phase boundary. The present results for ΔC_V and the data of Grilly and Mills yield the points in Figs. 6 and 7. In general, these results are somewhat lower than the average values over the phase. However, both α and K when calculated from Eqs. (7) and (8) are very sensitive to systematic errors in dV/dT. For this reason it is not certain that the difference between the values at the phase boundary and the average values over the phase are real.

It is interesting to note that above 1.65° K, both α and K decrease with increasing temperature. However, α decreases more rapidly than K, and thus the temperature dependence of α/K is qualitatively consistent with the volume dependence of the heat capacity [Eq. (6)].

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Phenomenological Model for the Electronic Thermal Conductivity of Superconductors

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A phenomenological model is proposed within the framework of BCS theory and the Boltzmann equation approach for the electronic thermal conductivity of superconductors limited by phonon scattering. Values of the parameters of the model are determined from comparison with the experimental data. In the case of weak coupling of electrons and lattice vibrations, it is found that τ_s , the time a quasiparticle takes to relax to the equilibrium flow of supercurrent, is comparable with τ_n in the normal state. In the case of strong electron-phonon interaction, it is found that τ_s is 10¹⁴ times τ_n at the reduced temperature t=0.80.

I. INTRODUCTION

R ECENTLY Tewordt^{1,2} has obtained theoretical expressions for the lifetime. expressions for the lifetime of a quasiparticle in a superconductor at finite temperatures and has applied successfully the results^{2,3} to the problem of intrinsic electronic thermal conductivity of tin and indium, where the electron-phonon interaction is weak. But the problem of very large slopes (~ 5 or 6) of K_s/K_n versus T/T_c curves for mercury and lead, the two typical cases of strong electron-phonon interaction, remains still unsolved.

It has been argued³ that the large limiting slopes of K_s/K_n measured for lead and mercury cannot be explained completely within the scope of the BCS model and a modification of the theory is strongly needed to include the strong-coupling cases. In the absence of such a theory it seems desirable to propose a phenomenological model and obtain some information regarding the behavior of the quasiparticles from the experimental data on transport properties. The proposed phenomenological model is within the framework of the BCS theory and conventional Boltzmann equation approach.

Recently doubts have been expressed regarding the applicability of the quasiparticle picture and the Boltzmann equation approach to the transport problems of



FIG. 1. Theoretical curves for the ratio of the thermal conductivity in the superconducting state K_s to that in the normal state K_n versus the reduced temperature T/T_c . Solid lines represent the theoretical results while the experimental points are shown as black dots. The curve designated by Hg,Pb is calculated by taking the ratio 2 $\epsilon_0(0)/kT$ equal to 4.1, while all other curves are with the value of the ratio equal to 3.52.

 ¹ L. Tewordt, Phys. Rev. **127**, 371 (1962).
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FIG. 2. Theoretical curves for the ratio of the relaxation time of a normal state excitation τ_n to that of a quasiparticle in the superconducting state τ_s , at different reduced temperatures $t=T/T_c$, in the weak-coupling case of indium.

the electron-phonon systems especially when the lifetimes are small in the strong electron-phonon coupling case or at high temperatures.^{4,5} But Prange⁶ has given justifications for the use of the Boltzmann equation approach throughout the entire temperature range with proper Landau corrections taken into account.

In Sec. II we deduce a general expression for the electronic thermal conductivity, limited by phonon scattering, in the two states by assuming a suitable general form for the relaxation time of a quasiparticle. Comparison of the phenomenological expression with the experimental K_s/K_n versus T/T_c curves is made and the values of the parameters are obtained. From these the ratio of the relaxation times, τ_s/τ_n , in the two states is obtained. The results are discussed in Sec. III.

II. PHENOMENOLOGICAL MODEL

Oualitatively the relaxation time of the quasiparticle is expected to depend on the excitation energy of the quasiparticle and the temperature. The temperature dependence is both explicit and implicit. The explicit temperature dependence comes from the phonon spectrum and the matrix elements of electron-phonon interaction. The implicit dependence is included in the dependence of the BCS energy gap on temperature, since $\epsilon_0(T)$ occurs in the quasiparticle energy

$$E_{\mathbf{k}} = \left[\epsilon_{\mathbf{k}}^{2} + \epsilon_{0}^{2}(T)\right]^{1/2}$$

This energy and the temperature dependence of the quasiparticle relaxation time is expected to be different in the normal and the superconducting state.

Using the relaxation-time approximation, the thermal conductivities in the two states are given by

$$K_{s} = \frac{A}{T^{2}} \int_{\epsilon_{0}}^{\infty} \tau_{s} E_{\mathbf{k}} (E_{\mathbf{k}}^{2} - \epsilon_{0}^{2})^{3/4} \operatorname{sech}^{2} \frac{1}{2} \beta E_{\mathbf{k}} dE_{\mathbf{k}} ,$$
$$K_{n} = \frac{A}{T^{2}} \int_{0}^{\infty} \tau_{n} \epsilon_{\mathbf{k}} \operatorname{sech}^{2} \frac{1}{2} \beta \epsilon_{\mathbf{k}} d\epsilon_{\mathbf{k}} ,$$

where τ_s and τ_n are the relaxation times in the two

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⁵ L. P. Kadanoff, Phys. Rev. 133, A1070 (1964).
⁶ R. E. Prange, Technical Report No. 331, Department of

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FIG. 3. Theoretical curves for the ratio of the relaxation time of a quasiparticle τ_s to that of a normal state excitation τ_n , at different reduced temperatures $t = T/T_c$, for the typical strong electron-phonon coupling case of mercury.

states. We assume that the relaxation time of the quasiparticle in the superconducting state is of the form

$$\tau_s \propto E_k^a T^b$$
.

Since the normal-state electronic thermal conductivity is proportional to T^2 , one obtains the following form for the relaxation time of the normal-state excitation:

 $\tau_n \propto \epsilon_k^m T^{(\frac{1}{2}-m)}$.

We shall now assume that the explicit temperature dependence of τ_s is same as that of τ_n (temperature dependence enters into picture through the phonon spectrum which we assume is not changed appreciably). Substituting for τ_s and τ_n , we obtain for the ratio K_s/K_n

$$K_{s}/K_{n} = \int_{\epsilon_{0}}^{\infty} E_{\mathbf{k}}^{a+1} (E_{\mathbf{k}}^{2} - \epsilon_{0}^{2})^{3/4} \operatorname{sech}^{2\frac{1}{2}} \beta E_{\mathbf{k}} dE_{\mathbf{k}} / \int_{0}^{\infty} \epsilon_{\mathbf{k}}^{(m+\frac{5}{2})} \operatorname{sech}^{2\frac{1}{2}} \beta \epsilon_{\mathbf{k}} d\epsilon_{\mathbf{k}},$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant. By putting $m + \frac{5}{2} = p$ and $a + \frac{5}{2} = p'$, we have

$$K_s/K_n = \int_1^\infty x^{p'} \left(1 - \frac{1}{x^2}\right)^{3/4} \operatorname{sech}^2 cx dx \\ / \int_0^\infty x^p \operatorname{sech}^2 cx dx,$$

where $c = \frac{1}{2}\beta\epsilon_0(T)$.

The above expression can be evaluated by numerical integration for chosen values of p and p'. For temperatures just below the transition temperature p may be taken equal to p'; p can now be fixed by fitting the experimental value of K_s/K_n at that temperature. Next for all temperatures p is taken as fixed and p' is determined empirically by curve fitting.

It is found that the above expression for K_s/K_n can be used to explain all the available experimental data of intrinsic electronic thermal conductivity. The results are shown in Fig. 1. It is found that in weak coupling case of Sn and In,⁷ we need take only p = p' for temperatures down to the reduced temperature t=0.75. The values obtained are p=1.1 for Sn₁, p=1.0 for In and p = 0.9 for Sn₁₁. But in the case of strong electronphonon interaction, Hg and Pb, we find that such is not the case. We have to take p = 0.25 and different values of p' at different temperatures. From these values of pand p' we can deduce information regarding the ratio of the relaxation times of the quasiparticles in the normal and the superconducting states. It is to be noted that thermal conductivity is not a very sensitive function of the relaxation time of the quasiparticle taking part in the transport of energy, so that we obtain only a rough knowledge of the relaxation times. We have

$$\tau_s/\tau_n = \left\lceil \epsilon_k^2 + \epsilon_0^2(T) \right\rceil^{(p'/2-5/4)} / \epsilon_k^{(p-5/2)}$$

The curves for different reduced temperatures are plotted in Fig. 2 for indium, as a typical weak coupling case and in Fig. 3 for Hg and Pb, typical strong electronphonon coupling cases.

⁷ A. M. Guenault, Proc. Royal Soc. (London), A262, 420 (1961).

III. DISCUSSION

The values of the parameters of the model in the weak coupling case as obtained by fitting the experimental curves⁷ for K_s/K_n versus T/T_c with the theoretical expression are such that p is approximately equal to p'and p is also nearly unity.

The values of τ_n/τ_s versus ϵ/k_BT at different reduced temperatures $t = T/T_c$ for weak electron-phonon coupling (indium) are presented in Fig. 2. It may be observed that τ_s is comparable with τ_n and is greater than τ_n for excitation energies $\epsilon/k_BT > 2$. For small excitation energies the relaxation time of the normal-state excitation is greater than that of the quasiparticle in the superconducting state at the same temperature.⁸ In the case of strong electron-phonon interaction it may be

⁸ It is interesting to note that this behavior is similar to that obtained by Tewordt for the ratio of the lifetime of the quasiparticle in the superconducting and the normal state. (See Fig. 2 of the Ref. 2.)

observed that for t=0.80, τ_s is as large as 10^{14} times the relaxation time of the normal-state excitation. The usual expressions for the rate of momentum transfer from the phonons to the quasiparticles do not provide an answer to such a large value of τ_s/τ_n even at 0°K. It appears that some other interaction is needed to decrease enormously the effective matrix elements for Hg and Pb.

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Energy Gap Measurements by Tunneling Between Superconducting Films. I. Temperature Dependence

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The electron tunneling technique was used to measure the energy gap $2\Delta(t)$ as a function of temperature in aluminum and tin films. The temperature dependence of the normalized gap $\Delta(t)/\Delta(0)$ for each film agreed rather well with the BCS theory, although a small consistent deviation was found in which the measured values of the gap were slightly larger than predicted by theory. In the case of aluminum, considerable random scatter in the absolute values of $2\Delta(0)$ for the various films was found.

I. INTRODUCTION

 $\mathbf{E}_{\mathrm{Nicol}\ et\ al.^2}^{\mathrm{XPERIMENTAL}\ \mathrm{measurements}\ \mathrm{by}\ \mathrm{Giaever^1}\ \mathrm{and}$ metals separated by a thin dielectric layer have shown that the density of (excited) states of each superconductor is reflected in the current-voltage characteristics in a dramatic way. They have shown that one can identify the energy gap of both metals more or less unambiguously. These early experiments were soon followed by additional measurements³⁻¹⁰ along with

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clarification of various theoretical points.¹¹⁻¹³ Measurements of the temperature dependence of the energy gap by this technique have been reported and the results have been compared with the predictions of the Bardeen, Cooper, and Schrieffer (BCS) Theory.¹⁴ For tin, the data of Giaever and Megerle³ and of Townsend and Sutton⁷ both indicate that the experimental values of the gap are larger than theoretical at intermediate temperatures. In the case of aluminum, good qualitative agreement is achieved with theory, but large scatter in the data prevented a quantitative comparison.

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