formula of Eck, Scalapino, and Taylor<sup>3</sup> for the height of their resonance-shaped peak in low Q junctions is essentially the special case of  $I_{de peak}$  evaluated at  $kL = m\pi$ .

From the regular spacing of the current steps, from their dependence on magnetic field, and from the other effects described, it seems probable to us that highfrequency electromagnetic fields exist within these junctions. Coupling of these fields to a detection instrument in the outside world would constitute proof of their existence. A preliminary attempt has been made to do this, using a transmission line smoothly tapering from the  $\sim 10$  Å separation of the junction to the macroscopic dimensions of a coaxial cable or wave guide. No ac power as large as 10<sup>-12</sup> W was detected, even though one junction was tunneling a current of 30 mA at 20  $\mu$ V. These experiments are continuing with greater emphasis on effecting smooth impedance transformation and reducing line losses.

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# Tunneling into Dirty Superconductors Near their Upper Critical Fields\*

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We describe experiments on tunneling into SnIn and PbBi alloys near their upper critical fields. In this regime, a theory by de Gennes predicts gapless superconductivity with a density of excited states whose energy scale is field-independent. We have experimentally investigated this density of states in detail, both in the superconducting sheath regime near  $H_{e3}$  (field parallel to the surface) and in the vortex regime near  $H_{c2}$  (field normal to the surface). We find excellent agreement between theory and experiment for the shape of the tunneling characteristic and reasonable agreement for its normalization.

# I. INTRODUCTION

R ECENTLY, de Gennes<sup>1</sup> and Maki<sup>2</sup> have shown that the domain of validity of the linearized Landau-Ginsberg<sup>3</sup> equations may be extended to arbitrarily low temperatures in dirty superconductors for the calculation of the geometry-dependent nucleation field  $H_{\rm cr}$  ( $H_{c2}$ , the bulk upper critical field or the nucleation field for surface superconductivity,4 He3). De Gennes<sup>1</sup> was further able to derive an expression for the density of states of excitations relative to the Fermi energy which is valid for fields just below  $H_{\rm er}$ , i.e., for small  $|\Delta|$ 

$$\frac{N(\mathbf{r},\omega)}{N(0)} = 1 + 2|\Delta(\mathbf{r})|^2 \tau^2 \frac{[(2\omega\tau)^2 - 1]}{[(2\omega\tau)^2 + 1]^2},$$
$$\left(\frac{H_{\rm er} - H}{H_{\rm er}} \ll 1\right), \quad (I.1)$$

where  $\hbar\omega$  is the excitation energy relative to the Fermi

energy, N(0) is the density of states at the Fermi surface in the normal metal, and  $\tau$  is a function only of temperature, given implicitly by

$$\ln(T/T_0) = \psi(\frac{1}{2}) - \psi(\frac{1}{2} + \hbar/4\pi k_B T\tau), \qquad (I.2)$$

where  $T_0$  is the critical temperature in zero field and

$$\psi(x) = \Gamma'(x) / \Gamma(x). \qquad (I.3)$$

The following points should be noted in connection with (I.1):

(1) The frequency dependence of the density of states (I.1) is quite different from the BCS density of states<sup>5</sup>

$$N(\omega)/N(0) = (\omega/[\omega^2 - (\Delta/\hbar)^2]^{1/2}). \quad (I.4)$$

Both forms have the same asymptotic behavior at large  $\omega$ , but the piling up of states at  $\hbar\omega = \Delta$  in (I.4) is smeared out. Note in particular that the density of states (I.1) shows no gap in the excitation spectrum  $[N(\omega) \text{ finite for } \omega \rightarrow 0]$ . A dirty superconductor near its upper critical field is predicted to be a gapless superconductor.

Early tunneling experiments displaying this type of gapless superconductivity have been performed by Tomasch<sup>6</sup> prior to the appearance of the theoretical

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<sup>&</sup>lt;sup>1</sup> P. G. de Gennes, Phys. Condensed Matter 3, 79 (1964).
<sup>2</sup> K. Maki, Physics 1, 21 (1964).
<sup>8</sup> See for example P. G. de Gennes, Superconducting Metals and Alloys (W. A. Benjamin, Inc., New York, to be published).
<sup>4</sup> P. G. de Gennes and D. St. James, Phys. Letters 7, 306 (1963).

<sup>&</sup>lt;sup>5</sup> J. Bardeen, L. Cooper, and J. Schrieffer, Phys. Rev. 108, 1175 (1957).

<sup>&</sup>lt;sup>6</sup> Tomasch, Phys. Letters 9, 104 (1964).

formula (I.1). We decided to repeat and extend those measurements, and to carry out a complete comparison of the results with (I.1). We used Al-Al<sub>2</sub>O<sub>3</sub>-S sandwiches where S was the dirty superconductor, in this case SnIn and PbBi alloys. The current-voltage characteristics of the junctions were measured as functions of temperature and magnetic field. The experiments were carried out both in fields perpendicular to the plane of the sandwich near  $H_{c2}$  and in parallel fields near  $H_{c3}$ . We find excellent qualitative and good quantitative agreement with (I.1). In fact, these nonmagnetic alloys in high fields appear to give us one of the cleanest experimental situations where gapless superconductivity can be displayed.

(2) Another remarkable property of (I.1) is that the density of states measured at one point **r** depends only on the order parameter  $\Delta(\mathbf{r})$  at the same point.<sup>1</sup> We have not been able to verify this property directly. However, we have calculated theoretically the values of  $\Delta(\mathbf{r})$  at the junction surface, and find reasonable agreement between these values and the ones which are required in (I.1) to account for the tunneling characteristics.

The theoretical calculations which are necessary to compare our experimental results with (I.1) are explained in Sec. II. Part A contains a calculation of the theoretical tunneling characteristics based on (I.1). In Part B we discuss the field dependence of the gap parameter  $|\Delta(\mathbf{r})|$  in both parallel and perpendicular fields just below the respective critical fields. Section III is devoted to the experimental procedure: Part A deals with the sample preparation, Part B contains a discussion of critical fields, Part C concerns the tunneling measurements. The results and comparison with theory are discussed in Sec. IV.

#### II. THEORY

#### A. Current-Voltage Characteristics

Here we present a calculation of the tunneling current as a function of the voltage applied across the junction when the excitation spectrum has the density of states given by (I.1). If we denote by  $\delta I$  the difference between the tunneling current in the normal and superconducting states, then

$$\delta I = C \int \delta N(\omega) \left| f(\hbar\omega) - f(\hbar\omega + eV) \right| d\omega, \quad (\text{II.1})$$

where C is a constant that depends on the junction,  $\delta N(\omega)$  is the difference between the normal and superconducting densities of states for excitations with energy  $\hbar \omega$  relative to the Fermi energy, V is the applied voltage,  $f(\hbar \omega)$  is the Fermi distribution function. The density of states (I.1) can be rewritten as

$$\delta N(\omega) = N(0) \frac{|\Delta|^2}{4\hbar^2} \left| \frac{1}{(\omega - i/2\tau)^2} + \frac{1}{(\omega + i/2\tau)^2} \right|. \quad (\text{II.2})$$

Then  $\delta I$  becomes

$$\delta I = -(I_n/V)G(V), \qquad (II.3)$$

where  $I_n$  is the normal current and

$$G(V) = (|\Delta|^2/4\hbar) \int d\omega \left[ f(\hbar\omega + eV) - \frac{1}{2} \right]$$

$$\times \left[ \frac{1}{(\omega - i/2\tau)^2} + \frac{1}{(\omega + i/2\tau)^2} \right]. \quad (\text{II.4})$$

By standard methods G(V) may be transformed into

 $G(V) = (|\Delta|^2/4\pi k_B T) \operatorname{Im} \psi_2(\frac{1}{2} + a - ib), \quad (\text{II.5})$ 

where  $\psi_2$  is the first derivative of the function defined in (I.3),  $a = (\hbar/4\pi k_B T \tau)$ , and  $b = eV/2\pi k_B T$ . The function G(V), Fig. (3), vanishes both at zero voltage and at high voltages (when  $I \rightarrow I_n$ ). The voltage for the maximum of G(V) is temperature-dependent and approaches  $eV = \hbar/2\tau = \Delta/2$  at absolute zero. Note that although the shape of G(V) is given entirely by  $\psi_2$ , its normalization depends upon  $|\Delta(0)|$ , i.e., the magnitude of the order parameter *at the surface* of the junction. In the range of validity of (I.1),  $\tau$  is independent of field and thus the only magnetic-field dependence occurs in  $|\Delta(0)|$  which, near  $H_{\rm er}$ , varies linearly as  $(H_{\rm er}-H)$ .

# B. Field Dependence of the Order Parameter

## i. Fields Parallel to the Surface

In this case we are interested in tunneling in the surface superconducting sheath just below  $H_{c3}$ .<sup>4</sup> In order to determine  $|\Delta(\mathbf{r})|$ , it is necessary to find a solution of the nonlinear Landau-Ginsberg equations. Our method essentially follows Abrikosov's' calculation of  $|\Delta(\mathbf{r})|$  in the mixed state just below  $H_{c2}$ . The principal approximation is to assume that the spatial dependence of the order parameter near  $H_{c3}$  preserves the form of the solution to the linearized problem, but only its normalization is field-dependent. A similar problem has been studied by Zuckerman<sup>8</sup> who has discussed the field distribution in the superconducting sheath. Maki<sup>2</sup> has generalized Abrikosov's calculation to arbitrary temperatures and finds that for  $T < T_0$ , the Landau-Gunsburg  $\kappa$  loses its unique meaning and becomes slightly temperature-dependent. Following Maki's notation,  $\kappa_1 = (1/\sqrt{2})(H_{c2}/H_c)$  (where  $H_c$  is the thermodynamic critical field) has been shown both by de Gennes and Maki to be about 20% larger at 0°K than at  $T_c$ . On the other hand, the parameter  $\kappa_2$  (related to the slope of the magnetization curve at  $H_{c2}$ ) decreases about 30% between  $T_0$  and absolute zero; at  $T=T_0$ ,  $\kappa_1 = \kappa_2 = \kappa$ . The free energy<sup>3</sup> of the superconducting state

<sup>&</sup>lt;sup>7</sup> A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **34**, 1442 (1957) [English transl.: Soviet Phys.—JETP **5**, 1174 (1957)]. <sup>8</sup> W. Zuckermann (to be published).

may be written in terms of the Landau-Ginsberg wave from the supercurrents and is approximately given by function  $\psi$  as

$$f = \int d\mathbf{r} \left( F_N + \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m} \left| \left( -i\hbar\nabla - \frac{2e\mathbf{A}}{c} \right) \psi \right|^2 + \frac{\hbar^2}{8\pi} \right). \quad (\text{II.6})$$

Just at the critical point,  $\psi$  satisfies the linearized Landau-Ginsburg equations

$$\alpha\psi + \frac{1}{2m} \left( -i\hbar\nabla - \frac{2e}{c}\mathbf{A} \right)^2 \psi = 0, \qquad (\text{II.7a})$$

$$\mathbf{j} = \frac{e\hbar}{im} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{4e^2}{mc} \psi^* \psi \mathbf{A}, \qquad (\text{II.7b})$$

where **j** is the current density and **A** the vector potential. The Landau-Ginsburg function  $\psi(\mathbf{r})$  is related to the pair potential  $\Delta(\mathbf{r})$  in a dirty superconductor by<sup>9</sup>

$$\psi = \left(\frac{\pi}{8} \frac{m}{k_B T} \frac{\sigma}{hc^2}\right)^{1/2} \Delta, \qquad (II.8)$$

where  $\sigma$  is the conductivity of the alloy in its normal state. The Abrikosov approximation lies in taking the eigenfunction  $\psi_0$  of (II.7a) having the lowest eigenvalue and finding its normalization by minimizing the free energy (II.6). In the case of surface superconductivity,  $\psi_0$  has been calculated by de Gennes and St. James,<sup>4</sup> but is a rather complicated Weber function. In order to simplify the subsequent calculations, we shall instead use a Gaussian centered at the surface. Kittel<sup>3</sup> and Zuckerman<sup>8</sup> have shown that such a function when used in a variational calculation of  $\psi_0$  gives results (for the nucleation field) which are in excellent agreement with the exact calculation. Using (II.7), and minimizing the free energy with respect to the normalization of  $\psi_0$ , we find

$$\beta \int |\psi_0|^4 d\mathbf{r} - \frac{1}{4\pi} \int h_1 h_s d\mathbf{r} = 0, \qquad (\text{II.9})$$

where the fields  $h_1$  and  $h_s$  are defined by

$$\mathbf{h}_{1} = \operatorname{curl} \mathbf{A}_{1},$$
  
$$\operatorname{curl} \mathbf{h}_{s} = (4\pi/c)\mathbf{j}_{0},$$
 (II.10)

where  $A_1$  is that part of the vector potential arising from the facts that (1) the applied field is slightly less than  $H_{c3}$  and (2) there also exist supercurrents which contribute to the fields. The field h, is the field arising

$$\operatorname{curl} \mathbf{h}_{s} \cong \frac{4\pi}{c} \mathbf{j}_{0} = \frac{4\pi e}{mc} \left[ \psi_{0}^{*} \left( -i\hbar \nabla - \frac{2e}{c} \mathbf{A}_{0} \right) \psi_{0} + \operatorname{c.c.} \right], (\text{II.11})$$

where  $A_0$  is the vector potential at  $H_{c3}$  and represents a uniform field. Thus

$$h_1 = H_{c3} - H + h_s$$
 (II.12)

and we find

$$\beta \int |\psi_0|^4 d\mathbf{r} + \frac{1}{4\pi} (H_{c3} - H) \int h_s d\mathbf{r} - \frac{1}{4\pi} \int h_s d\mathbf{r} = 0. \quad \text{(II.13)}$$

 $\beta$  is related to Maki's parameter  $\kappa_2$  by

$$\beta = 2\pi (2e\hbar/mc)^2 \kappa_2^2. \qquad (II.14)$$

The integration on the field arising from the supercurrents is related to the first moment of the supercurrent density by

$$\int_0^\infty h_s dx = \frac{4\pi}{c} \int_0^\infty x j_0(x) dx, \qquad (\text{II.15})$$

where  $h_s$  is directed along the z axis parallel to the surface of the sample, the current  $j_0$  flows also in the surface perpendicular to the fields and the x axis runs into the bulk of the sample. The integral of the square of the field over the sample was carried out approximately numerically using the Kittel variational function given below. In the gauge  $A_x = A_z = 0$ ,  $A_y = H_{c3}x$ , the linearized Landau-Ginsburg equation becomes

$$- (d^2 |\psi_0| / dx^2) + (2\pi H_{o3} / \phi_0)^2 (x - x_0)^2 |\psi_0|$$
  
=  $|\psi_0| / \xi^2$ , (II.16)

which is of the same form as the Schrödinger equation for a harmonic oscillator centered at  $x_0$ , where  $\phi_0$  is the flux quantum and we have taken  $\psi = e^{iky} |\psi|$ . The symmetry center of the potential  $x_0$  is given by  $x_0$  $= (hck/2eH_{c3})$ . The Kittel variational calculation gives

$$|\psi_k| \cong e^{-x^2/2\xi^2}, \qquad (\text{II.17})$$

where  $\xi$  is the temperature-dependent coherence length.

The Kittel function  $\psi_{\kappa}$  gives  $x_0 = 0.57\xi(T)$  and  $H_{c3}$ = 1.67 $H_{c2}$ . The exact values are  $x_0 = 0.59\xi(T)$  and  $H_{c3}$ =1.69 $H_{c2}$ : This approximation is quite good. Then, using  $\psi_{\kappa}$ , the current density becomes

$$j_0 = (2eH_{c3}/mc) |\psi_{\kappa}|^2 (x_0 - x).$$
 (II.18)

Using (II.13), (II.14), (II.15), (II.17), and (II.18), we find for the value of the Landau-Ginsburg function at the surface of the sample

$$|\psi_k(0)|^2 \cong 0.21 \left(\frac{mc}{eh}\right) \frac{(H_{e3}-H)}{\kappa_2^2 - 0.174}.$$
 (II.19)

Using (II.8), this gives for the gap parameter at the

<sup>&</sup>lt;sup>9</sup>L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. 37, 1407 (1959) [English transl.: Soviet Phys.—JETP 10, 998 (1960)]; C. Caroli, P. G. de Gennes, and J. Matricon, Phys. Condensed Matter 1, 176 (1963).

surface

$$|\Delta_k(0)|^2 \cong \frac{1.68}{(2\pi)^3} \frac{ec}{\sigma} \frac{H_{\epsilon 3} - H}{\kappa_2^2 - 0.174}.$$
 (II.20)

The numerical value (0.174) appearing in (II.20) can be more or less guessed even without a detailed calculation. The argument proceeds as follows: Consider, for simplicity, the region  $T \sim T_0$  where  $\kappa_1 = \kappa_2 = \kappa$ . When  $\kappa$ decreases,  $(H_{c3}/H_c) = 2.4\kappa$  decreases and becomes unity when  $\kappa = (1/2.4) = 0.42$ . Below this value of  $\kappa$  the transition is of first order. It is thus plausible to assume that, for that particular value of  $\kappa$ , the denominator in Eq. (II.20) vanishes. If this denominator is of the form  $(1/\kappa^2 - c)$  then  $c = (0.42)^2 = 0.174$ .

Finally, Eq. (II.20) can be used in the following way: Knowing the conductivity  $\sigma$  in the normal state, Maki's  $\kappa_2$ , and the upper critical field of the material  $H_{c3}$ , Eq. (II.20) predicts a definite value for the order parameter  $\Delta(0)$  at the surface. The tunneling experiments (in *Pb*Si and *Sn*In alloys) to be described below were designed to check the joint predictions of Eqs. (II.5) and (II.20).

# ii. Field Perpendicular to the Surface

When the magnetic field is applied perpendicular to the surface of the sample, there is no surface sheath. We are then interested in tunneling effects at fields just below  $H_{c2}$ . Then the sample is in the Shubnikov phase. Flux penetrates on throughout the sample in the form of Abrikosov vortices.<sup>10</sup> To compute explicitly the density of states (I.1) and the tunneling current (II.15), we must take the average value of  $|\Delta(0)|^2$  on the sample surface. This average differs from the average of  $|\Delta|^2$ in the bulk of the sample, since the magnetic lines of force "open up" near the surface. In the following, we neglect this difference and derive only  $\langle |\Delta(0)|^2 \rangle$  (where the brackets denote a spatial average). In the vortex state, (II.13) can be rewritten as

$$\beta \int |\psi|^4 d\mathbf{r} + \frac{e\hbar}{mc} (H - H_{c2}) \int |\psi|^2 d\mathbf{r} -4\pi \left(\frac{e\hbar}{mc}\right)^2 \int |\psi|^2 d\mathbf{r} = 0. \quad (\text{II.21})$$

This leads to a pair potential at the surface given by

$$|\Delta(0)|^{2} \cong \frac{1.55}{(2\pi)^{3}} \frac{ec}{\sigma} \frac{H_{e2} - H}{\kappa_{2}^{2} - 0.5}.$$
 (II.22)

We have taken the value of  $\langle |\psi|^2 \rangle^2 / \langle |\psi|^4 \rangle$  appropriate to the triangular lattice. Notice the remarkable result that in the limit  $2\kappa^2 \gg 1$ , (II.22) and (II.20) approximately coincide for a given  $\Delta H$ . As we shall see later, this is borne out by our experiments.

#### **III. EXPERIMENTAL PROCEDURE**

#### A. Preparation of the Samples

The specimens were prepared in a conventional evaporator of limit vacuum  $2 \times 10^{-7}$  Torr. They were deposited on a glass substrate at room temperature from a crucible heated by the Joule effect. A relatively thick film of Al was deposited first and then oxydized for several minutes in a glow discharge under a pressure of  $10^{-2}$  Torr of dry O<sub>2</sub>. The discharge current of several milliamperes occurs between a pure Al wire at a potential of 500 V and the bell jar at a zero potential. Then on top of the oxide layer we deposit the alloy of interest (PbBi 5% and SnIn at various concentrations). The alloy films are evaporated from a piece of bulk alloy. The problem is to check that the two elements evaporate together. For the lead alloys this was proven by isolating parts of the evaporation on different substrates during the experiment. For the Sn alloys we were able to prove, in comparing the normal state resistivity as well as the superconducting properties with those of the starting ingot, that the diffusion between Sn and In occurs very rapidly if the material is evaporated under a sufficient vacuum. Finally we emphasize that much attention was paid to the shape of the masks to avoid any edge effects on the alloy film that would enhance the residual superconductivity in high fields.

The resistivity ratio of the alloy films in the normal state was in good agreement with that determined from resistivity measurements<sup>11</sup> on the bulk alloy. In all cases of interest the mean free path is limited by scattering from the impurity atoms rather than by surface scattering (the thickness  $d\gg l$  in these experiments). Also the scattering by possible defects introduced during evaporation appears to be negligible in these alloys.

#### **B.** Critical Fields

The film thicknesses d are of order 4000 Å. In the domain of temperature which was used (from 0.5 to 3.4°K in the Sn base films) the thickness of the superconducting sheath  $\xi(T)^4$  is then much smaller than d. Then the parallel critical field is known to be<sup>12</sup>

$$H_{11} = H_{c3} = 1.69 H_{c2}$$

The perpendicular critical field is

 $H_1 = H_{c2}$ .

In the present work  $H_1$  and  $H_{11}$  were measured from tunneling.<sup>13</sup> The Landau-Ginsburg parameter  $\kappa$  of each

<sup>&</sup>lt;sup>10</sup> W. H. Kleiner, L. M. Roth, and S. H. Autler, Phys. Rev. 133, A1226 (1964).

 $<sup>^{11}</sup>$  A system devised by G. Deutscher using essentially the measurement of the normal skin depth of bulk cylinders of alloys has been used (to be published).

<sup>&</sup>lt;sup>12</sup> See, for example, J. P. Burger, G. Deutscher, E. Guyon, and A. Martinet, Solid State Commun. 2, 101 (1964).

<sup>&</sup>lt;sup>13</sup> The orientation can be obtained sensitively using a sharp maximum of the resistance in the intermediate state for  $H_{II}$  (see Ref. 14).



FIG. 1. The lower solid line is the theoretical variation of  $\frac{1}{2}\tau$  with reduced temperature. According to the theory of de Gennes,<sup>1</sup> this should be proportional to  $H_{e2}(T)$ . The open circles represent some of our measurements of this quantity, normalized such that one value of  $H_{e2}$  lies on the curve. The upper curve is a theoretical plot of the temperature variation of the maximum of G(V) deduced from (II.5). The error bars represent our measurements on SnIn.

sample of the Sn alloys was derived from a study of  $(H_1/H_c)$  in the limit  $T \rightarrow T_0$ . ( $H_c$  being taken as the value for the pure metal.)

For the lead alloy, this technique was not convenient: We measured the ratio  $(H_{\rm L}/H_c) = \kappa_1 \sqrt{2}$  at  $T = 4^{\circ}$ K, and derived the value of  $\kappa = \kappa_1(T_c)$  from  $\kappa_1$  (4°K) by theoretical formulas of Ref. 2 or Ref. 3. The resulting  $\kappa$ values for two typical alloys are shown in Table I and compared with the theoretical formula of Gorkov

$$\kappa = \kappa_0 + 7.5 \ 10^3 \gamma^{1/2} \rho$$

 $(\gamma = \text{Sommerfeld constant}, \kappa_0 = \text{value of } \kappa \text{ in the pure matrix}).$  We have also measured the complete curve  $H_1(T) = H_{c2}(T)$  for various SnIn alloys. Results are shown in Fig. 1, and compared with a theoretical

TABLE I. K values for two typical alloys.

	l	ĸgg	Kexp	$T_0$	$\Delta_0$	
Pb Bi 5% Sn In 5%	240 Å 390 Å	1.96 0.86	$\kappa_{4.2}^{\circ} \kappa = 2.2$ 0.92	3.75°K	1.3 meV 0.57 meV	

formula<sup>1</sup>

$$H_{c2} = (\Phi_0 \hbar/2\pi\tau D),$$

[where  $\Phi_0$  is the flux quantum,  $\tau$  is the dephasing time related to the temperature by Eq. (I.2), and D the diffusion coefficient for electrons at the Fermi level in the normal metal]. The predicted proportionality between  $H_{c2}$  and  $(1/\tau)$  is very well confirmed by the results of Fig. 1. For that particular case, the best fit corresponds to  $D=46 \text{ cm}^2/\text{sec.}$  The corresponding calculated value  $D=(\sigma/N(0)e^2)=32 \text{ cm}^2/\text{sec}$  is in satisfactory agreement.

### C. Tunneling Measurements

For a given field, we measured

$$G(V) = (I_n(V) - I_s(V))R_1,$$

where  $I_n(V)$  is the linear function representing the tunneling conductance in the normal state and  $I_s(V)$ that with the alloy film in the superconducting state with a field applied H. This was done using a bridge whose one arm contained the junction and which was balanced when the resistance was equal to its normal value  $(=R_1)$ . In the superconducting state the voltage across the bridge  $V' = (R_1R_3/R_3 + R_4)\delta I = (R_1/2)\Delta I = (G(V)/2),$  $R_3$  being taken as equal to  $R_4$ , is proportional to  $\Delta I$  and was recorded horizontally on a XY recorder after amplification through a dc amplifier. The higher sensitivity gives a full scale deviation for  $V'=50 \mu V$ . This procedure gives very sensitively the deviation of the I(V)characteristics from the linear form in the normal state; for the voltage at the maximum of the curve, we find typically 50  $\mu$ V for  $(\Delta H/H_{er}) \sim 10\%$ .

The bridge was balanced at a voltage high enough so that the IV characteristic is indistinguishable from the normal one. In the case of Sn base alloy, this voltage for the balance is taken as 10 mV. This operation is not so easy for the Pb base alloys because of the bumps in the IV characteristics due to phonon assisted tunneling.<sup>14</sup> Furthermore this last effect is—in high fields of the order of magnitude of the direct tunneling for V > 4 mV. The adjustment has to be done for every voltage as it is not possible to eliminate the resistance of the conducting arms of the junction from the bridge. The resistance of the superconducting arm varies with the field and has to be taken into account in  $R_1$ . Other effects to be taken into account in  $R_1$ —critical current effects and effect of the warming of the arms of the junction-can be minimized, provided one has a junction resistance large compared to them (small area of the junction, thick junction, thick arms of the junction).

It turns out that the determination of G(V) is as sensitive (and more direct) than the more standard measurements of the differential conductivity dI/dV. However, to compare experiment and theory, it is

<sup>&</sup>lt;sup>14</sup> See, for example, J. M. Rowell, P. W. Anderson, and D. E. Thomas, Phys. Rev. Letters 10, 334 (1963).

sometimes convenient to present results in terms of dI/dV (in particular, for  $T \ll T_0$ , dI/dV gives directly the density of states). For this reason, some of our later results will be given in the form of dI/dV curves.

### IV. RESULTS AND DISCUSSION

To compare theory and experiment we focus our attention on the following points:

(1) For a given temperature, the experimental G(V) curve normalized to its maximum amplitude  $G(V)/G(V_{\text{max}})$  is independent of both the magnitude and the orientation of the field [within a range  $(H_{\text{er}}-H/H_{\text{er}}) \approx 0.3$ ]. This is shown in Fig. 3. Changes in H change only the amplitude of G(V), not its shape. In particular, when  $H \to H_{\text{er}}$ , the order parameter  $\Delta \to 0 G(V) \to 0$  but the potential  $V_{\text{max}}$  at which G is a maximum is *finite*.

All these properties are in agreement with the predictions of (I.1) and (II.5). Since  $\tau$  [as defined in (I.2)] depends only on temperature, the only field-dependent term in G(V) is  $\langle |\Delta|^2 \rangle$  which acts as a scaling factor.

Note incidentally that a similar property has been found in tunneling experiments by Goldstein<sup>15</sup> on the surface sheath in nearly pure lead. Unfortunately, the theoretical density of states has not yet been calculated for such a "clean" superconductor near  $H_{c3}$ .

(2) The G(V) curve *cannot* be interpreted in terms



FIG. 2. The points represent the measured ratio of the differential conductivity in the superconductor to the differential conductivity in the normal state. The heavy line passing through the points represents the theory deduced from (II.5). The light line is the corresponding BCS tunneling curve having the same initial slope. Note that this BCS curve gives very bad agreement for the voltage at which G(V) is maximum. In fact, there *does not* exist a value of the gap  $\Delta$  for which the BCS characteristic is in reasonable agreement with experiment.

Alox.<u>Sn</u> ln 5%  $T_{\pm}1.4^{\circ}K$ G(V) arb. units  $H_{\perp} = \begin{vmatrix} 0 & 315 & g \\ 0 & 350 & g \\ + & 350 & g \\ 2 \\ + & 350 & g$ 

FIG. 3. The line represents G(V) for an arbitrary normalization. The points are the measured values in SnIn normalized to the maximum for the various indicated samples, fields, and orientations. Note that the shape of G(V) is independent of all of these parameters as predicted.

of a BCS type density of states

 $N(\omega) = N(0) \left( \hbar \omega / \left| (\hbar \omega)^2 - \epsilon_0^2 \right|^{1/2} \right)$ 

whatever choice of  $\epsilon_0$  is made. This is shown in Fig. 2. If we try to fit the initial slope  $(dG/dV)_V = 0$  we cannot fit the position of the maximum and vice versa.

On the other hand, G(V) is correctly described by (II.5) as shown in Fig. 3.

(3) The temperature variation of the characteristic time  $\tau$  can be obtained from a study of  $V_{\text{max}}$  as a function of T. The theoretical curve  $V_{\text{max}}(T)$  as deduced from Eq. (II.5) is shown on Fig. 1. Note first that for  $T \rightarrow 0$ 

$$eV_{\rm max} \rightarrow (\hbar/2\tau(T=0)) = \frac{1}{2} (\epsilon_0)_{\rm BCS} = (3.5/4)kT_0.$$

But for nonzero T,  $V_{\text{max}}$  and  $(1/\tau)$  behave differently:  $V_{\text{max}}$  increases while  $(1/\tau)$  decreases. Our experimental results on tin alloys are also shown on Fig. 1. The relatively wide error bars are due to the difficulty of locating a maximum. Still, we may conclude that the agreement is rather good (there is no adjustable scale factor in this comparison). These results, together with the measurements of  $H_{c2}(T)$  quoted in Sec. III give a direct verification of the fundamental laws (I.1) and (I.2) over the whole temperature range.

For the lead base alloys (Fig. 4), the situation is more complicated. Again properties (1) and (2) are well verified, but the experimental (tunneling) and theoretical values of  $(1/\tau)$  at T=1.4°K differ by a factor of 40%. This may be due to strong coupling effects which are known to be important for lead.

(4) Effect of the field on the amplitude of G(V). To verify quantitatively the  $\Delta^2$  dependence on field calculated in (II.20) and (II.22), we evaluated the coefficients in these formulas only from resistivity measurements in the normal state and from the determination of the Landau-Ginsburg parameter  $\kappa$  at  $T_e$  already de-

<sup>&</sup>lt;sup>15</sup> Y. Goldstein, LT 9 Proceedings of the Low Temperature Conference, Columbus, Ohio, 1964 (unpublished).

scribed. We have used Eq. (II.8) relating the Landau-Ginsburg  $\psi$  to the order parameter  $\Delta$  involving the experimental resistivity rather than Gorkov's expression for free electrons. A use of the latter expression would give serious discrepancies with the experimental results.

Then, taking into account the theoretical variation of  $\kappa_2$  given by Maki, in Fig. 5 we plot the value of the maximum of G(V) as a function of  $\Delta H = H - H_{\rm er}$  in the two cases of parallel and perpendicular geometry. We can verify first the following *qualitative* features:

(1) All the points for a given sample orientation, and temperature fit on a straight line in high field.

(2) The ratio of the slope between the perpendicular and parallel orientation for the same sample increases when the temperature decreases. As

$$\frac{G_{\rm L}(V_{\rm max})}{G_{\rm H}(V_{\rm max})} \simeq \frac{\kappa_2^2 - 0.17}{\kappa_2^2 - 0.5}$$

this is a proof of the decrease of  $\kappa_2$  when the temperature decreases as predicted by Maki.

(3) For different samples at a given temperature corresponding to an increasing Ginsburg-Landau parameter from sample 3 to sample 1 (i.e., to a decreasing resistivity ratio), the parallel slope is much less affected than the perpendicular one which decreases quite rapidly due to the rapid variation of  $(1/\kappa_2^2 - 0.5)$  when  $\kappa_2 \sim 1/\sqrt{2}$ .

Quantitatively, we can say that the agreement is good provided the  $\kappa_2$  is known very precisely. In Fig. 5 we



FIG. 4. G(V) for *Pb*Bi alloys, again normalized to the maximum. The discrepancy is probably associated with strong coupling effects and phonon-assisted tunneling.



FIG. 5. (a) The amplitude of G(V) as a function of field in Sn In at  $T=2.4^{\circ}K$  in both parallel and perpendicular fields. The dashed and continuous lines represent the theory for parallel and perpendicular fields, respectively. The given  $\kappa$  was determined from critical-field measurement. (b) The corresponding amplitudes at 1.4°K. The two dashed (or straight) lines represent the two  $\kappa_2$ 's deduced from the application of Maki's theory to the extreme admissible value of  $\kappa_2$ . Note that the perpendicular-field results are more sensitive to slight differences in  $\kappa$  than the parallel field results at low  $\kappa$  ( $\kappa \sim 1$ ) in agreement with theory.

find very good agreement at 2.4°K, where  $\kappa_2$  is not very different from the experimental  $\kappa$ . At lower temperature, the agreement is not so good and we have plotted the two theoretical curves corresponding to the possible limit between which our results fit.  $\kappa_2 = 0.9$  would correspond for sample 3 to the value deduced from Maki's formula using  $\kappa_2$   $(T=2.4^{\circ}\text{K})=0.98$ .

To conclude, the main difficulty with the tin alloys is that the  $\kappa$  values are low: factors such as  $(1/\kappa_2^2-0.5)$ are then extremely sensitive to our choice of  $\kappa_2$ ; furthermore our theoretical formulas for perpendicular fields neglect the expansion of flux lines near the surface; this may bring in serious corrections when  $\kappa \sim 1/\sqrt{2}$ .

It is thus not surprising to find that in the *PbBi* alloys (where  $\kappa \gg 1/\sqrt{2}$ ) the agreement between theory and experiment on that particular problem of  $\langle |\Delta|^2 \rangle$  is more satisfactory. In particular, we measure a ratio  $(G_1(V_{\max})/G_{11}(V_{\max})) \simeq 1$  as we expect from the above formula when  $\kappa \gg 1$ .

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