ture may occur from a cluster of critical points in the energy region near  $\Gamma$ . For the energy bands of GaAs, the cluster consists of

$$M_0$$
 at  $k_0 = (0.25, 0, 0)$  and 4.08 eV,

 $M_1$  at  $k_1 = (0.2, 0.2, 0)$  and 4.21 eV.

It therefore seems possible that the small peak  $E_{Cp}$  seen in this work results from such a cluster of critical points in this energy region. Extrapolation of the  $E_{Cp}$  transition to GaP gives an energy of 3.5 eV, and if such clustering occurs in GaP, one would expect to find evidence of it at approximately this energy. It is possible that the  $E_{Cp}$  transition in GaP, as well as the  $E_0' + \Delta_0$  peaks in both GaAs and GaP, could be found by means of the newer techniques reported recently, such as field effects in the reflectivity<sup>15,16</sup> and piezoreflectivity.<sup>17,18</sup>

The authors wish to thank Dr. T. E. Fischer<sup>14</sup> of Bell Telephone Laboratories, and Dr. E. W. Williams<sup>19</sup> of Texas Instruments for useful discussions and information on their unpublished data, and Dr. Forrest Williams of Monsanto for the epitaxial samples. (Dunod, Paris, 1964).

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## GEOMETRICAL RESONANCE IN THE TUNNELING CHARACTERISTICS OF SUPERCONDUCTING Pbt

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Film diodes of the form Al-AlO<sub>X</sub>-Pb have been investigated extensively in the past.<sup>1</sup> Highsensitivity measurements have, however, invariably involved Pb films only a few thousand angstroms thick. This Letter describes a damped oscillation in  $d^2V/dI^2$  which is periodic in V and which is observed only in much thicker Pb films (Pb and Al both superconducting). Over the range covered (2.9-9.7  $\mu$ ) the voltage period  $h\nu$  was found to vary inversely with Pb thickness d(Pb). This effect is not to be confused with previously reported phonon phenomena<sup>2</sup> which were also very prominent in the present measurements but which are insensitive to film thickness.

Relatively high-impedance diodes (10-100

 $\Omega$  for 0.01-cm<sup>2</sup> junctions) were prepared by standard methods.<sup>3</sup> Thin Al films (~300 Å) were commonly utilized so that magnetic field effects could be studied with both Pb and Al superconducting. Diode pairs fabricated simultaneously were compared to investigate the influence of planar junction dimensions and barrier thickness. The latter could be varied by storing one Al film in argon during part of the air-exposure period. Conventional modulation techniques were employed to measure dV/dI and  $d^2V/dI^2$ .

Figure 1 presents plots of dV/dI and  $d^2V/dI^2$ over the range in which oscillations were observed for a Pb film 4.3  $\mu$  thick. Peaks in  $d^2V/dI^2$  have been indexed by integers  $\eta$  with  $\eta = 1$ 

<sup>&</sup>lt;sup>1</sup>M. Cardona, in <u>Proceedings of the International Con-</u> ference on the Physics of Semiconductors, Paris, 1964



FIG. 1. Voltage dependence of dV/dI and  $d^2V/dI^2$ for an Al-AlO<sub>X</sub>-Pb tunnel diode. Modulation levels were 10  $\mu V$  (rms) and 50  $\mu V$  (rms), respectively. Integers  $\eta$  index peaks in  $d^2V/dI^2$  with  $\eta = 1$  corresponding to the first peak of the series. Voltages  $V_{\eta}$  denote points of maximum negative slope in  $d^2V/dI^2$  and correspond to local maxima in dI/dV. These are relatively weak, as can be seen from the plot of dV/dI.

corresponding to the first and strongest peak. Although the effect in dV/dI is rather weak, structure corresponding to  $\eta = 5$  could be detected in the original data. Under conditions of the experiment, points of maximum negative slope in  $d^2V/dI^2$  correspond to local maxima in dI/dV and are labeled  $V_{\eta}$ . A plot of  $V_{\eta}(\eta)$ yields a straight line. The half-sum of the energy gaps,  $\delta = \langle \Delta(Pb) \rangle + \Delta(Al)$ ,<sup>4</sup> was determined from an independent dV/dI measurement. Figure 1 indicates that  $V_{\eta}(\eta)$  has an intercept  $V_0$ quite near  $\delta$ , so that  $V_{\eta}$  can be described by

$$e(V_{\eta}-\delta) = \eta h \nu. \tag{1}$$

A plot of  $h\nu$  vs 1/d (Fig. 2) yields a straight line which extrapolates to zero.

The following factors have no significant effect on  $h\nu$ : (1) polarity of V; (2) planar dimensions of the junction; (3) thickness of the barrier region (as indicated by resistance measurements); and (4) thickness of the Al film (300-1500 Å). Application of a longitudinal magnetic



FIG. 2. Variations of oscillation period  $h\nu$  with inverse Pb film thickness. Interpretation of these data in terms of standing wave modes of wavelength d(Pb) yields a velocity  $\nu$  which is comparable to the Fermi velocity  $u_{\rm F}$ . [A conceivable indexing problem for two diodes could result in  $h\nu$  being ambiguous by a factor of two. The lower values (solid circles) yield a smooth curve and have been selected as the more plausible alternatives.]

field equal to 90% of the bulk critical field (1.1°K) does not affect  $h\nu$  or cause appreciable peak broadening. No structure is observed when the Pb has been driven entirely normal. Warming from 1.1 to 1.35°K causes severe structural smearing, and the attendant experimental uncertainty could mask a modest  $h\nu$  temperature dependence. No structure of the type under consideration is observed at 1.4°K (Al normal). A film 5.7  $\mu$  thick and containing 5 at.% Tl does not exhibit structure at 1.06°K. Diodes examined directly after preparation often exhibit only traces of structure. After several days annealing at room temperature (in vacuum), pronounced structural enhancement is observed.

For many purposes, it is fruitful to associate dI/dV with the effective tunneling density of states  $N_{\circ}$  Equation (1) then suggests additional contributions to N(Pb) at regular intervals  $h\nu$  from the gap edge. Such a result would be anticipated if the tunneling electrons were coupled to a reasonably monochromatic energy reservoir, as in the Dayem-Martin (DM) experiment<sup>5</sup> (tunnel diode inside a driven micro-

wave cavity). One must, in fact, demonstrate that the present effects do not stem from a cavity resonance in the dielectric barrier. That they do not can be seen from the insensitivity of  $h\nu$  to changes in junction planar dimensions and barrier thickness.<sup>6</sup> Furthermore,  $h\nu$  should not depend on d(Pb) because of the great thickness of the Pb films.<sup>6</sup> An important departure from the DM type of result is that no transitions corresponding to quantum absorption are observed in the present experiment. This is because the driven cavity can easily supply quanta for absorption, whereas the reservoir to be proposed can probably only supply quanta by thermal excitation which is weak at 1.1°K. Although a consistent interpretation of the present data results from a simple quasiparticle tunneling picture, it is not as yet possible to rule out alternative mechanisms. It seems plausible, however, that the physically important quantity  $h\nu$  (a characteristic of the Pb film) should be independent of the tunneling "interrogation" mechanism.

The linear relationship between  $h\nu$  and 1/d, together with Eq. (1), strongly suggests that the Pb films exhibit geometrical resonances (standing wave modes), and that these serve as monochromatic (or harmonic) reservoirs to which tunneling electrons may lose energy. This fits in well with observed annealing and alloying effects since short mean free paths should damp the resonance.<sup>7</sup> If one assumes a wavelength  $\lambda$  equal to d(Pb), the data of Fig. 2 yield a velocity ( $v = 3.75 \times 10^7$  cm/sec), which is comparable to the Fermi velocity<sup>8</sup> ( $u_{\rm F} = 5.0$  $\times 10^7$  cm/sec) and appreciably greater than the velocity of sound ( $\sim 2 \times 10^5$  cm/sec). This suggests that the phenomenon is basically electronic in nature. It would also appear that collective excitations are important in view of the long wavelengths required.<sup>9</sup> Temperature and magnetic effects do not conflict with this interpretation. The former are simply attributed to the reduction of  $\Delta(Al)$  with rising temperature. Diamagnetic shielding probably insures a small magnetic effect on  $h\nu$  since field penetration can at best alter surface boundary conditions.10

Bogoliubov<sup>11</sup> and Anderson<sup>12</sup> (BA) have proposed an acoustic collective mode which physically corresponds to a long-wavelength density modulation of the pair gas and which is associated with a velocity  $u \approx (u_F/\sqrt{3}) \approx 2.9 \times 10^7$  cm/sec. Unfortunately, inclusion of the long-range

Coulomb interaction appears to convert the BA mode into a plasma mode of very high energy.<sup>12</sup> There does seem to be some agreement, however, that low-lying modes should exist.<sup>13</sup> It is believed that the present data generally support the view that low-energy collective modes exist in Pb.

The author is indebted to T. Wolfram for valuable discussions, and to R. R. Hargrove for preparing the diodes.

<sup>4</sup>Thick Pb films appear to exhibit two sharp energy gaps  $\Delta_2 > \Delta_1$ . Since the peak widths of Fig. 1 exceed  $\Delta_2 - \Delta_1$ , use of an average gap  $\langle \Delta(Pb) \rangle$  is justified. In several instances, however, peak widths were less than  $\Delta_2 - \Delta_1$  and two series of peaks were observed, one much stronger and better resolved than the other. Both yielded the same value of  $h\nu$  and had intercepts  $V_0$  quite near  $V = \langle \Delta(Pb) \rangle + \Delta(Al)$ .

<sup>5</sup>A. H. Dayem and R. J. Martin, Phys. Rev. Letters <u>8</u>, 246 (1962); P. K. Tien and J. P. Gordon, Phys. Rev. <u>129</u>, 647 (1963); M. H. Cohen, L. M. Falicov, and J. C. Phillips, in <u>Proceedings of the Eighth Inter-</u> <u>national Conference on Low-Temperature Physics,</u> <u>London, 1962</u>, edited by R. O. Davies (Butterworths Scientific Publications, Ltd., London, 1962), p. 178. The present effect (Fig. 1) is much weaker than that observed by Dayem and Martin.

<sup>6</sup>J. C. Swihart, J. Appl. Phys. 32, 105 (1961).

<sup>7</sup>Because of the long wavelength involved, the mean free path is most likely determined by extended defects (dislocations, etc.). These are probably stabilized by pinning in the alloy. For thinner Pb films (shorter wavelengths), localized defects should contribute to scattering. This probably accounts for the absence of oscillations in thinner Pb films, even though  $h\nu < 2\Delta_1$ (Pb).

<sup>8</sup>J. Bardeen and J. R. Schrieffer, in <u>Progress in</u> <u>Low Temperature Physics</u>, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1961), Vol. III, Chap. VI, p. 243.

<sup>9</sup>The linear form of the dispersion relationship (Fig. 2) probably also implies that bosons (condensed

<sup>†</sup>Based on work sponsored by the Division of Research, Metallurgy and Materials Programs, U. S. Atomic Energy Commission, under Contract No. AT-(11-1)-GEN-8.

<sup>&</sup>lt;sup>1</sup>Space limitations preclude presentation of a comprehensive bibliography. A partial bibliography may be found elsewhere [W. J. Tomasch, Phys. Rev. <u>139</u>, A746 (1965)].

<sup>&</sup>lt;sup>2</sup>I. Giaever, H. R. Hart, Jr., and K. Megerle, Phys. Rev. <u>126</u>, 941 (1962); J. M. Rowell, A. G. Chynoweth, and J. C. Phillips, Phys. Rev. Letters <u>9</u>, 59 (1962); J. M. Rowell, P. W. Anderson, and D. E. Thomas, Phys. Rev. Letters <u>10</u>, 334 (1963); J. M. Rowell and L. Kopf, Phys. Rev. <u>137</u>, A907 (1965).

<sup>&</sup>lt;sup>3</sup>I. Giaever and K. Megerle, Phys. Rev. <u>122</u>, 110 (1961).

pairs) are involved.

<sup>10</sup>It may be interesting to study Pb films having a thin normal-metal overlay.

<sup>11</sup>N. N. Bogoliubov, V. V. Tolmachov, and D. V. Sirkov, in <u>Theory of Superconductivity</u>, edited by

N. N. Bogoliubov (Gordon and Breach Publishers, Inc., New York, 1962), p. 278. <sup>12</sup>P. W. Anderson, Phys. Rev. <u>112</u>, 1900 (1958). <sup>13</sup>J. M. Blatt, <u>Theory of Superconductivity</u> (Academic

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## GAPLESS SUPERCONDUCTIVITY INDUCED BY METALLIC CONTACTS\*

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Numerous experiments<sup>1</sup> performed over the last few years show that superposition of normal and superconducting metal films can alter the superconducting properties of the films which are in contact. So it was shown that the transition temperature  $T_c$  of such a system depends on the thickness  $D_s$  and  $D_n$  of the superconducting and normal film, respectively, and theoretical investigations by de Gennes and Guyon<sup>2</sup> and Werthamer<sup>3</sup> are in good quantitative agreement with experiments. We are here primarily concerned with another sort of experiment with such contacts, as performed by Reif and Woolf,<sup>4</sup> in which the tunneling density of states of a superconducting film backed by a paramagnetic film is measured.

In order to get a theoretical understanding of such a situation, we first determine the tunneling density of states for a superconducting film in contact with a nonmagnetic normal film assuming that the mean free path in the metals is small compared with the coherence distance. Our calculations, which are done in the vicinity of the second-order phase transition point where the order parameter is small, show that the tunneling density of states of such a contact is similar to the one found for superconductors containing paramagnetic impurities.<sup>5</sup> This reveals that the essential influence of a metallic contact on superconductivity is a tendency to break electron pairs. We should like to point out that we have here, quite unexpectedly, an example of gapless superconductivity which

is not caused by an interaction which breaks time-reversal symmetry. In fact, even for large order parameters where our expressions do not hold, we expect a tunneling characteristic similar to the one for superconductors with paramagnetic impurities. Interesting experiments-for example, tunneling measurements-to prove this point are suggested. Second, our calculations are extended to the case of contacts between superconducting films and paramagnetic metals. No qualitative difference arises in that case, but quantitatively paramagnetic metals exert an order of magnitude larger pair-breaking effect upon the superconducting electrons as compared with nonmagnetic normal metals.

We express the tunneling density of states  $N(\mathbf{\tilde{r}}, \omega)$  in terms of the Green's function  $G(\mathbf{\tilde{r}}_1 \mathbf{\tilde{r}}_2, \omega)$  as

$$N(\mathbf{\tilde{r}},\omega) = (1/\pi) \operatorname{Im} G(\mathbf{\tilde{r}},\mathbf{\tilde{r}},\omega), \qquad (1)$$

where  $G(\mathbf{\tilde{r}}, \mathbf{\tilde{r}}', \omega)$  formally can be written up to terms of second order in the order parameter  $\Delta(\mathbf{\tilde{r}})$  as

$$G = \{G_0\}_{rs} + \{G_0 \Delta G_0^{-} \Delta^+ G_0\}_{rs}$$

Here  $G_0$  is the Green's function for a normal metal, and  $\{\cdot \cdot \cdot \}_{\gamma S}$  indicates that an average over randomly distributed scattering centers has to be taken. This averaging process can be carried out by using a renormalization procedure developed by one of the authors (K.M.).<sup>6</sup> We find

$$G(\mathbf{\tilde{r}},\mathbf{\tilde{r}}',\omega) = \int \frac{d^{3}p}{(2\pi)^{3}} \frac{e^{i\mathbf{\tilde{p}}(\mathbf{\tilde{r}}-\mathbf{\tilde{r}}')}}{\tilde{\omega}-\xi_{\mathbf{\tilde{p}}}} - \int \frac{d^{3}p}{(2\pi)^{3}} d^{3}r_{1}r_{2}\frac{e^{i\mathbf{\tilde{p}}(\mathbf{\tilde{r}}-\mathbf{\tilde{r}}_{1})}}{\tilde{\omega}-\xi_{\mathbf{\tilde{p}}}} \times \eta_{\mathbf{\tilde{q}}_{1}}\Delta(\mathbf{\tilde{r}}_{1})\frac{e^{i(\mathbf{\tilde{p}}+\mathbf{\tilde{q}}_{1})(\mathbf{\tilde{r}}_{1}-\mathbf{\tilde{r}}_{2})}}{\tilde{\omega}+\xi_{\mathbf{\tilde{p}}+\mathbf{\tilde{q}}_{1}}}\eta_{\mathbf{\tilde{q}}_{2}}\Delta^{+}(\mathbf{\tilde{r}}_{2})\frac{e^{i(\mathbf{\tilde{p}}+\mathbf{\tilde{q}}_{1}-\mathbf{\tilde{q}}_{2})(\mathbf{\tilde{r}}_{2}-\mathbf{\tilde{r}}')}}{\tilde{\omega}-\xi_{\mathbf{\tilde{p}}}+\mathbf{\tilde{q}}_{1}-\mathbf{\tilde{q}}_{2}}},$$
(2)