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Ultrasonic-Surface-Wave Attenuation of Gapless Superconductors

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The ultrasonic attenuation of gapless superconducting films has been measured with acoustic surface waves. The following systems have been investigated: thin films in parallel and perpendicular magnetic fields, superconductors in close contact with magnetic layers, and films showing surface superconductivity. Qualitatively the experiments exhibit the characteristic features derived theoretically for gapless superconductors. But quantitative comparisons show that the measured pair-breaking effect is stronger than expected from theory in all cases investigated.

I. INTRODUCTION

In their study on superconductors containing magnetic impurities Abrikosov and Gorkov[1] have first pointed out that superconductivity may exist even in the absence of an energy gap. This "gapless" superconductivity[2] occurs in the presence of various perturbations, if the transition from the superconducting to the normal state is of second order.

During the past years much effort has been spent on the theoretical investigation of ultrasonic attenuation in gapless superconductors. In this paper we limit ourselves to the case of "dirty" superconductors, where the electronic mean free path l is small compared to the coherence length ξ_0. The ratio of the electronic attenuation coefficients in the superconducting and normal state α_s/α_n for superconductors containing magnetic impurities was calculated by Kadanoff and Falko[3] and Griffin and Ambegaokar.[4] These authors found characteristic deviations from the BCS behavior, e.g., finite values of α_s/α_n at $T=0$ for certain impurity concentrations and finite slopes of α_s/α_n at the transition temperature T_c. Owing to experimental difficulties no ultrasonic measurements on superconductors containing magnetic impurities have been published so far.

By reinterpreting the pair-breaking parameter Maki and Fulde[5] have shown that the acoustic attenuation for superconductors containing magnetic impurities is equivalent to the case of thin superconducting films in a parallel magnetic field. Preliminary experimental results[6] on the ultrasonic-surface-wave attenuation are in qualitative agreement with theory.

In the gapless superconducting systems mentioned so far the order parameter Δ is spatially constant. The acoustic attenuation of dirty gapless superconductors with spatially varying order parameter has been calculated by Maki and Fulde[7] and McLean and Houghton[8] for temperatures near T_c. Typical examples for this situation are a thin film in a perpendicular magnetic field, a film exhibiting surface superconductivity, and a superconducting film in close contact with a magnetic film.

The absorption of thin superconducting layers can be measured rather simply with acoustic surface waves.[9] In this paper we report on such measurements using gapless superconducting films with both spatially constant and spatially varying order parameter and we compare the experimental results with theory.

II. THEORY

For short mean free paths ($l \ll \xi_0$) the different pair-breaking mechanisms lead to equivalent results. The transition temperature T_c in the presence of a perturbation can be described by the universal function[1]

$$\ln(T_c/T_{c0}) = \psi(\tfrac{1}{2}) - \psi(\tfrac{1}{2} + \Gamma/2\pi T_c) \ , \qquad (1)$$

where T_{c0} is the transition temperature in the absence of the perturbation and ψ is the digamma function. The pair-breaking parameter Γ depends on the physical situation. Superconductivity is destroyed for $\Gamma = \frac{1}{2}\Delta_{00}$, where Δ_{00} is the order parameter at $T=0$ in the absence of the perturbation. All equations are expressed in terms of units where $\hbar = c = k = 1$.

A. Spatially Constant Order Parameter

In the presence of a pair-breaking mechanism leading to a spatially constant order parameter the ultrasonic attenuation is determined by the number of normal electrons as in the absence of the perturbation (we only consider ultrasonic waves with energies small compared to the binding energy of the Cooper pairs). For longitudinal waves the attenuation may be written[3,4]

$$\frac{\alpha_s}{\alpha_n} = \int_0^\infty \frac{d\omega}{2T} \cosh^{-2}\left(\frac{\omega}{2T}\right) \frac{1}{2}\left(1 + \frac{|u|^2 - 1}{|u^2 - 1|}\right) \ , \qquad (2)$$

where $u(\omega/\Delta, \zeta)$ is the solution of the basic equation of the Abrikosov–Gorkov theory,

$$\frac{\omega}{\Delta} = u[1 - \zeta/(1-u^2)^{1/2}] \ , \tag{3}$$

with $\zeta = 1/\tau_s\Delta$, and τ_s is the exchange scattering time. The ratio of attenuation α_s/α_n has been calculated numerically[4] for pair breaking caused by magnetic impurities with a concentration n_i using the quantity $n = 2\Gamma/\Delta_{00} = n_i/n_{cr}$ as parameter, where n_{cr} is the critical impurity concentration at which superconductivity is destroyed. Initially these calculations have been carried out only for the case $ql > 1$ (q is the wave vector of the sound wave), but they have been shown to be valid for all ql values.[3]

This theory is applicable also to the case of a thin superconducting film in a parallel magnetic field,[5] provided the following conditions are satisfied:

$$\begin{aligned} &l \ll \xi_0 && \text{(dirty limit),} \\ &d \ll (l\xi_0)^{1/2} && \text{(constant order parameter over the specimen),} \\ &d \ll \lambda_{eff} = \lambda_L(\xi_0/l)^{1/2} && \text{(nearly perfect penetration of the magnetic field),} \end{aligned} \tag{4}$$

where d is the film thickness and λ_L is the London penetration depth. The condition $d \gg l$ (local electrodynamics) is not necessarily required in this context.[10] The normalized pair-breaking parameter for a thin film in a parallel magnetic field is given by

$$n = 2\Gamma/\Delta_{00} = H_\parallel^2/H_{c\parallel}^2(0) \ , \tag{5}$$

where $H_{c\parallel}(0)$ is the critical magnetic field at $T = 0$.

B. Spatially Varying Order Parameter

For gapless superconducting systems with spatially varying order parameter $\Delta(\vec{r})$ until now no calculations of the transport properties exist which are valid in the whole superconducting temperature region. Only in the range near the transition temperature T_c is a power-series expansion in terms of the order parameter possible. By these means the ultrasonic attenuation of longitudinal waves has been calculated[7,8]:

$$\alpha_s/\alpha_n = 1 - \frac{\langle|\Delta(\vec{r})|^2\rangle}{2(2\pi T)^2}\left[\rho^{-1}\psi^{(1)}(\tfrac{1}{2}+\rho) - \psi^{(2)}(\tfrac{1}{2}+\rho)\right] ; \tag{6}$$

$\rho = \Gamma/2\pi T$, $\psi^{(1)}$ is the trigamma function, and $\psi^{(2)}$ is the tetragamma function.

The spatially averaged square of the order parameter $\langle|\Delta(\vec{r})|^2\rangle$ is computed from the generalized Ginsburg–Landau equation[11]

$$[\psi(\tfrac{1}{2}+\rho) - \psi(\tfrac{1}{2}) - \ln T_{c0}/T]\langle|\Delta|^2\rangle + [1/2(2\pi T)^2]f_1(\rho)\langle|\Delta|^4\rangle = 0. \tag{7}$$

The function $f_1(\rho)$ depends on the physical situation. We obtain from Eq. (7)

$$\langle|\Delta(\vec{r})|^2\rangle = 2(2\pi T)^2\,\frac{1-\rho\psi^{(1)}(\frac{1}{2}+\rho)}{\beta f_1(\rho)}\left(1 - \frac{T}{T_c}\right). \tag{8}$$

The quantity $\beta = \langle|\Delta|^4\rangle/\langle|\Delta|^2\rangle^2$ is a measure for the spatial variation of the order parameter.

As examples for superconducting systems with spatially varying order parameter we consider (i) a thin film in a perpendicular magnetic field, (ii) a superconductor in close contact with a magnetic layer, and (iii) a film showing surface superconductivity in a parallel field (superconducting sheaths on both sides of the film). For these physical situations the quantities $\rho = \Gamma/2\pi T$, $f_1(\rho)$, and β are listed in Table I.

With the help of the Eqs. (6) and (8) and Table I the α_s/α_n values near T_c can be calculated numerically. The quantity ρ may be expressed in the following way:

$$\rho = \frac{\Gamma}{2\pi T} = \frac{2\Gamma}{\Delta_{00}}\,\frac{\Delta_{00}}{4\pi T} = n\,\frac{1.76}{4\pi}\,\frac{T_{c0}}{T} \ .$$

For the m-γ functions we have used the tables of

TABLE I. Quantities ρ, $f_1(\rho)$, and β for various physical situations with spatially varying order parameter. Here τ_{tr} = transport collision time, v_F = Fermi velocity, l = mean free path, ξ_0 = coherence length, H_{c3} = nucleation field of the surface sheath, d_s = thickness of the superconducting film, $\psi^{(m)}$ = mth derivative of the digamma function.

Physical situation	$\rho = \frac{\Gamma}{2\pi T}$	$f_1(\rho)$	$\beta = \frac{\langle\lvert\Delta\rvert^4\rangle}{\langle\lvert\Delta\rvert^2\rangle^2}$	Conditions
Thin film in perpendicular magnetic field	$\frac{\tau_{tr}v_F^2 eH}{6\pi T}$	$-\frac{1}{2}\psi^{(2)}(\frac{1}{2}+\rho)$	1.16	$l \ll \xi_0$
Contact between superconductor and magnetic film	$\frac{\tau_{tr}v_F^2}{12\pi T}\left(\frac{\pi}{2d_s}\right)^2$	$-\frac{1}{2}\psi^{(2)}(\frac{1}{2}+\rho) + (\rho/18)\psi^{(3)}(\frac{1}{2}+\rho)$	1.5	$l \ll \xi_0$ $d_s > (1\ \xi_0)^{1/2}$
Surface sheaths on both sides of the film	$\frac{0.59\ \tau_{tr}v_F^2 eH}{6\pi T}$	$-\frac{1}{2}\psi^{(2)}(\frac{1}{2}+\rho)$	$d_s\ [0.59\ e\ H_{c3}(t)/\pi]^{1/2}$	$l \ll \xi_0$ $d_s \gg [2e\ 0.59\ H_{c3}(t)]^{-1/2}$

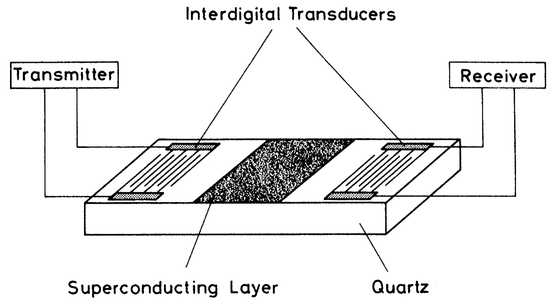

FIG. 1. Experimental arrangement for surface-wave-attenuation measurements of superconducting layers.

Abramowitz and Segun.[12] The results are shown in comparison to the experimental data.

C. Attenuation of Surface Waves

Until now we have treated the ultrasonic attenuation in dirty superconductors for longitudinal waves. We compare these results to attenuation measurements of surface waves which contain both longitudinal and transversal components and we want to justify the comparison.

In our measurements the ql values are always smaller than 0.05. For this limit $ql \ll 1$ in superconductors without perturbations the ratio α_s^L/α_n^L for longitudinal waves and the ratio α_s^T/α_n^T for transversal waves[13] follow the BCS relation

$$\alpha_s^L/\alpha_n^L = \alpha_s^T/\alpha_n^T = 2f(\Delta) \quad , \tag{9}$$

where f is the Fermi function. Equation (9) is confirmed by many experiments[14] with bulk waves.

In the presence of a perturbation leading to gapless superconductivity α_s^L/α_n^L and α_s^T/α_n^T also differ by the factor $g(ql)$ only,[3] where $g(z) = \frac{3}{2} z^{-3}[-z + (z^2+1)\arctan z]$ is the Pippard function. In the limit $ql \ll 1$ this factor $g(ql)$ is nearly unity [$g(0.05) = 0.995$] and we again find $\alpha_s^L/\alpha_n^L = \alpha_s^T/\alpha_n^T$.

In our evaporated films the crystalline regions are small compared to the wavelength and we can treat these films similar to isotropic materials. Then the absorption α of the surface waves is simply related to α^L and α^T by the expression[15]

$$\alpha = a^L \alpha^L + a^T \alpha^T \quad , \tag{10}$$

where, as Poisson's ratio varies from zero to one-half, a^L varies from 0.72 down to 0.02 and a^T varies from 0.63 up to 1.05.[16]

Under these conditions the ratio α_s/α_n for surface waves is equal to α_s^L/α_n^L:

$$\frac{\alpha_s}{\alpha_n} = \frac{a^L\alpha_s^L + a^T\alpha_s^T}{a^L\alpha_n^L + a^T\alpha_n^T} = \frac{\alpha_s^L}{\alpha_n^L}\,\frac{a^L + a^T(\alpha_s^T/\alpha_s^L)}{a^L + a^T(\alpha_n^T/\alpha_n^L)} = \frac{\alpha_s^L}{\alpha_n^L} \quad . \tag{11}$$

This relation is confirmed by our experimental results.

III. EXPERIMENTAL METHOD

A. Measuring Technique

Acoustic surface waves on X-cut quartz, propagating along Y direction, with frequencies up to 1 GHz were generated and detected piezoelectrically using interdigital transducers.[17] The transducers were fabricated from a vacuum-deposited Al film by photoresist technique. The superconducting film was evaporated between the transducer gratings (Fig. 1).

To separate the surface-wave signal from direct electromagnetic coupling between the transducers, rf voltage pulses were applied to the transmitter grating and the received pulse was time selected. The ratio α_s/α_n is determined according to the relation

$$\frac{\alpha_s(T)}{\alpha_n(T)} = 1 - \frac{\log_{10}A_s(T) - \log_{10}A_n(T)}{\log_{10}A_s(0) - \log_{10}A_n(0)} \quad , \tag{12}$$

where A_s and A_n are the amplitudes of the surface-wave signal when the film is in the superconducting and normal state, respectively. The amplitude A_n is nearly constant in the temperature range investigated. In all experiments the thickness of the superconducting layer is very small compared to the wavelength of the ultrasonic surface waves.

The layers on the quartz substrates were cooled down in a helium cryostat by helium exchange gas with pressures ranging between 10^{-1} and 10^{-2} Torr. The temperatures were measured by carbon resistors and were varied by suitably changing the power of an electrical heater.

B. Film Preparation

The experiments in a parallel magnetic field were carried out with rather thin layers. Initially Sn and Pb films with thicknesses of about 400 Å were evaporated on quartz substrates at room temperature, but with these films we did not succeed in measuring the ultrasonic attenuation. Some of the layers did not show electrical conductivity at all; in other cases the electronic mean free paths in these films were too small. This is caused not only by scattering of the electrons at the film boundaries, but, more important, the structural disorder in thin films is much stronger than in thicker layers. Variation of the deposition rate (up to 100 Å/sec) did not lead to the desired results. To obtain thin layers suitable for our ultrasonic measurements in parallel magnetic fields we cooled the quartz substrate to about 120 K during evaporation, warmed it up after the film had been deposited, and cooled down again for the measurements. In a few cases the quartz substrate was presensitized by thin Ag or Cu films with thicknesses of about 20 Å.

In order to study superconductors in close con-

TABLE II. Experimental realization of conditions (4) (values in Å).

	$l \ll \xi_0$	$d \ll (l\ \xi_0)^{1/2}$	$d < \lambda_L (\xi_0/l)^{1/2}$
Sn	200 < 2300	400 < 680	400 < 1200
Pb	300 < 830	400 < 500	400 < 1000

tact with magnetic layers we chose Sn/Cr and Pb/Mn films. These metals constitute suitable systems for such studies, because they hardly mix and do not form intermetallic compounds. The magnetic film was vacuum deposited on the superconducting film a few seconds after this layer had been fabricated. The normal metals Cr and Mn are antiferromagnets. But the magnetic order is highly disturbed in the evaporated films and antiferromagnets and ferromagnets act in a similar way.

The attenuation for the case of surface superconductivity is investigated in Sn films, doped with In, and in Pb films, doped with Bi. Because the vapor pressures of Pb and Bi do not differ very much the Pb : Bi films have been fabricated by evaporating a Pb : Bi mixture of a certain composition. In the case of the Sn : In layers this method is not practicable because of the different vapor pressures. For this reason we have evaporated Sn and In from two separate sources simultaneously regulating the deposition rates by a monitor. The impurity concentration has been determined by chemical analysis. Film thicknesses were measured interferrometrically by the Tolanski method.

The electronic mean free path l in the residual-resistivity range has been determined for each layer from electrical-resistivity measurements in the normal state. For this purpose a test strip has been evaporated simultaneously. The thickness dependence of l is taken into account according to the Fuchs–Sondheimer theory[18] assuming diffuse scattering at the surface. In this way the mean free path l_∞, extrapolated to the bulk, is determined additionally. Different values of l_∞ for the same material indicate different structures of the films.

In the case of single crystals, Peverley[19] has observed that the acoustic mean free paths are smaller than those determined from electrical-conductivity measurements. If this also holds for our evaporated layers, the dirty-limit condition is satisfied even better. It is not clear, however, whether such a difference is of any importance at small ql values.

IV. EXPERIMENTAL RESULTS

A. Thin Films in Parallel Magnetic Field

We have investigated the ultrasonic-surface-wave attenuation of various Sn and Pb films in a parallel magnetic field. The measurements on films of thickness $d = 400$ Å were performed at 700 MHz; the total change of attenuation from the normal to the superconducting state at low temperatures and in the absence of perturbations was about 0.5 dB/cm for these layers. We determined the following electronic mean free paths:

$$l_{\rm Sn} = 200 \text{ Å}, \quad l_{\infty\,\rm Sn} = 250 \text{ Å},$$

$$l_{\rm Pb} = 300 \text{ Å}, \quad l_{\infty\,\rm Pb} = 450 \text{ Å} .$$

A comparison with theory requires the conditions (4) to be valid. Table II shows to which extent these conditions are satisfied experimentally. Furthermore, the theoretical α_s/α_n values[3,4] for this situation have been derived under the assumption of the BCS relation in the weak-coupling limit

$$2\Delta_{00} = 3.5 T_c \quad . \tag{13}$$

For Sn films, Eq. (13) is satisfied rather well. For the strong-coupling superconductor Pb, however, the relation

$$2\Delta_{00} = 4.3 T_c \tag{14}$$

holds and in this case no quantitative comparison with the theory under consideration is possible. On the other hand, the rather high transition temperature of Pb (7.2 K) is favorable for measurements in the presence of perturbations, because relatively low T/T_c values may be easily reached for a given value of $n = 2\Gamma/\Delta_{00} = H_\parallel^2/H_{c\parallel}^2(0)$.

In Fig. 2 the square of the critical field $H_{c\parallel}^2$ is plotted versus the normalized pair-breaking parameter $2\Gamma/\Delta_{00}$. The critical fields have been determined by measuring the ultrasonic attenuation of these films as a function of parallel magnetic field at various temperatures.[9] The normalized pair-

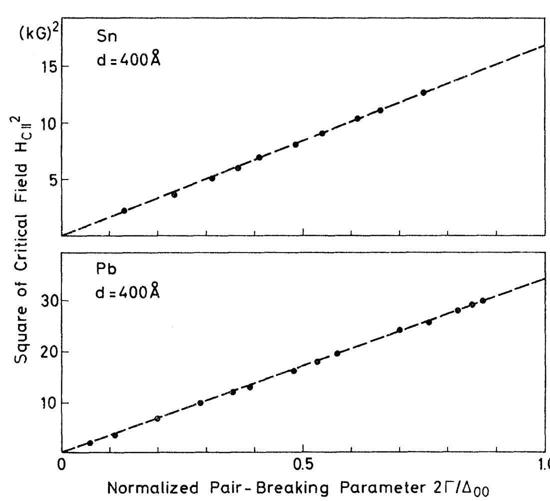

FIG. 2. Square of parallel critical magnetic field vs normalized pair-breaking parameter.

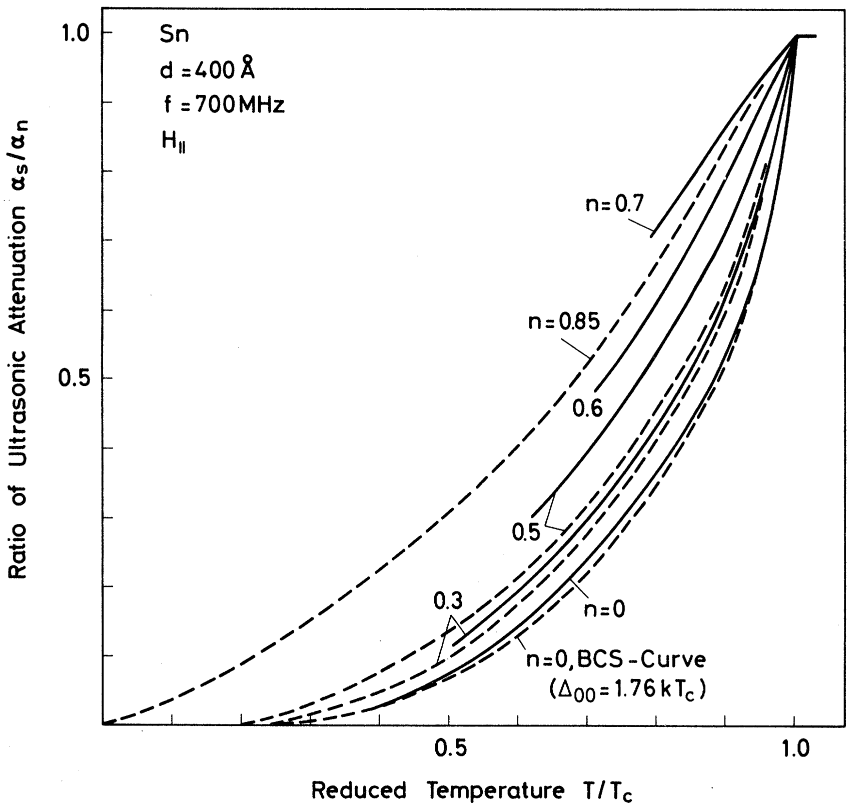

FIG. 3. Ultrasonic attenuation of a thin Sn film in parallel magnetic field vs reduced temperature for various values of $n = H_{\parallel}^2/H_{c\parallel}^2(0)$. Solid curve, experimental values; dashed curve, calculated according to Griffin and Ambegaokar (Ref. 4).

breaking parameter has been calculated from Eq. (1) with the transition temperature T_c in the presence of the magnetic field. The relation $\Gamma(T) \sim H_{c\parallel}^2$ is satisfied rather well experimentally and we obtain for the parallel critical fields $H_{c\parallel}(0)$ at $T = 0$

$$H_{c\parallel\,\mathrm{Sn}}(0) = 4.13 \text{ kG}, \quad H_{c\parallel\,\mathrm{Pb}}(0) = 5.86 \text{ kG}.$$

Figures 3 and 4 show the ratio of attenuation α_s/α_n as a function of reduced temperature T/T_c for various values of $n = 2\Gamma/\Delta_{00} = H_{\parallel}^2/H_{c\parallel}^2(0)$. The deviation from the parallel field direction was less than 0.2 deg. For Sn the theoretical α_s/α_n curves[3,4] are also plotted. The experimentally found pair-breaking effect is stronger than expected from theory.

For thicker films ($d \approx 1000$ Å) a better agreement between measurements and theory is simulated. This results from the insufficient penetration of the magnetic field and the violation of the condition $d \ll \lambda_{eff}$.

B. Thin Films in Perpendicular Magnetic Field

The thin Sn and Pb films investigated in parallel magnetic fields have been used also for the measurements in perpendicular fields. In this case only the dirty-limit condition is assumed to be valid (compare Table II).

In Fig. 5 the critical perpendicular magnetic field is plotted versus the normalized pair-breaking parameter $2\Gamma/\Delta_{00}$. The values of $H_{c\perp}$ and

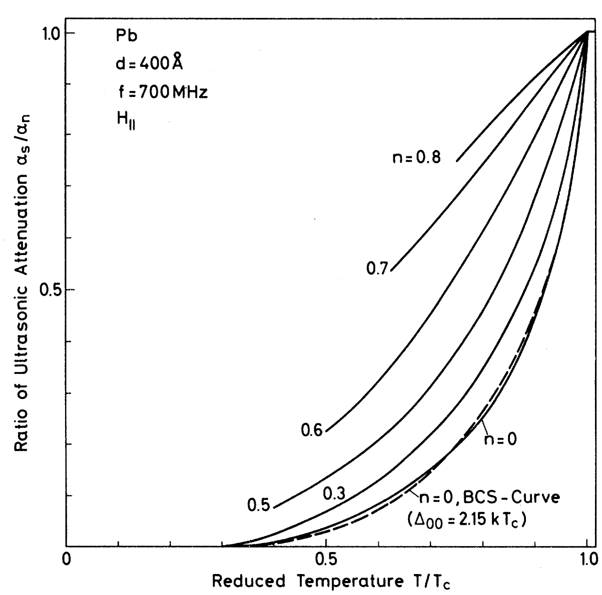

FIG. 4. Measured ultrasonic attenuation of a thin Pb film in a parallel magnetic field vs reduced temperature for various values of $n = H_{\parallel}^2/H_{c\parallel}^2(0)$.

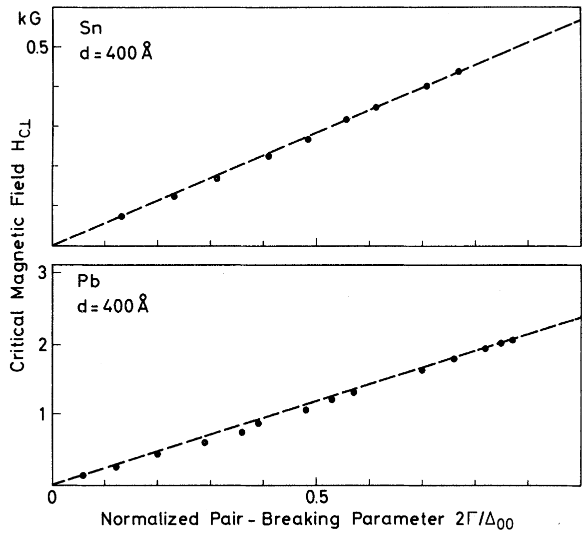

FIG. 5. Perpendicular critical magnetic field vs normalized pair-breaking parameter.

$2\Gamma/\Delta_{00}$ have been determined as described in Sec. IV A. The relation $\Gamma \sim H_{c\perp}$ is satisfied rather well experimentally and we obtain for the perpendicular critical field $H_{c\perp}(0)$ at $T=0$

$$H_{c\perp\,\mathrm{Sn}}(0)=0.57\ \mathrm{kG}, \quad H_{c\perp\,\mathrm{Pb}}(0)=2.34\ \mathrm{kG}.$$

Figure 6 shows the ratio of attenuation α_s/α_n as a function of reduced temperature T/T_c for various values of $n = H_\perp/H_{c\perp}(0)$ in a perpendicular magnetic field. For Sn the theoretical α_s/α_n values near T_c for a given n are also plotted. These values have been calculated from Eqs. (6) and (8) and Table I. The measured pair-breaking effect is stronger than expected from theory as in the case of thin films in parallel fields.

A similar behavior of the α_s/α_n curves is found for thicker Sn and Pb films ($d \approx 2000$ Å), where the dirty-limit condition is highly violated. The temperature dependence of $H_{c\perp}$ in these thicker films, however, is much better described by the relation $H_{c\perp} \sim (1-t^2)/(1+t^2)$ derived from the Ginzburg–Landau theory[20] than by the relation $H_{c\perp} \sim \Gamma(T)$ derived from the microscopic theory for the dirty limit.

C. Superconductors in Close Contact with Magnetic Films

These measurements have been performed with Sn/Cr and Pb/Mn films. The transition temperatures of these double layers have been found to be independent of the thickness d_L of the magnetic layers, if d_M is larger than about 50 Å. The thicknesses of the superconducting Sn and Pb films have been varied from 1600 to 2500 Å and from 750 to 1300 Å, respectively. For this case the conditions (Table I)

$$l \ll \xi_0, \quad d_s > (l\xi_0)^{1/2} \tag{15}$$

must be satisfied. Table III shows for various thicknesses of the superconducting film to which extent these conditions could be realized experimentally.

In Fig. 7 the quantity l/d_s^2 is plotted versus $2\Gamma/\Delta_{00}$. In this case the electronic mean free path l has to be taken into account because different

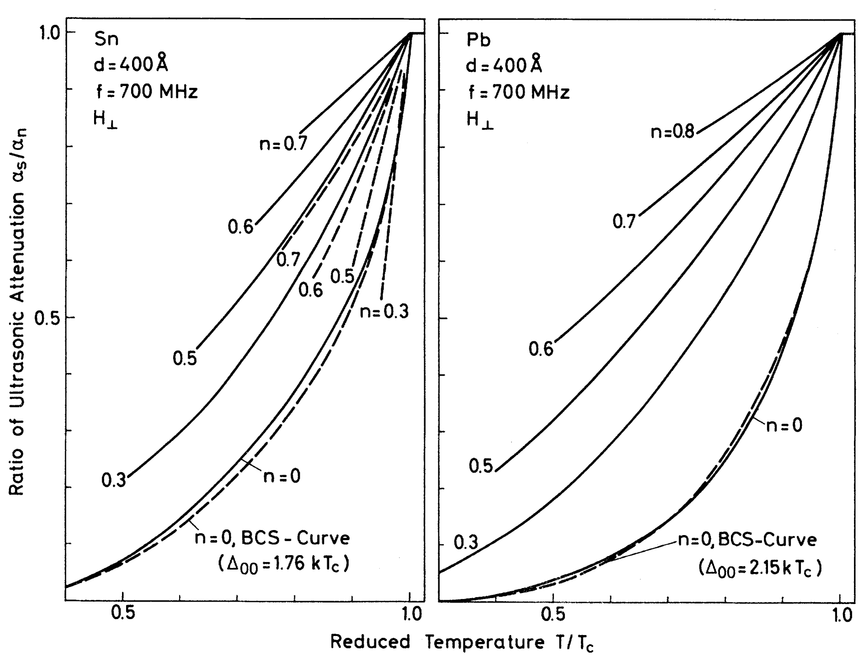

FIG. 6. Ultrasonic attenuation of thin films in perpendicular magnetic field for various values of $n = H_\perp/H_{c\perp}(0)$. Solid curve, experimental values; dashed curve, calculated from Eqs. (6) and (8) and Table I (valid near T_c).

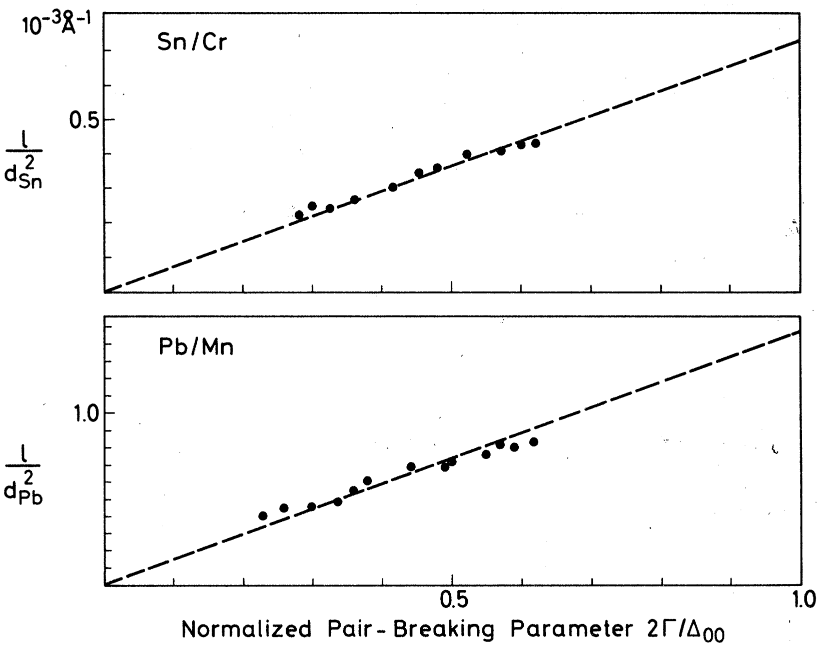

FIG. 7. Electronic mean free path divided by the square of the superconducting film thickness vs normalized pair-breaking parameter.

layers have been compared. The experimental points lie approximately on a straight line through the origin (dotted line in Fig. 7).

The experimental verification of the relation $\Gamma \sim \tau_{tr}/d_s^2 \sim l/d_s^2$ further indicates that for different layers similar conditions at the boundary have been realized experimentally.

Figure 8 shows the ratio of attenuation α_s/α_n of these double layers for various values of $n = 2\Gamma/\Delta_{00}$. The calculated α_s/α_n values near T_c are also plot-

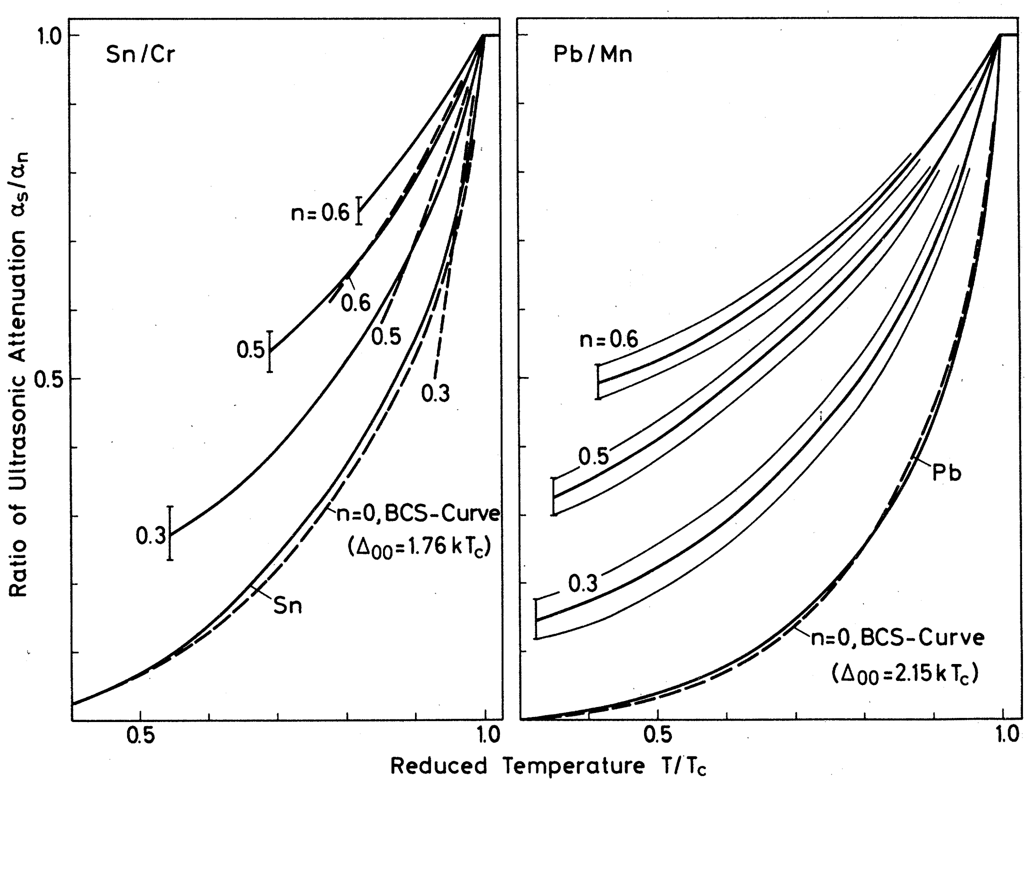

FIG. 8. Ultrasonic attenuation of double-layer superconductor magnetic film vs reduced temperature for various values of $n = 2\Gamma/\Delta_{00}$. Solid curve, experimental values; dashed curve, calculated from Eqs. (6) and (8) and Table I (valid near T_c).

TABLE III. Experimental realization of conditions (15) (values in Å).

	d_s	l	l_∞	$l \ll \xi_0$	$d_s > (l\ \xi_0)^{1/2}$
Sn	1600	1000	1400	1000 < 2300	1600 > 1500
	2500	1500	2000	1500 < 2300	2500 > 1860
Pb	750	450	600	450 < 830	750 > 610
	1300	700	950	700 < 830	1300 > 760

TABLE IV. Experimental realization of the conditions given in Table I for the case of surface superconductivity (values in Å).

	$l \ll \xi_0$	$d_s \gg (2e\ 0.59\ H_{c3})^{-1/2}$
Sn : In (3 wt% In)	250 < 2300	$n=0.3$: 3900 > 770 $n=0.8$: 3900 > 1300
Pb : Bi (2 wt% Bi)	500 < 830	$n=0.3$: 4400 > 500 $n=0.8$: 4400 > 820

ted. The experimental determination of the α_s/α_n values raises some difficulties in this case, because the attenuation of the pure superconducting film is required. Therefore, we have deposited a pure Sn or Pb film at each evaporation, too, and have measured the attenuation of this film for comparison. From various experiments we have estimated the uncertainties indicated in Fig. 8, which originate in this method.

The theory used includes the assumption that the order parameter is zero at the boundary between the superconductor and the magnetic film.[21] Deutscher *et al.*[22] have measured finite penetration depths of the Cooper pairs in the magnetic layer (about 4 Å) for In : Bi layers in close contact with a Mn film. A modification of $\langle|\Delta(\vec{r})|^2\rangle$ according to these results leads to slightly smaller theoretical α_s/α_n values. But the deviations are only about 2% and therefore we have not taken into account these α_s/α_n values in Fig. 8.

D. Surface Superconductivity

Surface superconductivity[23] may occur if the Ginzburg–Landau parameter κ of a superconductor [the ratio of temperature-dependent penetration depth $\lambda(T)$ and temperature-dependent coherence length $\xi(T)$] is larger than 0.42. In a parallel magnetic field $H_\parallel$ a film which is already normal conducting in the bulk $\{d_s \gg [2e\ 0.59\ H_{c3}(T)]^{-1/2}\}$ may exhibit superconducting surface sheaths on both sides of the film.

The surface-wave absorption is an excellent tool for the study of surface superconductivity.[9] Figure 9 shows the attenuation of a Pb film as an example. At rather high temperatures $T(7.2 > T > 4\ \mathrm{K})$ the Ginzburg–Landau parameter κ is smaller than 0.42 and no surface superconductivity occurs. The attenuation as a function of $H_\parallel$ shows an abrupt change at $H_{c\parallel}$ indicating a first-order phase transition. At lower temperatures ($T < 4$ K) κ is larger than 0.42. The surface-wave attenuation then again shows an abrupt change at $H_{c\parallel}$ but now followed by a gradual increase until the critical field H_{c3} is reached. The abrupt change corresponds to the first-order phase transition of the interior of the Pb film, the gradual increase to the transition of the superconducting surface sheath.

The quantitative comparison of these measurements with the theoretical expressions given above does not appear to be reasonable because for pure Pb films of these thicknesses the dirty-limit condition is highly violated. For this reason we have doped Pb films with a few percent Bi. In this case surface superconductivity is observed too (Fig. 9), but the distinction from bulk superconductivity is not so obvious because now the phase transition is of second order. The same is true for Sn films doped with a few percent In, though in pure Sn films no surface superconductivity is observed because κ is too small.

Table IV shows to which extent the conditions of

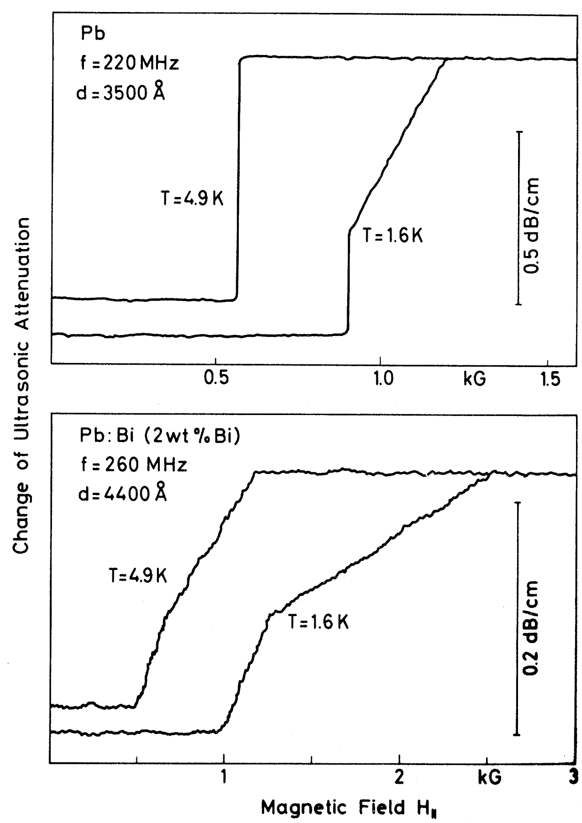

FIG. 9. Change of ultrasonic attenuation for Pb and Pb : Bi (2-wt%-Bi) films vs parallel magnetic field at various temperatures.

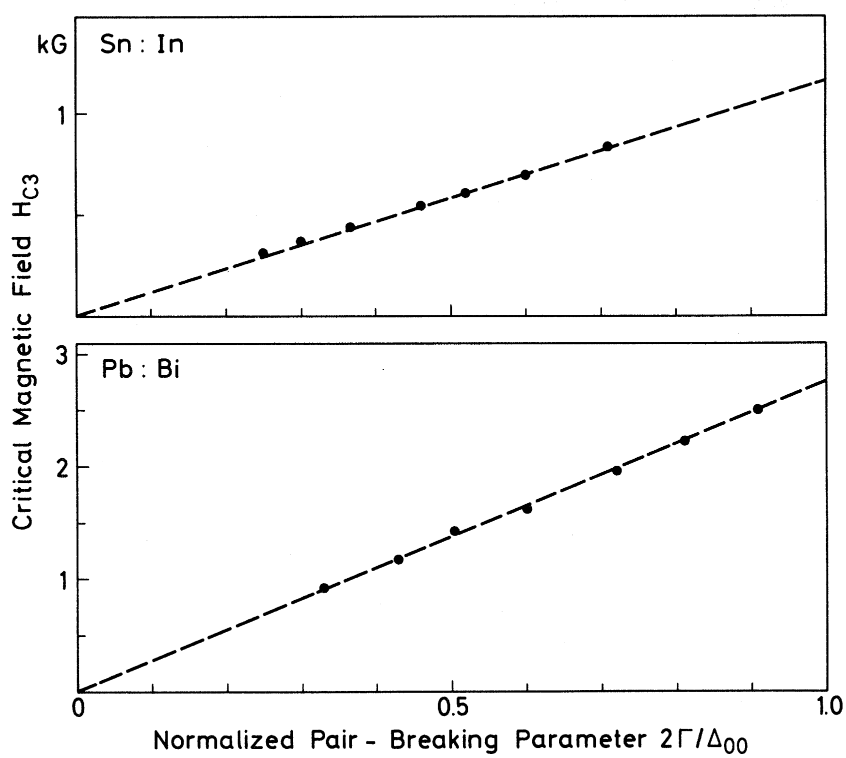

FIG. 10. Critical magnetic field of the superconducting surface sheath vs normalized pair-breaking parameter.

Table I are satisfied for the Sn : In (3-wt%-In) and the Pb : Bi (2-wt%-Bi) films used at the measurements. In this case different values of $n = H_{c3}(T)/H_{c3}(0)$ have to be taken into account because H_{c3} strongly depends on temperature.

In Fig. 10 the critical field H_{c3} is plotted versus $2\Gamma/\Delta_{00}$. The relation $H_{c3} \sim \Gamma$ is satisfied rather well and we obtain for these films

$$[H_{c3}(0)]_{\mathrm{Sn:In}} = 1.17\ \mathrm{kG}, \quad [H_{c3}(0)]_{\mathrm{Pb:Bi}} = 2.75\ \mathrm{kG}.$$

Figure 11 shows the ratio of attenuation as a function of temperature for various values of $n = H_{c3}(T)/H_{c3}(0)$. The α_s/α_n curves are only plotted for temperatures where the occurrence of superconducting surface sheaths has been established by the magnetic field dependence of the attenuation. The theoretical α_s/α_n values near T_c are also plotted. The α_s/α_n curves for $n = 0$ show that the ratio Δ_{00}/kT_c has been enlarged by doping the superconductors with the impurities In and Bi, respectively. But in the case of the Sn : In this increase is rather small and a reasonable comparison with theory is still possible.

V. DISCUSSION

The theory of gapless superconductivity predicts the following characteristics for the ultrasonic attenuation.

(a) The α_s/α_n values are considerably larger than those calculated from the BCS equation (9).

(b) A finite slope appears at the transition temperature.

(c) The attenuation at $T = 0$ attains finite values for sufficiently strong perturbations.

(d) The strongest deviations from the BCS behavior (9) for a given $n = 2\Gamma/\Delta_{00}$ occur in the case of a superconductor in contact with a magnetic layer, slightly weaker deviations are predicted for films in a perpendicular magnetic field, and the smallest differences are calculated for thin films in a parallel magnetic field. The behavior of films showing surface superconductivity cannot be compared directly to the previous three situations, since in this case the film thickness and the absolute value of the critical magnetic field H_{c3} additionally enter into the calculations.

Theoretical predictions (a)–(d) are confirmed experimentally. (We infer the nonzero attenuation at $T = 0$ from the comparison of experimental and theoretical curves at finite temperatures.) Furthermore, the measured values of the normalized pair-breaking parameter agree with theory rather well (Figs. 2, 5, 7, and 10). However, the quantitative comparison of theory and experimental results exhibits considerable discrepancies as already mentioned in the part on the experimental results. In all cases investigated the measured pair-breaking effect is stronger than calculated. Especially large deviations are observed for films in a perpendicular field (Fig. 6), but the attenuation mea-

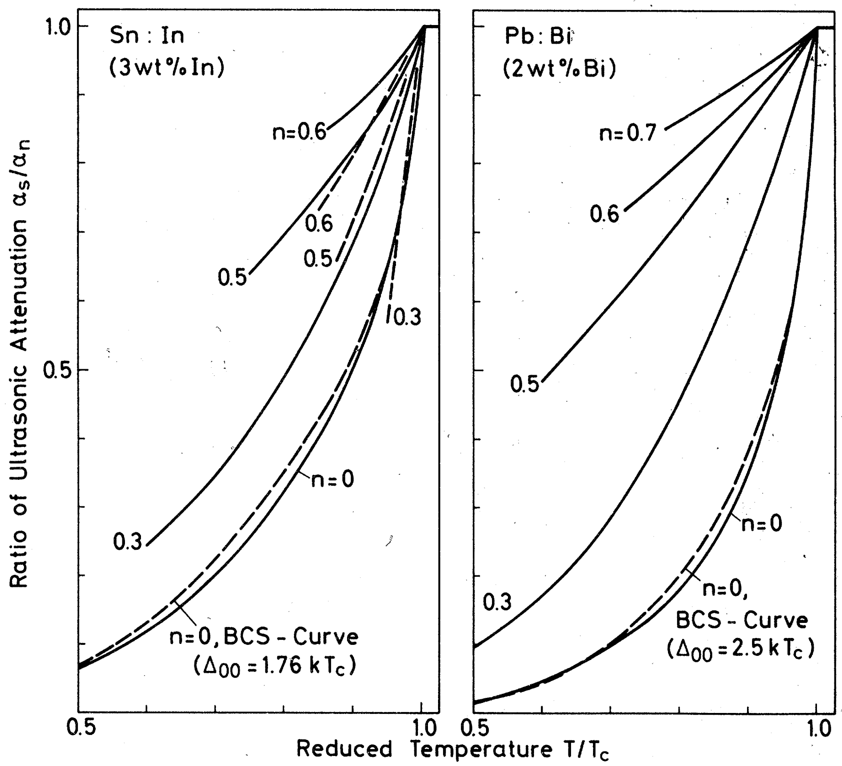

FIG. 11. Ultrasonic attenuation of the superconducting surface sheath vs reduced temperature for various values of $n = H_{c\parallel}/H_{c3}(0)$. Solid curve, experimental values; dashed curve, calculated from Eqs. (6) and (8) and Table I (valid near T_c).

surements on films in parallel fields also differ appreciably from theory (Fig. 3). In the cases of superconductors in contact with a magnetic layer and of surface superconductivity better agreement is found (Figs. 8 and 11). But this agreement refers to the slope of the α_s/α_n curves at T_c only; already at slightly lower temperatures the measured α_s/α_n values are larger than the calculated curves.

The reasons for these discrepancies between theory and experiments are not yet understood. In an earlier letter[6] we suggested that the insufficient realization of the dirty-limit condition ($l \ll \xi_0$) might be responsible for the deviations. This is supported by calculations of Strässler and Wyder,[24] who showed that even for $l/\xi \approx 0.1$ the influence of the pair-breaking effect is considerably stronger than in the limit $l \to 0$. But the following experiments confirm this explanation only partly: We have investigated various layers with different electronic mean free paths. Within certain limits mean free paths have been varied by different evaporation rates and different substrate temperatures during vacuum deposition. In the case of surface superconductivity the impurity concentration has been changed, too. At all measurements the α_s/α_n values for a given $n = 2\Gamma/\Delta_{00}$ grow with increasing mean free path as expected.

But we infer from these results that the insufficient realization of the dirty-limit condition may not account completely for the discrepancies between theory and experiments. We suppose that quantitative disagreement would remain even if the experiments were fully in the dirty limit. Evidence for this is provided by the following example: We consider the slope of $\alpha_s(T)/\alpha_n(T)$ at $T = T_c$ for two Sn films (ξ_0 = 2300 Å) with different mean free paths in a perpendicular magnetic field. At $n = 0.6$ we find for the film with $l/\xi \approx 0.5$ a slope $d(\alpha_s/\alpha_n)/d(T/T_c) = 1.1$ at $T = T_c$. This slope increases only moderately for a film with $l/\xi_0 \approx 0.1$ to a value of 1.35, which is still far below the theoretical slope of 3.0 calculated for the dirty limit.

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[1] A. A. Abrikosov and L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. 39, 1781 (1960) [Sov. Phys. JETP 12, 1243 (1961)].

[2] A detailed summary of gapless superconductivity is given by K. Maki, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Chap. 18.

[3]L. P. Kadanoff and J. J. Falko, Phys. Rev. 136, 1170 (1964).

[4]A. Griffin and V. Ambegaokar, Low Temp. Phys. 9A, 524 (1964).

[5]K. Maki, Progr. Theoret. Phys. (Kyoto) 31, 731 (1964); K. Maki and P. Fulde, Phys. Rev. 140, A1586 (1965).

[6]E. Krätzig, Phys. Letters 37A, 21 (1971).

[7]K. Maki and P. Fulde, Solid State Commun. 5, 21 (1967).

[8]F. B. McLean and A. Houghton, Phys. Rev. 157, 350 (1967).

[9]E. Krätzig, K. Walther, and W. Schilz, Phys. Letters 30A, 411 (1969).

[10]R. S. Thompson and A. Baratoff, Phys. Rev. Letters 15, 971 (1965).

[11]P. Fulde, in *Tunneling Phenomena in Solids*, edited by E. Burstein and S. Lundqvist (Plenum, New York, 1969), Chap. 29.

[12]*Handbook of Mathematical Functions*, edited by A. Abramowitz and J. Segun (Dover, New York, 1965).

[13]M. Levy, Phys. Rev. 131, 1497 (1963); L. T. Claiborne, Jr. and R. W. Morse, *ibid.* 136, A893 (1964).

[14]A summary of ultrasonic-attenuation measurements in superconductors is given by D. M. Ginsberg and L. C. Hebel, in Ref. 2, Chap. 4.

[15]F. Press and J. Healy, J. Appl. Phys. 28, 1323 (1957).

[16]R. M. White, IEEE Trans. Electron Devices 14, 181 (1967).

[17]R. M. White and F. W. Voltmer, Appl. Phys. Letters 7, 314 (1965).

[18]See, for instance, A. von Bassewitz and G. von Minnigerode, Z. Physik 181, 368 (1964); A. M. Toxen, M. J. Burns, and D. J. Quinn, Phys. Rev. 138, A1145 (1965).

[19]J. R. Peverley, Phys. Rev. 173, 689 (1968).

[20]M. Tinkham, Phys. Rev. 129, 2413 (1963).

[21]P. Fulde and K. Maki, Phys. Rev. Letters 18, 675 (1965); Phys. Kondensierten Materie 5, 380 (1966).

[22]G. Deutscher, P. Lindenfeld, and R. D. McConnell, Phys. Rev. B 1, 2169 (1970).

[23]D. Saint James and P. G. de Gennes, Phys. Letters 7, 306 (1963).

[24]S. Strässler and P. Wyder, Phys. Rev. 158, 319 (1967).

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Thomas–Fermi Screening in One Dimension*

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The Thomas–Fermi method has been applied to the problem of screening due to an electron gas confined to a filament and a coaxial infinite cylinder. Using parameters derived for $K_2Pt(CN)_4Cl_{0.32}\cdot 2.6H_2O$, the potential in the region between the filament and cylinder due to a source charge in the filament was evaluated and was found to vary approximately as $e^{-\kappa_{eff} r}/r$ with an effective screening length about ten times that of metallic platinum. The isotropic form of the screened potential shows the close relationship to screening in three dimensions.

I. INTRODUCTION

The nature of screening in compounds which have less than three-dimensional freedom of motion for the conduction electrons has been treated by several authors.[1–3] The one-dimensional case is treated by Kuper[1] using a single-filament model and by Dzyaloshinskii and Katz[2] using an array of filaments. Materials whose structures exhibit this one-dimensional nature include a variety of radical-anion charge-transfer complexes of tetracyanoquinodimethan (TCNQ)[4] and platinum chain compounds such as $K_2Pt(CN)_4Cl_{0.32}\cdot 2.6H_2O$ characterized by Krogmann.[5] Graphite systems are represented by the two-dimensional model of Visscher and Falicov.[3]

To a large extent the possibility of superconductivity in the one-dimensional systems has motivated the previous treatments. Kuper,[1] on the basis of a single-filament model, concluded that dielectric screening would be insufficient to reduce the Coulomb repulsion between conduction electrons to a point where it could be dominated by an attractive interaction as proposed by Little.[6] Dzyaloshinskii and Katz,[2] on the other hand, considered the effect of interaction with neighboring filaments in their model of an array of filaments and found solutions which exhibit superconductivity, thereby pointing out the necessity of also dealing with the long-wavelength interactions. In the present paper we reinvestigate the model of Kuper and extend its scope in a manner which recognizes not only the one-dimensional nature of the individual conducting filaments, but also the obvious three-dimensionality of the bulk material.

II. MODELS

We consider two models in the present treatment. The first is that of Kuper which involves a single filament of radius R_1 lying along the z axis. The region within the filament is designated as metallic and in the absence of source