's method, the relaxation times for scattering of electrons by phonons and by impurities are denoted $[2\Gamma_{\rm ph}^s(\mathbf{k})]^{-1}$ and $\tau_{\rm imp}^s$, respectively, so that the Boltzmann equation takes the form

$$\frac{k_z}{m}\frac{\epsilon_k}{T}\frac{\partial f_k^0}{\partial E_k}\frac{dT}{dz}=\left\{2\Gamma_{\rm ph}^s(\mathbf{k})+\frac{1}{\tau_{\rm imp}^s}\right\}(f_k-f_k^0). \tag{II.2}$$

The various quantities making up this expression have the meanings given by Tewordt in his equation (4.1). Solving for $f_k-f_k^0$ and substituting into Tewordt's equation (4.6), one obtains

$$K_e^s=-\frac{1}{4}\frac{[\cos\xi_s]^{-1}}{m^2kT}\int k_z^2\epsilon_k^2 \times\operatorname{sech}^2\left[\frac{(\epsilon_k^2+\Delta_k^2)^{1/2}}{2kT}\right]\frac{d^3k}{2\Gamma_{\rm ph}^s(\mathbf{k})+1/\tau_{\rm imp}^s} \tag{II.3}$$

for the superconducting-state thermal conductivity. Here, Δ_k is the energy gap which is a function of crystal direction Ω as well as quasiparticle energy ω. The normal-state thermal conductivity is found simply by taking $\Delta_k=0$. Transforming the momentum integrations into energy and angular integrations, and forming the ratio K_e^s/K_e^n, one obtains

$$\frac{K_e^s(T)}{K_e^n(T)}=\frac{9\cos\xi_n}{8\pi^3\cos\xi_s}\left[1+a\left(\frac{T}{T_c}\right)^3\right] \times\int_0^{2\pi}d\phi'\int_0^{\pi}\cos^2\theta'\sin\theta'd\theta' \times\int_0^{\infty}\frac{\operatorname{sech}^2(\omega/2kT)}{a(T/T_c)^3+\epsilon/\omega}\epsilon^2d\epsilon. \tag{II.4}$$

[7] L. P. Kadanoff and P. C. Martin, Phys. Rev. **124**, 670 (1961).
[8] L. Tewordt, Phys. Rev. **128**, 12 (1962).

We have used

$$\omega^2=\epsilon^2+[\Delta(\Omega',\omega,T)]^2. \quad \text{(II.5)}$$

In (II.4) $\Omega'=(\theta',\phi')$ are the polar and azimuthal angles, measured relative to the sample axis. This expression is therefore a function of the orientation of the sample axis relative to some arbitrary direction. As pointed out in Ref. 4, the parameter a is the ratio of the thermal resistivity due to scattering of electrons by phonons to that due to scattering by impurities, evaluated at $T=T_c$. The remaining quantities have the same meanings as in Ref. 4. The full dependence of Δ_k upon all the parameters of interest can be denoted by writing

$$\Delta_k=\Delta(\Omega,\omega,l,T), \quad \text{(II.6)}$$

i.e., angle, energy, mean free path, temperature.

III. ENERGY GAP IN PURE TIN

Having determined an expression for the thermal conductivity of a superconductor in terms of an arbitrary energy gap, it is necessary to examine the anisotropy of the gap in the pure substance. In the pure material, $\Delta(\omega)\approx\Delta(\Delta)$ for energies ω of interest. The variation of the energy gap [i.e., $\Delta(\Delta)$], evaluated at $T=0$, with crystal direction in pure tin has been the object of extensive experimental investigation. These investigations include the work of Morse,[9] Mackintosh,[10] and Bezugli.[11]

The experimental results have been tabulated by Douglass and Falicov[1] in their figure 5.16. Since the data came from acoustic-attenuation measurements, the gap reported is actually an average over a plane perpendicular to the direction of sound propagation. In the text accompanying Fig. 5.16 of Douglass and Falicov, they present further gap values obtained from tunneling, a technique which sees the gap in a specific direction.

Using the values presented there, one must unfold the equatorial averages to obtain $\Delta(\Omega)$. There are simply not enough data to do a thorough unfolding. However, the twin assumptions of an elliptical θ dependence and a simple φ dependence having the symmetry of Fig. 5.16 (which has the symmetry of the crystal, as it must) allow us to write down a formula consistent with the bulk of the data:

$$2\Delta(\Omega)/(kT_c)=3.1+1.2\cos^2\theta-0.3\sin^2\theta\cos 8\varphi \quad \text{(III.1)}$$

at $T=0$. We find that $\langle 2\Delta(\Omega)\rangle=3.5kT_c$, which happens to agree with the BCS value. (Angular brackets denote an average around the Fermi surface.) If we put $\Delta(\Omega)=\langle\Delta(\Omega)\rangle[1+a(\Omega)]$, we find $\langle[a(\Omega)]^2\rangle=0.012$. We recall that the theory of MK[2] determined that the value of $\langle a^2\rangle$ for tin which produced best agreement with critical temperature measurements on impure samples is $\langle a^2\rangle=0.019$. It should be noted that the value of $\langle a^2\rangle$ is probably underestimated by the present procedure since properly unfolding the equatorial averages should produce greater variations in $a(\Omega)$. [Notice that the function $a(\Omega)$ is not to be confused with the parameter a defined in Sec. II.]

As far as the temperature dependence of the anisotropic gap is concerned, we assume that

$$\Delta(\Omega,T)=\Delta(\Omega)f(T), \quad \text{(III.2)}$$

where $f(T)$ is the temperature variation given by the BCS theory[12] for the isotropic gap. This assumption is consistent with the theory of MK as well as with the experimental results of Hebel,[13] Masuda,[14] and Masuda and Redfield.[15]

IV. THERMAL CONDUCTIVITY IN PURE TIN

Upon substituting Eq. (III.1) into Eq. (II.4) and performing the integrations, one obtains the thermal conductivity as a function of temperature. However, if (II.4) is used in the form shown above, the result will be valid only for the particular case of the sample axis lying parallel to the [001] axis. To obtain K_e^s/K_e^n for an arbitrary direction it is necessary to express the angles θ, φ in terms of the angles θ', φ' and the orientation (α,β) of the sample axis relative to the [001] axis. This is easily done by using the Euler transformation matrix for coordinate system rotations which gives

$$\cos\theta=\sin\alpha\sin\varphi'\sin\theta'+\cos\alpha\cos\theta', \quad \text{(IV.1a)}$$

$$\cos\varphi\sin\theta=\cos\beta\cos\varphi'\sin\theta'-\sin\beta\cos\alpha\sin\varphi'\sin\theta'+\sin\beta\sin\alpha\cos\theta', \quad \text{(IV.1b)}$$

$$\sin\varphi\sin\theta=\sin\beta\cos\varphi'\sin\theta'+\cos\beta\cos\alpha\sin\varphi'\sin\theta'-\cos\beta\sin\alpha\cos\theta'. \quad \text{(IV.1c)}$$

These expressions together with (II.4) can now be used to find the thermal conductivity for any crystal direction in pure tin. However, the presence of the parameter a in (II.4) unnecessarily complicates the analysis and for the present purposes it will be sufficient to assume that $a=0$. Inspection of the values of a in Ref. 4 shows that this assumption is not too bad an approximation for any of the samples. It is even fairly good for the "pure" sample where $a=0.28$. At any rate, the effect of a small a in Eq. (II.4) is negligible except near $T=T_c$.

Assuming that $a=0$, and ignoring ξ, Eq. (II.4) then reduces to the simple form

$$\frac{K_e^s}{K_e^n}=\frac{9}{\pi^3}\int_0^{2\pi}d\varphi'\int_0^{\pi/2}\cos^2\theta'\sin\theta'd\theta'\times[G_1'+G_2'+2G_3'], \quad \text{(IV.2)}$$

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

[10] A. R. Mackintosh, in *Proceedings of the Seventh International Conference on Low Temperature Physics* (University of Toronto Press, Toronto, Canada, 1961), p. 240.

[11] P. A. Bezugli, A. A. Galkin, and A. P. Korolzuk, Zh. Eksperim. i Teor. Fiz. **39**, 7 (1960) [English transl.: Soviet Phys.—JETP **12**, 4 (1961)].

[12] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[13] L. C. Hebel, Phys. Rev. **116**, 79 (1959).

[14] Y. Masuda, Phys. Rev. **126**, 1271 (1962).

[15] Y. Masuda and A. G. Redfield, Phys. Rev. **125**, 159 (1962).

with

$$G_1'=y^2[1+\exp(y)]^{-1}, \quad \text{(IV.3)}$$

$$G_2'=2y\ln[1+\exp(-y)], \quad \text{(IV.4)}$$

$$G_3'=\int_0^\infty \frac{xdx}{1+\exp(x+y)}, \quad \text{(IV.5)}$$

where $y=\Delta(\Omega,T)/kT$. The integral G_3' has been tabulated by Rhodes.[16] In this work the temperature dependence of the gap is assumed to be the same as that given by the BCS theory.[12] Equation (IV.2) can then be evaluated numerically and the results of these calculations are shown in Fig. 1.

The two solid curves represent the upper and lower limits on the spread of the theoretical results. The lower solid curve is for $\alpha=0°$. The higher solid curve is for $\alpha=90°$ regardless of the value of β. That is, on the basis of the anisotropy function (III.1), the thermal conductivity is completely insensitive to the value of β. This is a completely expected and satisfying result since, for a uniaxial crystal, there should be no azimuthal dependence of conductivity.

The comparison of theory to the data of Guénault is also shown in Fig. 1. We made the particular choices of Guénault's samples as follows. We selected two samples having $\alpha=90°$ (denoted by $\perp$ in the figure) and two having $\alpha=0°$ (denoted by $\|$). The samples were required to have a small in accord with previous discussion, but not so small that the samples could not be considered "pure." Agreement between theory and experiment is satisfactory. If one were to increase the variation of $a(\Omega)$ in order to make $\langle a^2\rangle=0.019$ instead of 0.012 (see Sec. III), one would find better agreement in a comparison like that of Fig. 1.

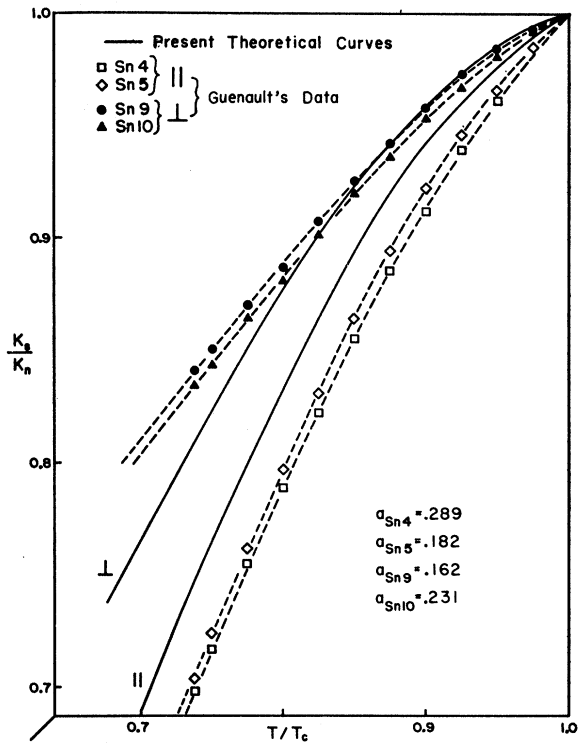

FIG. 1. Theoretical curves for the ratio $K_e^s(T)/K_e^n(T)$ as calculated using the anisotropic energy gap in pure tin. Also shown are some experimental points of Guénault. The parameter a is the ratio of the thermal resistivity due to scattering of electrons by phonons to that due to scattering by impurities, evaluated at $T=T_c$.

V. ENERGY GAP IN IMPURE TIN

We need to know the behavior of the gap with regard to variations in four quantities. These are energy ω, angle Ω, mean free path l, and temperature T. In the case of the pure material where $l\to\infty$, the standard model of an anisotropic superconductor[2] yields a gap which is independent of ω and whose T dependence is given simply by multiplying $\Delta(\Omega)$ by the BCS T dependence. These simplifying features are no longer present when l is finite. What we have available to us is the current model of a doped anisotropic superconductor which has been solved at $T=0$ [6] and at $T=T_c$.[2] In fact the kind of solution depends upon the range of ω or l considered. We therefore specialize our considerations immediately to the ranges of interest to us. The range of l is large ($l\gg\xi_0$) corresponding to low doping. Regarding Δ as a function of ω, we note that Eq. (II.4) requires knowledge of different ranges of ω at low than at high temperatures: i.e., $\omega\approx\Delta(T)$ for low T and $\omega\approx kT$ for high T. This originates in the Fermi factors.

We need to know the gap over essentially the entire temperature range. We can extend the solutions at $T=0$ and $T=T_c$ over a large range by *assuming* that the BCS T dependence is a multiplicative factor as it is in the pure case. Notice that this may very well be true in each limited energy range of interest to us whereas we stated before it is not true in general. The final result over the entire temperature range is a smooth connection of these two solutions. We rely heavily in this section on the papers of MK and Hohenberg.

According to MK a good approximation for Δ is

$$\Delta(\Omega,\omega,l)=\Delta_0(l)+\Delta_1(\omega,l)a(\Omega), \quad \text{(V.1)}$$

at least when $T\to T_c$. Since we plan to use a multiplicative temperature factor, we suppress the symbol T. In the ideally pure case, when $l\to\infty$, $\Delta_1(\omega)=\Delta_0$. Because Δ_0 is independent of ω, Eq. (V.1) reduces to the BCS result when $a(\Omega)=0$. Equation (V.1) is exact when the impurities scatter isotropically. Notice that it says that the angular dependence $a(\Omega)$ of the pure material is preserved while the effect of doping is to reduce Δ_1. We see that the condition which allows us to solve our enormously complicated problem is that the full dependence of Δ on Ω, ω and T breaks up into dependences that are separately specifiable.

[16] P. Rhodes, Proc. Roy. Soc. (London) **A204**, 396 (1950).

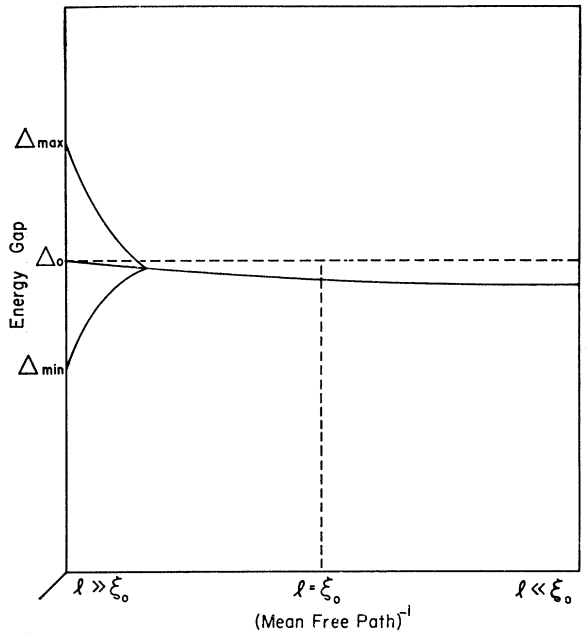

FIG. 2. Schematic theoretical curves for $\Delta(\Omega,l,T)$ at a fixed temperature for extreme and average gap values, plotted versus reciprocal mean free path; ξ_0 is the superconducting coherence length. Adapted from Hohenberg, Ref. 6.

Using Eq. (V.1), MK find

$$\Delta(\Omega,\omega,l)=\Delta_0\left\{1+\frac{a(\Omega)}{1-i/(2\omega\tau)}\right\}, \qquad (V.2)$$

where τ is the mean free time corresponding to l. For properties such as the density of states or the quasiparticle energies, the important quantity is the real part of Δ^2. This contains in its denominators the expression

$$d=1+(2\omega\tau)^{-2}. \qquad (V.2')$$

(It is not essential to change from l to τ. Theoretical papers generally use τ while experimentalists prefer l. The connection between them is $l/\xi_0=\pi\Delta_0\tau$.)

We know that Eqs. (V.1) and (V.2) must be reasonable in a finite range below T_c since we can always perform an expansion of the integral equation for the gap in powers of Δ^2, whereupon the zeroth-order solution is exactly that at T_c and the correction terms are of order $(\Delta(T)/kT)^2$. This is a standard trick used when working near T_c. It was used most effectively (and originally) by Gor'kov[17] to derive the Ginzburg-Landau[18] equations from the microscopic theory. We thus have a formula for the "high-temperature gap."

By far the greater temperature range below T_c is not accessible through this trick. This range may be reached by extending the Hohenberg theory, which he works out in great detail for $T=0$. His results may be summarized as follows. For *any* finite l the gap is strictly isotropic, which means that for any direction of propagation there exists an excitation having a minimum energy E_g and this energy is independent of direction. However, there is a circumstance which completely overthrows this apparent isotropy and that is that the density of states near E_g is exceedingly small for those directions Ω such that $\Delta(\Omega)$ is much different from E_g when $l\to\infty$.

Thus we are to some extent justified in making the following assumption for the "effective gap," which we still denote by $\Delta(\Omega,l)$ and which is the energy at which the density of states has a sharp increase; we assume that Eq. (V.1) applies also at $T=0$. (Again we are concerned with the value $\omega=\Delta$.) This assumption is consistent with the results of Hohenberg. Adapting his Eq. (31) to the special notation and assumption of this paper, we have

$$\Delta_1(l)\approx\Delta_0(\infty)\{1-\langle\alpha^2\rangle^{-1/4}(2\tau\Delta_0|_{T=0})^{-1}\}, \qquad (V.3)$$

for concentrations small enough that the right-hand side is not close to zero. We outline a derivation of (V.3) in an appendix.

For the same region of concentration, his Eq. (38) tells us that

$$\Delta_0(l)=\Delta_0(\infty)\{1-\pi\langle a^2\rangle(16\tau\Delta_0|_{T=0})^{-1}\}. \qquad (V.4)$$

Since $a^2\approx\langle 0.02\rangle$ for tin (as well as typically), we see that $\Delta_1(l)$ decreases far more rapidly than $\Delta_0(l)$ with reduction in mean free path. The complete behavior of $\Delta(\Omega,l)$ is shown qualitatively in Fig. 2 for three values of Ω. The three directions are chosen to represent the extreme and the average values of $a(\Omega)$. On the abscissa l^{-1} is plotted. Our figure is adapted from Fig. 1 of Hohenberg's paper, but one point of difference is that we are making use of the knowledge of the correct cutoff procedure, which appears in MK. This procedure is to cut off frequency integrations at $\pm\omega_D$, as did BCS. When this is done $\Delta_0(l)$ flattens out at a relatively high value instead of continuing to decrease as l becomes small. We call the gap which appears in Eqs. (V.3) and (V.4) the "low-temperature gap."

Before we introduce the low- and high-temperature gaps into the formula for thermal conductivity, we call attention to two related surprising features of the MK and Hohenberg model. One feature appears in Fig. 2 and that is that anisotropy in the gap edge $\Delta|_{\omega=\Delta}$ disappears at an impurity concentration very much smaller than the concentration needed to cause the average gap Δ_0 to level off. The other feature becomes manifest when we compare the behavior of Δ_1 to the behavior of T_c. If we eliminate τ and Δ_0 in Eq. (V.3) in favor of l and ξ_0, we find $\Delta_1\to 0$ when $\xi_0/l\approx\frac{1}{4}$. This is in marked contrast to the prediction of MK that it takes a value $\xi_0/l\approx 3$ to effectively saturate the reduction in T_c.

These features may be understood by noting that it is only right at the gap edge that anisotropy is eliminated

[17] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **36**, 1918 (1959) [English transl.: Soviet Phys.—JETP **9**, 1364 (1959)].
[18] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).

at low doping. This is undoubtedly due to the singular density of states. Anisotropy in Δ_1 away from the gap edge persists to much higher concentrations. Since both Δ_0 and T_c are related to the entire gap function, $\Delta_0+\Delta_1 a(\Omega)$, over the entire energy range $-\omega_D<\omega<\omega_D$ through the integral equation known as the gap equation, this implies that both Δ_0 and T_c should continue to decrease at the higher concentrations.

We now return to considerations of importance to thermal conductivity. It is apparent that the value of τ which reduces the low-temperature value of Δ_1 in Eq. (V.3) to zero brings $(2\omega\tau)^{-2}$ in (V.2a) (the high-temperature expression) to a value $(\Delta_0|_{T=0}/\omega)^2\langle a^2\rangle^{1/2}$. But the important values of ω are of order kT and therefore, typically,

$$(2\omega\tau)^{-2}\lesssim(\Delta_0|_{T=0}/kT_c)^2\langle a^2\rangle^{1/2}\approx 0.4\ll 1. \quad \text{(V.5)}$$

It thus appears that relatively little anisotropy is lost to important excitations near T_c for the same value of τ. In this paragraph we have allowed ourselves the simplification of extrapolation of the linear dependence in τ^{-1} in (V.3).

What do we mean by "low temperature" and "high temperature"? The low-temperature extension of the gap equation inserts $\tanh(\frac{1}{2}\omega/kT)$ into the integrand. But the tanh factor ≈ 1 if $\omega/kT\approx 1$; also the minimum value of ω is $\Delta(T)$. Moreover, it has been remarked that the high-temperature-gap equation contains terms of order $(\Delta(T)/kT)^2$. Clearly the terms mean lower or higher than the temperature for which $\Delta(T)\approx kT$, which occurs when $T\approx 0.9T_c$.

In summary we present our formulas for the low-temperature and high-temperature gaps. These are, respectively,

$$\Delta(\Omega,\omega,l,T)\approx\Delta_0(\infty)f(T)\times[1+a(\Omega)\{1-\langle a^2\rangle^{-1/4}\pi\xi_0(2l)^{-1}\}] \quad \text{(V.6)}$$

and

$$\Delta(\Omega,\omega,l,T)\approx\Delta_0(\infty)f(T)[1+a(\Omega)]. \quad \text{(V.7)}$$

$f(T)$ is the BCS temperature dependence, while for tin $a(\Omega)$ is given by

$$a(\Omega)=3.5^{-1}\{-0.4+1.2\cos^2\theta-0.3\sin^2\theta\cos 8\varphi\}. \quad \text{(V.8)}$$

VI. THERMAL CONDUCTIVITY OF IMPURE TIN

We are now in a position to compute the thermal conductivity of impure tin using Eq. (II.4) in the same fashion as for pure tin. We use Eqs. (V.6)–(V.8) to obtain so-called "low-temperature" and "high-temperature" solutions. In a temperature range around $0.9T_c$ we interpolate smoothly between the two. The machine calculation is hardly more complicated than in the pure case.

In Fig. 3 we plot two of the many possible curves yielded by our machine program. The higher one is for the pure material with orientation $\alpha=90°$. The lower one is for doping heavy enough to eliminate anisotropy

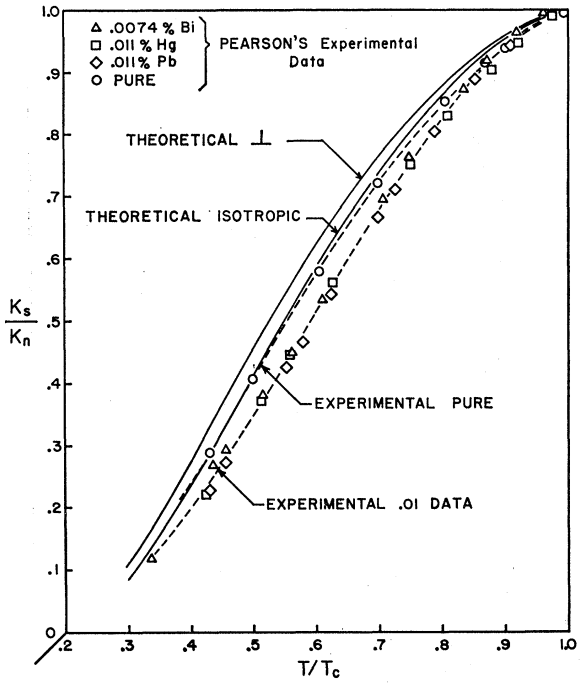

FIG. 3. Theoretical curves for $K_e^s(T)/K_e^n(T)$ in pure and moderately impure tin. The data is that of Pearson for pure and slightly impure tin.

in the low-temperature region $T<0.9T_c$. We have reason to believe that these are the most sensible curves to compare with the data of Pearson *et al.*[4] We shall discuss this point after we have made the comparison. Also in Fig. 3 we have plotted the data of Pearson *et al.* for their purest sample as well as for their low-doping samples, those having roughly 0.01% of impurities. The data of Guénault, obtained only for pure and ultrapure samples, do not appear on this graph because we feel it is most meaningful to confine ourselves to a case where the pure and impure measurements were performed by the same group.

If we contend that the experimental impurity concentrations and orientation correspond to the theoretical curves in Fig. 3, then it is seen that theory is consistently higher than the data. However, the comparison does not end there because it is possible that there exists a systematic discrepancy common to both the pure and impure cases. If we wish to isolate the effect attributed to the washing out of anisotropy by impurities, it is sensible to plot the difference curve between pure and impure theoretical results. This we show in Fig. 4. Similarly we plot the difference between pure and impure data. (Included in Fig. 4 for comparison are some relevant data taken by Hulm.[19]) The favorable feature of Fig. 4 is the similarity in the shapes of the curves. In particular they both reach a maximum in the vicinity of $T=0.5T_c$. The unfavorable feature is

[19] J. K. Hulm, Proc. Roy. Soc. (London) **A204**, 98 (1950).

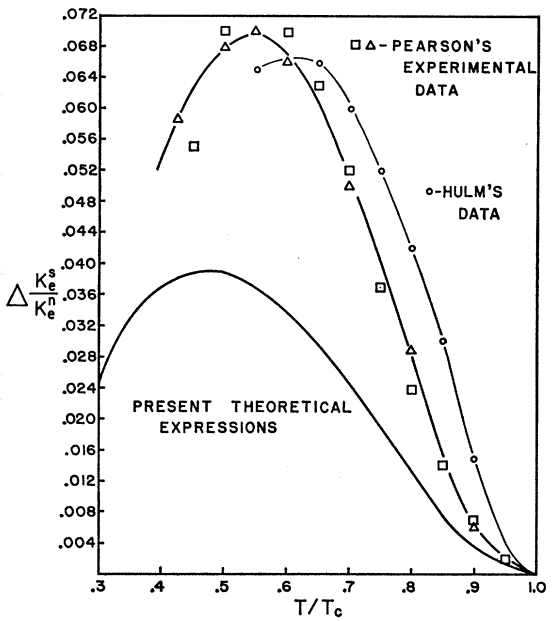

FIG. 4. Comparison of theory to experiment. Theoretical curve is shift in K_e^s/K_e^n predicted for moderate doping. Experimental points are shifts obtained by Pearson between his pure and his lightly doped samples, and also by Hulm between his pure and 0.033 at.% Hg sample.

that even the assumption of total destruction of anisotropy in the gap edge fails by a factor of almost 2 in bringing theory into line with experiment. We have yet to criticize this assumption but we shall do so toward the end of this section.

We now address ourselves to the question of the orientation of the samples which we included in our comparison. The value of α for Pearson's four samples is frankly unknown, but more recent samples of tin and tin alloys have been shown to grow preferentially in directions perpendicular to the [001] axis.[20] However, Tearson's samples were not grown but were extruded. Pherefore such a preference cannot be assumed. At least it is clear that all four samples have common orientations, from the fact that the room-temperature resistivity was the same for all four samples. Since this quantity is rather anisotropic itself, clearly this means that the value of α is about the same for all. The comparison in Figs. 3 and 4 would be senseless if this were not so.

The foremost weakness in the present analysis resides in the fact that the gap edge would have to become isotropic at 0.01% of impurity in order to fit experiment. This concentration corresponds to $\xi_0/l=0.03$ which is $\frac{1}{8}$ of the necessary value according to theory. We are therefore far from quantitative agreement with experiment. Further experiments with doped *single* crystals of tin are in progress.

[20] J. E. Gueths, C. A. Reynolds, and M. A. Mitchell, Phys. Rev. (to be published).

VII. CONCLUDING REMARKS

The first major conclusion of this paper is that Guénault's measurements of thermal conductivity in relatively pure crystals are well explained quantitatively by a model which simply injects anisotropy in the gap into the standard theory. The second major conclusion is that the changes in the thermal conductivity ratio with light doping may be fitted qualitatively by a model which simply injects impurity-dependent anisotropy in the gap into the standard theory. As noted in the introduction, if the thermal conductivity ratio were assumed to be isotropic, one could infer an average gap which increases with light doping, apparently contrary to the theory of Anderson. However, we now understand this effect as resulting from the elimination of anisotropy in the thermal conductivity ratio, which imperfectly reflects the actual gap anisotropy. Thus an effective gap inferred from the thermal conductivity ratio is itself anisotropic, and is not the true average gap. The samples used in Pearson's experiments were evidently oriented such that the effective gap was near a minimum, and consequently increased when the anisotropy was reduced.

The failure of the model to produce quantitative agreement breaks up into two quite separate questions. The first has to do with a discrepancy of order 2 and may well be due to the circumstance, already cited, that our anisotropy function $a(\Omega)$ underestimates the variations in the gap. As further information is reported on this quantity, a more complete $a(\Omega)$ is bound to improve the agreement. The second concerns the factor of 8 in the doping strength. This poses a real problem. We recall that the decrease in Δ_0 and T_c saturates at a doping of 1% or so. The surprising prediction (which by now is no longer surprising) that anisotropy in the gap edge vanishes at a doping of 0.1% gives us the benefit of an order of magnitude. There is evidently another order of magnitude to account for to bring theory into line with the samples of 0.01% doping. If, for a reason we do not yet understand, scattering at the gap edge is even stronger than it is in our model, here again the agreement will improve.

It should be emphasized that we see no reason to abandon the current model of a doped anisotropic superconductor in order to seek a resolution of this puzzle since the model has been triumphant in explaining the observed behavior of T_c and Δ_0, as discussed in great detail by MK and Hohenberg. The present paper is the first sustained attempt at an understanding of the detailed angular variations in the gap rather than just its mean-square value around the Fermi surface. It should come as no surprise that there are important points left to clear up.

We should remark that this entire analysis is made possible by the fact that the nominally pure sample of Pearson is not pure but is sufficiently impure to make the parameter a, discussed previously, smaller than 0.3.

Ordinarily the largest effect produced by doping a pure material would be to drastically reduce a. (Such is the case for Guénault's purer samples.) This reduction is not important when a is already much less than one.

We wish to call attention to the fact that we have ignored anisotropy in the normal density of states. This quantity enters both in the gap equation and in the equation for thermal conductivity, where it really enters twice: in the number of carriers and in their mobility. A more complete theory will have to take account of this.

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APPENDIX

Equation (V.3) expresses the dependence on τ of the anisotropic part of the gap, Δ_1. We here outline a derivation of (V.3). To understand the derivation the reader should already be familiar with the article by Hohenberg.[6]

Hohenberg's Eq. (31) says, in our notation,

$$\Delta_{\min}(l)\approx\Delta_{\min}(\infty)\{1+\langle a^2\rangle^{1/4}/(2\tau\Delta_0)\}. \quad \text{(A1)}$$

But $\Delta_{\min}(\infty)=\Delta_0[1+a_{\min}]$. This is a definition of $a_{\min}$, the value of $a(\Omega)$ for the direction (Ω) in which the gap has its minimum value. We are interested in a linear approximation for the decrease in Δ_1 between $\tau=\infty$ and $\tau=$ the value at which $\Delta_1\to 0$ in this approximation. We therefore find the value of τ for which $\Delta_{\min}(l)\approx\Delta_0$ and Eq. (V.3) immediately follows. Hohenberg's Fig. 2 shows that this result is fairly good for all directions Ω. Equation (V.3) results from an approximation which coalesces the effects of doping on a complex gap into the real part alone.

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Mixed State of Type-I Superconducting Films in a Perpendicular Magnetic Field

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Thin films of type-I superconductors are shown to exist in a variety of quite distinct mixed states, depending on their thicknesses. The most interesting of these states consist of hexagonal arrays of vortices of larger than unit quantum number. Their general character falls between that of the ordinary mixed state, a triangular array of unit vortices which occurs for sufficiently thin films, and the intermediate states consisting of islands of superconducting phase in a matrix of normal phase which occurs for sufficiently thick films. The theory is developed in Abrikosov's high-field approximation, which gives solutions of the Ginzburg-Landau equations that are exact in the limit as the applied field approaches the second critical field H_{c2}. Two critical thicknesses are found and determined as functions of the Ginzburg-Landau parameter κ. The first and smaller critical thickness is the maximum film thickness for which the ordinary mixed state will exist near H_{c2}. The second critical thickness is the maximum for which a second-order field transition occurs at H_{c2}. The new types of mixed state are stable for values of film thickness intermediate between these two.

INTRODUCTION

A THEORETICAL model given by Tinkham[1] has indicated that sufficiently thin type-I films assume the mixed state when placed in a magnetic field normal to their surface. Maki[2] has recently shown that the Ginzburg-Landau (GL) equations predict this. He derived an approximate value for the maximum thickness a film may have in order that it should have a second-order transition to the mixed state at the upper critical field H_{c2}. We have looked in greater detail at the solutions of the GL equations in the neighborhood of the upper critical field using Abrikosov's high-field approximation[3] properly modified as in Maki's paper to take into account the field energy. In brief, our results, which apply near H_{c2}, are that very thin films exist in the state consisting of a triangular array of vortices which was first determined by Kleiner, Roth, and Autler (KRA).[4] Films of intermediate thickness, however, make a second-order transition as the field is decreased

[1] M. Tinkham, Phys. Rev. **129**, 2413 (1963); Rev. Mod. Phys. **36**, 268 (1964). Experiments on narrow strips of Sn by R. D. Parks and J. M. Mockel, Phys. Rev. Letters **11**, 354 (1963), show structure in resistance versus perpendicular magnetic field due to the presence of vortex structure. J. Pearl, Appl. Phys. Letters **5**, 65 (1964), discusses a model for such vortices and the forces between them.

[2] Kazumi Maki, Ann. Phys. (N. Y.) **34**, 363 (1965).

[3] A. A. Abrikosov, Zh. Eksperim. i. Teor. Fiz. **32**, 1442 (1957) [English transl.: Soviet. Phys.—JETP **5**, 1174 (1957)].

[4] W. H. Kleiner, L. M. Roth, and S. H. Autler, Phys. Rev. **133**, A1236 (1964).