Tunneling Measurements of Phonon Spectra and Density of States in Superconductors

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Using the technique of electron tunneling between superconducting films, we have measured the density-of-states variation with energy in a number of soft superconductors. In lead we show that the density-of-states variation suggests the form of the phonon spectrum which is effective in the coupling of the Cooper pairs. The spectrum has transverse and longitudinal peaks located at 4.4 and 8.5 meV, respectively. A solution of the Eliashberg gap equation using this phonon spectrum and reasonable values for coupling constants gives good agreement between theoretical and experimental density-of-states plots, as shown by Schrieffer *et al.* In addition to the density-of-states variation due to the two main peaks in phonon density, we resolve fine structure which is the effect of the Van Hove critical points in the phonon spectrum. Reasonable agreement is found between the energy and type of structure observed in the density-of-states variation and the occurrence of critical points in the dispersion curves obtained by neutron scattering. From similar experiments we suggest that the tin phonon spectrum extends to 17.7 meV with critical points as low as 3.4 meV. In indium the end of the spectrum appears to be 14.8 meV with a transverse peak between 3 and 7 meV and a longitudinal peak from 11 to 14 meV.

INTRODUCTION

THE existence of an attractive interaction between electrons in a metal in the superconducting state is regarded as basic to an understanding of the phenomenon of superconductivity. Cooper[1] showed that when the attraction overcomes the Coulomb repulsion between the electrons a net attractive interaction exists and the electrons then form bound pairs with an energy below the ground state of the single electrons. From the existence of these "Cooper pairs," Bardeen, Cooper, and Schrieffer[2] (BCS) developed their very successful theory of superconductivity.

The attraction between the electrons arises from interactions between the electrons and phonons. This attraction has been discussed by Fröhlich[3] and by Bardeen[4] and the role of the lattice vibrations is experimentally confirmed by the observation[5] of the isotope effect, the dependence of transition temperature on (isotope mass)$^{-1/2}$ for many superconductors.

The description of the electron-phonon interaction developed somewhat slowly. The form used by BCS was that of Bardeen and Pines,[6] a perturbation-theoretical approximation which is adequate for many purposes; but it turns out that the more complete field-theoretical approach of Eliashberg,[7] taking into account retardation and damping effects and not using the quasiparticle assumption, is essential for detailed application to superconductivity. However, the BCS theory, which takes account of the electron-phonon interaction only through the critical temperature T_c, was so successful in describing most of the available experimental data that it seemed unnecessary to extend the description of the interaction to include any details of the actual phonon spectrum of individual superconductors. Indeed no aspect of the superconducting state appeared to contain detailed information about the electron-phonon interaction susceptible to experimental investigation, although critical field curves[8] did indicate that lead and mercury in particular do display some individuality which could arise from an unusually strong electron-phonon interaction.

The discovery of the electron-tunneling technique in 1961 by Giaever[9] introduced an exceptionally powerful tool with which to examine the properties of superconductors. In particular one can measure directly the density-of-states variation with energy in a superconductor with a precision and detail which is apparently only limited by one's experimental techniques, or by noise. Giaever *et al.*[10] obtained density-of-states measurements for Sn, In, Al, and Pb, and showed that the variation with energy was close to that of BCS but with noticeable deviations in the case of Pb. The wealth of data contained in the density-of-states variation can be realized by examining the integral equation for the energy-gap parameter $\Delta(E)$ which is

$$\Delta(E)=\frac{dn}{d\epsilon}\int_{\Delta_0}^{\infty}dE'V(E-E')\,\mathrm{Re}\left[\frac{\Delta(E')}{[E'^2-\Delta^2(E')]^{1/2}}\right], \quad (1)$$

where E is the actual quasiparticle energy, Δ_0 is the value of the gap parameter at the energy gap. The interaction between the electrons, both Coulomb repulsion and phonon attraction, is described in $V(E-E')$ which contains the appropriate phonon spectrum effective in the coupling.

[1] L. N. Cooper, Phys. Rev. **104**, 1189 (1956).
[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[3] H. Fröhlich, Phys. Rev. **79**, 845 (1950), Proc. Roy. Soc. (London) **A215**, 291 (1952).
[4] J. Bardeen, Phys. Rev. **80**, 567 (1950).
[5] E. Maxwell, Phys. Rev. **78**, 477 (1950). C. A. Reynolds, B. Serin, W. H. Wright, and L. B. Nesbitt, *ibid.* **78**, 487 (1950).
[6] J. Bardeen and D. Pines, Phys. Rev. **99**, 1104 (1955).
[7] G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **38**, 966 (1960) [English transl.: Soviet Phys.—JETP **11**, 696 (1960)].
[8] D. K. Finnemore, D. E. Mapother and R. W. Shaw, Phys. Rev. **118**, 127 (1960).
[9] I. Giaever, Phys. Rev. Letters **5**, 147 (1960).
[10] I. Giaever, H. R. Hart, and K. Mergerle, Phys. Rev. **126**, 941 (1962).

The variation in density of states (ρ_s) with energy in a superconductor is obtained experimentally by a tunneling experiment and is related to the gap parameter by the expression given by Schrieffer *et al.*[11]:

$$\rho_s(E)=\rho_n \operatorname{Re}\left(\frac{E}{[E^2-\Delta^2(E)]^{1/2}}\right), \qquad (2)$$

where ρ_n is the density of states in the normal metal. For a gap parameter independent of energy, this reduces to $\rho_s(E)=\rho_n E/(E^2-\Delta^2)^{1/2}$ which is the BCS expression for the density-of-states variation. (This is plotted as curve 1 in Fig. 4.)

The relationships (1) and (2) above show that from a tunneling measurement of $\rho_s(E)/\rho_n$ one can study the phonon spectrum involved in the interaction $V(E-E')$ if the solution of the gap equation is carried out to obtain $\Delta(E)$ from $V(E-E')$. Alternatively, if the phonon spectrum is known, a measurement of $\rho_s(E)$ allows careful investigation of the interaction $V(E-E')$ and the form of the gap equation.

We describe first experimental techniques used in preparing the tunnel junctions and in measuring their current versus voltage (I versus V) and derivative (dI/dV versus V, d^2I/dV^2 versus V) characteristics. We next show how in the case of lead the density of states versus energy variation measured experimentally agrees well with that found from a solution of the gap equation using a reasonable model for the phonon spectrum. A further refinement of experimental technique allows observation of fine structure in density-of-states, and the evidence relating this to Van Hove critical points in the phonon spectrum of lead is presented. Harmonics of the phonon peaks, rather than the critical points, are shown to extend to quite high energies. We discuss in less detail similar measurements for Sn and In and are able to predict some characteristics of the phonon spectra.

EXPERIMENTAL

The preparation of the tunnel units follows the techniques outlined by Giaever.[10] An Al-I-Pb unit is shown as an example in Fig. 1. (In this paper we will use A-I-B to describe a tunnel junction formed by evaporation of metal A first, oxidation to form insulator I and evaporation of metal B last. We consider the designation of the insulator as I to be more realistic than specification of oxide composition as the layer may be mostly adsorbed gas in some cases. M will be used to indicate a metal which is normal at the temperature of measurement, S to indicate a superconductor.) The aluminum film is evaporated onto a sapphire or glass substrate at a pressure of about 10^{-6} Torr. and is approximately 2000 Å thick. The insulating layer is aluminum oxide grown by exposure of the film at room temperature to air for one or two minutes. The crossing lead films are also 2000 Å thick, evaporated at 10^{-7}–10^{-6} Torr. Electrical contact to the films is made using 0.0002-in.-thick aluminum foil leads attached with silver paste, both ends of all films being used to give a four-terminal connection to each junction. The mounted sample is immersed in liquid helium which can be pumped to 1.3°K.

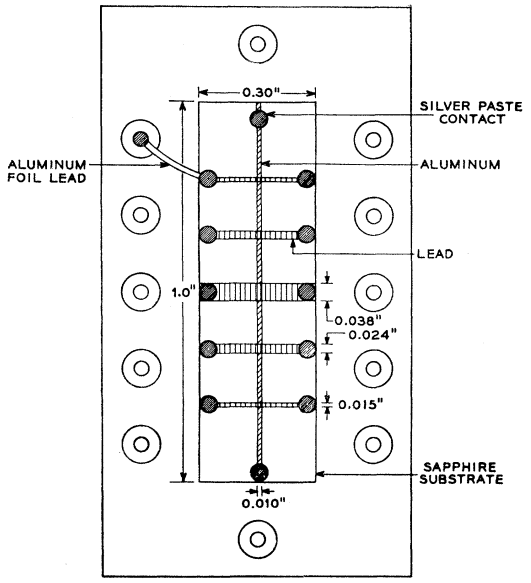

FIG. 1. A typical layout of Al and Pb films to form five Al-I-Pb junctions.

In order to prepare samples of Pb-I-Pb or Sn-I-Sn, the oxidation of the first film is hastened by placing the sample on a small hot plate at ~50°C in a stream of dry oxygen for 5–30 min. For Pb-I-Pb samples this method consistently yields very uniform low-resistance junctions (<0.1 Ω-mm²) which exhibit large Josephson currents. However, the junction resistance can be increased by reduction of the film widths and hence, the junction area. Recent junctions have dimensions 0.002 in.×0.002 in.

The current (I) versus voltage (V) characteristics are taken on an X-Y recorder and the junctions with suitable resistance (10–100 Ω) selected for differentiation. The dI/dV versus V curves are obtained as a continuous X-Y recorder trace using a self-balancing bridge network described by Thomas and Klein.[12] This apparatus has the advantage of plotting directly dI/dV (dV/dI is generally obtained) but the disadvantage of a rather large ac sensing signal (~½ mV peak-to-peak). The dc voltage can vary slowly in this case and an example of performance is given by Thomas and Klein for an Al-I-Pb junction.

The second differential curves, d^2I/dV^2 versus V, can also be obtained with this apparatus, but the second derivative signal is proportional to the rate of dc bias

[11] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters **10**, 336 (1963).

[12] D. E. Thomas and J. M. Klein, Rev. Sci. Inst. **34**, 920 (1963).

sweep and for high sensitivity a loss of resolution results. Recently harmonic detection[13] has been used with vastly improved resolution and with sensitivity equal to that of the bridge network. A 500-cps signal is fed to the sample and the 1000-cps harmonic detected with a lock-in amplifier. The amplitude of this harmonic signal is proportional to d^2I/dV^2 (except when dI/dV varies very rapidly) and this signal is traced on an X-Y recorder against a dc voltage being swept very slowly across the sample. The dc voltage is typically swept at the rate of 1 mV/min. Traces are usually taken for both biases in order to check the symmetry of the I-V plot and to give more accurate location of structure. Small difficulties in reproducibility of the traces (≤ 0.05 mV) probably arise from thermal emfs generated in the leads to the sample.

In order to resolve the very fine structure in the d^2I/dV^2 versus V plot the amplitude of the 500-cps signal is generally kept of the order of kT. Structure much narrower than this signal is resolved, but its shape may be somewhat smeared.

THE DIFFERENTIAL CURVES

It was realized by Giaever[9] that the current-voltage characteristic for tunneling between a metal and superconductor through a thin insulating layer (M-I-S junction) could be elegantly explained in terms of the single-particle density of states versus energy diagrams shown at the top of Fig. 2. He assumed that the tunneling probability for a particle depends directly on the density-of-states at its initial and final state and that the tunneling transition probability is not bias-dependent over the small bias ranges of interest. Study of the diagrams then leads directly to the general shape of the current-voltage characteristics shown below them.

At a temperature of 1.3°K the gap characteristic of the Al-I-Pb junction is smeared because of the singularity in the lead density-of-states moving against a thermally smeared Fermi edge in the aluminum. The form of the Pb-I-Pb characteristic is much sharper as thermal excitation across the gap ($\sim$20 kT) is small and two singularities move against each other. However, the rise in current at a bias 2Δ(2.75 mV) is not discontinuous as might be expected if the gaps were uniform over the junction area. Possibly this variation in gap is due to strain induced by differential contractions of films and substrates. The width of the rise in our Pb-I-Pb junctions is typically 0.15 mV from 10 to 90% of the current jump. We believe that even more striking differential curves could be obtained if this slight nonuniformity in the gap were eliminated.

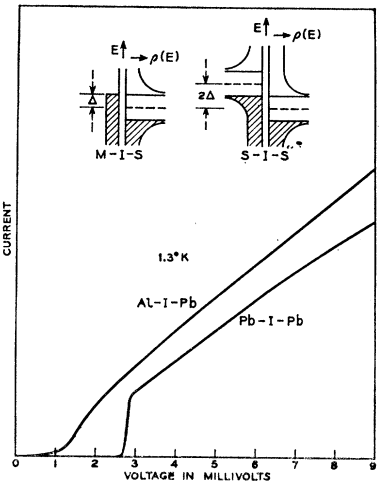

FIG. 2. The density of states versus energy diagrams for M-I-S and S-I-S tunnel junctions. The current-voltage characteristics are for an Al-I-Pb and a Pb-I-Pb junction at 1.3°K.

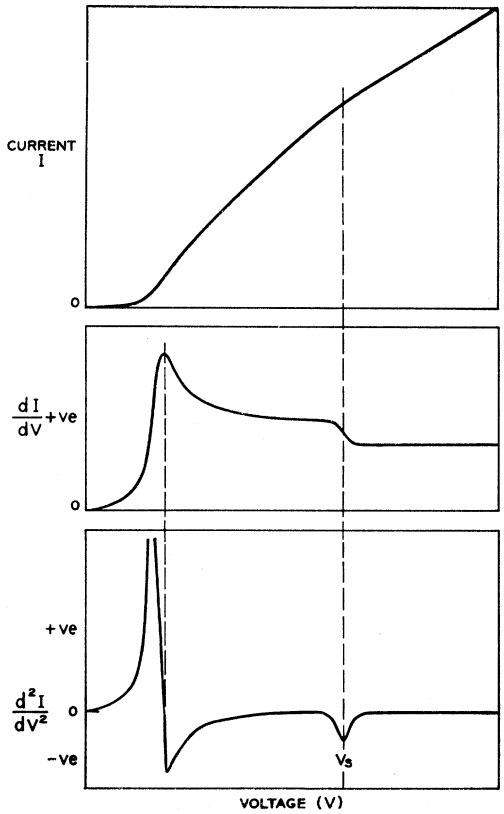

FIG. 3. The current-voltage (I versus V) characteristic for a M-I-S tunnel junction with corresponding first (dI/dV) and second derivative (d^2I/dV^2) plots. The effect of a drop in density of states at an energy greater than the gap is shown.

For a M-I-S junction, the dI/dV versus V plot represents closely the density-of-states variation with energy in the superconductor. As shown in Fig. 3, there is considerable thermal smearing of the singularity at $E=\Delta$ unless measurements are made at much lower temperatures than 1.3°K, as reported by Giaever *et al.*[10] But if, for example, there is a step in the density of states at some energy greater than the gap (represented diagrammatically in Fig. 3), then at a voltage V_s corresponding to this energy the I versus V characteristic changes slope, the dI/dV versus V plot has a step, and the d^2I/dV^2 versus V plot exhibits a relatively sharp

[13] D. E. Thomas (to be published).

negative peak. In this way, second derivative curves can be used to locate structure which cannot be observed in either I versus V or dI/dV versus V plots.

DENSITY OF STATES IN LEAD— THE PHONON SPECTRUM

A number of solutions of the gap equation have been obtained recently which yield an energy-dependent gap parameter $\Delta(E)$ and hence a density-of-states versus energy variation different from that of BCS. Swihart[14] considered the Bardeen-Pines,[6] Bogoliubov,[15] and Eliashberg[7] interactions with both Debye and Einstein phonon spectrums. Culler *et al.*[16] derived a solution of the Eliashberg gap equation using a Debye phonon spectrum and plotted the density-of-states variation for this case. In general these solutions showed that structure should occur in the density of states versus energy variation at energies approximately $\Delta+E_D$ and $\Delta+E_E$ for the Debye and Einstein spectrums, respectively, E_D being the Debye cutoff and E_E the energy of the Einstein peak. Morel and Anderson,[17] in their solution of the gap equation using a retarded interaction, found that for the Eliashberg gap equation and a single Einstein phonon peak, density-of-states structure should be observed not only at $\Delta+E_E$ but at $\Delta+2E_E$, $\Delta+3E_E$, $\cdots$, etc.

As mentioned above, tunneling measurements of the density-of-states variation in Sn, In, and Al by Giaever *et al.*[10] gave good agreement between experimental results and the BCS plot. In the case of Pb, however, small deviations from this plot were observed. With a more sensitive experimental technique, we have observed these deviations in detail and the density of states variation with energy in Pb is shown in Fig. 4, curve 2. The striking features are the two relatively sharp drops in density of states below the BCS value (curve 1) which are followed by smeared "humps" as the density of states approaches its value for the normal metal. Consideration of this behavior, in the light of the solutions of the gap equation mentioned above, leads to the conclusion that the phonon spectrum of lead effective in the electron interaction may be roughly approximated by two Lorentzian peaks located at 4.4 and 8.5 mV. It should be borne in mind that the interaction $V(E-E')$ is weighted by a coupling constant which is very small for long-wavelength phonons, so that the main concern is with the distribution of short-wavelength phonons. The locations 4.4 and 8.5 mV are in the centers of the two drops in density of states, and an estimate of the widths of the phonon peaks is made from the widths of the drops. Thus the widths taken for the transverse and

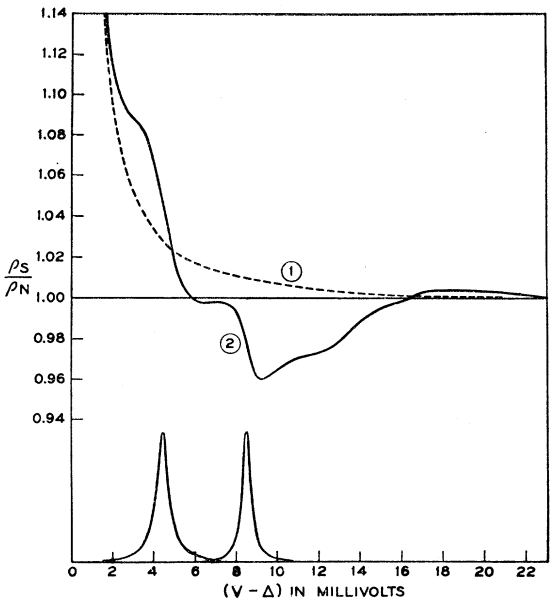

FIG. 4. The variation with energy of the ratio of density of states in superconducting lead to that in the normal metal. Curve 1 is the BCS plot, curve 2 the tunneling measurement. Also shown is the phonon spectrum suggested by the experimental density-of-states plot.

longitudinal peaks (assumed Lorentzian) are 0.75 and 0.5 mV, respectively, as shown at the bottom of Fig. 4. The broader "humps" in density-of-states at energies greater than 9 meV are attributed to sum and harmonic structure of the two fundamental phonon peaks. A phonon spectrum of the form shown in Fig. 4 was used by Schrieffer *et al.*[11] in a detailed solution of the gap equation. The phonon density of states $F(\omega)$ used is

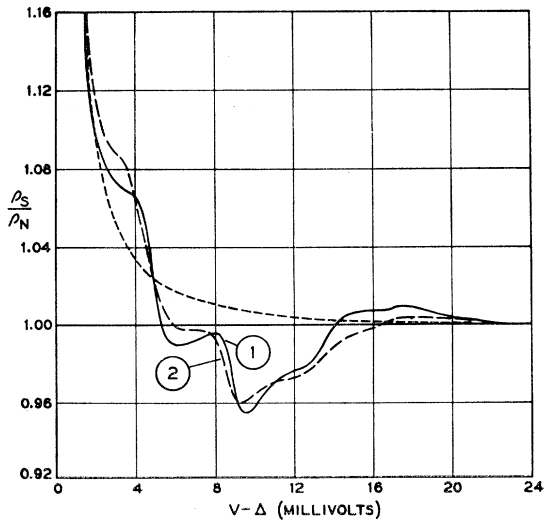

FIG. 5. Comparison of: (1) The density of states versus energy variation calculated by Schrieffer *et al.*—solid line, and (2) the tunneling result—long dashed line. The BCS variation is shown as the short dashed line.

[14] J. C. Swihart, Phys. Rev. **131**, 73 (1963).
[15] N. N. Bogoliubov, Nuovo Cimento **7**, 794 (1958). N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *A New Method in the Theory of Superconductivity* (1958) [English transl.: Consultants Bureau, Inc., New York, 1959.]
[16] G. J. Culler, B. D. Fried, R. W. Huff, and J. R. Schrieffer, Phys. Rev. Letters **8**, 399 (1962).
[17] P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

given by

$$F(\omega)=2f_T(\omega)+f_L(\omega),$$

where

$$f_T(\omega)=\frac{W_T/\pi}{(\omega_T-\omega)^2+W_T^2},$$

with $W_T=0.75$ mV, $\omega_T=4.4$ mV, and

$$f_L(\omega)=\frac{W_L/\pi}{(\omega_L-\omega)^2+W_L^2},$$

with $W_L=0.50$ mV, $\omega_L=8.5$ mV.

The coupling constant (α^2) was taken to be the same for both the transverse and longitudinal modes and was adjusted to give the correct gap parameter at the gap edge. In the solution obtained, both the real and imaginary parts of the gap parameter exhibit large variations over the energy range of interest and the resulting density of states variation is shown in Fig. 5 (curve 1). Comparison of this result with the experimental trace (Fig. 5, curve 2) shows that agreement is good not only in the neighborhood of the two phonon peaks (the region of the two sharp decreases in density of states), but also at higher energies where the broad structures are due to sum and harmonic effects. The theoretical solution is sensitive to the Coulomb interaction over this high-energy range, but a more detailed comparison should await a tunneling measurement at 0.3°K of a M-I-Pb junction.

The lead density of states versus energy curve can be examined in more detail by plotting d^2I/dV^2 versus V as shown in Fig. 6 (curve 2) for an Al-I-Pb junction (Al not superconducting). The two drops in density of states (curve 1) associated with the phonon peaks are resolved as two strong negative peaks in second derivative. The problem of deriving a more detailed phonon spectrum from this second derivative curve is far from straightforward as a solution of the gap equation is involved.

THE VAN HOVE SINGULARITIES—GENERAL CONSIDERATIONS

A general prediction made by Van Hove[18] is that for three-dimensional crystals there exists in the phonon spectrum [plot of phonon density $g(\nu)$ against frequency ν] at least two infinite discontinuities in $dg/d\nu$ and at the upper end of the spectrum $dg/d\nu=-\infty$. These critical points occur at saddle points, maxima and relative minima in the dispersion curves and have been discussed in detail by Phillips[19]; generally there are many more than two.

The effect of these critical points on the second derivative versus voltage plot of the tunneling characteristic of M-I-S and S-I-S junctions has been considered

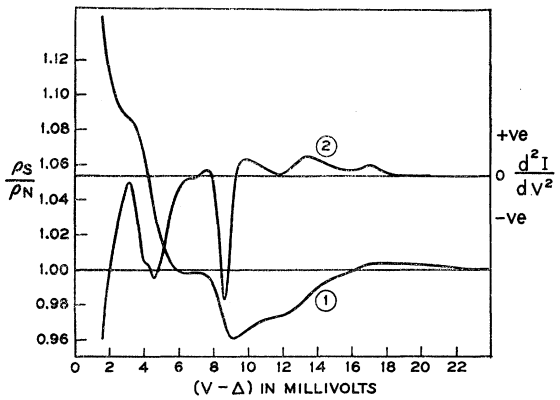

FIG. 6. Comparison of the density-of-states variation with energy (ρ_s/ρ_n versus E or dI/dV versus V) with the second derivative plot (d^2I/dV^2 versus V) for an Al-I-Pb junction at 1.3°K.

by Scalapino and Anderson.[20] Their result is that superimposed on the density-of-states variation which is attributed to the general shape of the phonon spectrum there should be singularities of the following types: for a critical point where an infinite discontinuity in $dg/d\nu$ occurs, the d^2I/dV^2 versus V plot for a M-I-S junction should exhibit a logarithmic singularity and jump discontinuity (at a voltage corresponding to the gap Δ plus the energy E_c of the critical point) and for a S-I-S junction an inverse square-root singularity should be displayed (at $2\Delta+E_c$ for identical films). Weaker critical points (finite discontinuity in $dg/d\nu$) produce logarithmic singularities in d^2I/dV^2 versus V for the S-I-S case.

Second derivative versus voltage plots for an Al-I-Pb junction (Al not superconducting, curve 1) and a Pb-I-Pb junction (curve 2) junction at 1.3°K are shown in Fig. 7. The plots are not to the same vertical scale.

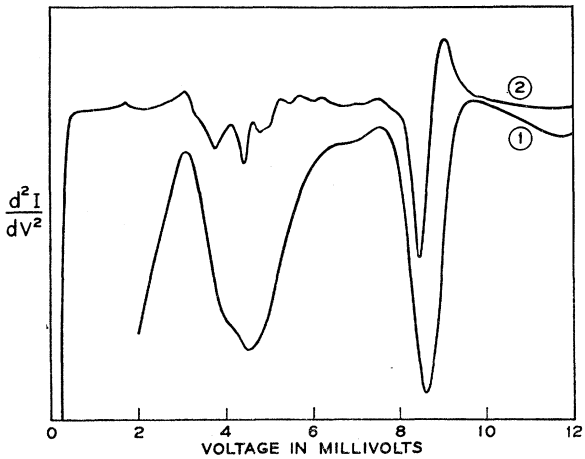

FIG. 7. Second derivative versus voltage plots for (1) Al-I-Pb and (2) Pb-I-Pb junctions at 1.3°K. Voltage is measured from Δ for (1), from 2Δ for (2).

[18] L. Van Hove, Phys. Rev. **89**, 1189 (1953).
[19] J. C. Phillips, Phys. Rev. **104**, 1263 (1956).
[20] D. J. Scalapino and P. W. Anderson, Phys. Rev. **133**, A921 (1964).

The Al-I-Pb trace is considerably smeared at this temperature and no singularities can be located with certainty, but in the Pb-*I*-Pb case, on the other hand, extensive structure is resolved. This is due in part of the fact that in a *S-I-S* junction a gap edge and singularity, rather than a Fermi edge, are being presented to the structure in density-of-states by changing voltage. Moreover, if the two superconducting films of the junction are identical then the structure in the tunneling characteristic is enhanced, as one can see by a consideration of a density-of-states diagram for this type of junction. Similarly Sn-*I*-Sn junctions are much more interesting than Al-*I*-Sn, and for the most detailed study of structure the junction of two identical superconductors is a necessity unless very low temperatures are available. Preparation of such junctions depends, of course, on the possibility of forming an insulating oxide of the metal or of depositing uniform layers of some other insulator only 15–20 Å thick.

OBSERVATION OF SINGULARITIES IN LEAD

A recorder trace of d^2I/dV^2 versus V for a Pb-*I*-Pb junction at 1.3°K is shown in Fig. 8. The arrows mark voltages corresponding to the energies of the Van Hove critical points which are taken from the dispersion curves given by Brockhouse *et al.*[21] In this way only critical points along symmetry directions have been considered and it is probable that more points contribute to the tunneling data. The energy of the critical points and the behavior of the second derivative plot near these points as calculated by Scalapino and Anderson is shown in Table I.

The general agreement in position between the critical points and resolved structure in the d^2I/dV^2 plot is good. Two main structures are observed in d^2I/dV^2 and these are located in regions where a number of critical points are found, namely the region 3–5.5 mV where five transverse critical points are reported by Brockhouse *et al.* and that from 7.5 to 9.5 mV where two transverse and four longitudinal critical points are seen. (A number of points occur at the same energy, see Table I.)

A detailed interpretation of the d^2I/dV^2 versus V plot in terms of the critical points and their resulting singularities is, however, very difficult. As noted previously, the rise in current at a bias 2Δ is not discontinuous but typically 0.15 mV wide so it is not expected that singularities will be observed with much greater resolution than this, or that infinite singularities will be observed. This smearing of the gap and hence, probably, the singularities, leads to difficulty of interpretation especially where a number of critical points are located close in energy. As an example, consider the voltage range from 9.0 to 9.7 mV. Scalapino and Anderson have found that a good fit to the experimental plot is a square-root singularity located at 8.85 mV, but such an interpretation assumes that only one critical point is contributing to the density of states variation over this range which is unlikely in view of the numerous critical points in the symmetry directions. Rather than attempt a complete explanation of the curve, we can see if any noticeable disagreement exists between the theoretical conclusions and the experimental results by the following simple approach. We assume that between 7 and 10.5 mV the seven critical points of the Brockhouse data (including the point for π wave in the square face) are the only ones effective in producing singularities in the d^2I/dV^2 versus V plot and that all these produce singularities of equal magnitude. The position and form of the singularities is then as shown in Fig. 9(a) taking $\beta=3\gamma$ (see Scalapino and Anderson) and assuming that the singularities are cut off at a width 0.1 mV, consistent with the smearing of the gap. We add the effect of all seven critical points by summing these singularities and obtain the result, Fig. 9(b). This curve, the effect of the critical points on the tunneling characteristic, is to be combined with the effect of the over-all longi-

TABLE I. The frequency and energy of critical points expected in the lead phonon spectrum, taken from the dispersion curves of Brockhouse *et al.* (Ref. 21). The resulting type of singularity in the (d^2I/dV^2) (versus) V plot for a Pb-*I*-Pb junction is found from Scalapino and Anderson (Ref. 20).

Direction	Dispersion curve behavior	(d^2I/dV^2) versus V behavior	Frequency cps	Energy meV
$100T$	min	$-\surd$	0.89 10^{12}	3.68
$111T$	max	$+\surd$	0.89	3.68
$110T_1$	min	$-\surd$	0.89	3.68
$100T$	max	$+\surd$	1.115	4.61
$110T_1$	max	$+\surd$	1.25	5.16
$100L$	min	$-\surd$	1.89	7.68
$110T_2$	min	$-\surd$	1.86	7.68
$110T_2$	max	$+\surd$	2.02	8.34
π_1	max	$+\surd$	2.10	8.67
$110L$	max	$+\surd$	2.10	8.67
$100L$	max	$+\surd$	2.16	8.92
$111L$	max	$+\surd$	2.185	9.03

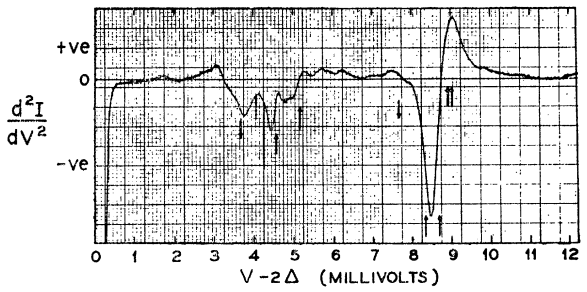

FIG. 8. Photographed recorder trance of second derivative versus voltage for a Pb-*I*-Pb junction at 1.3°K. The 500-cps measuring signal was 42 μV rms. Arrows mark the position of the critical points from Brockhouse *et al.* and the direction of the expected square-root singularity.

[21] B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. 128, 1099 (1962).

tudinal peak in the phonon spectrum to obtain a resulting d^2I/dV^2 versus V plot. The longitudinal peak, as described above, produces a drop in density-of-states or broad negative peak in second derivative. We therefore take as the effect of the peak the behavior of second derivative versus voltage for an Al-I-Pb junction at 1.3°K. This is reasonable as long as effects due to critical points are weak in this case, as they apparently are. Another difficulty is that the harmonic behavior of the transverse peak falls in the longitudinal peak region, but this is also a weak effect. Thus the combination of the trace for an Al-I-Pb junction at 1.3°K

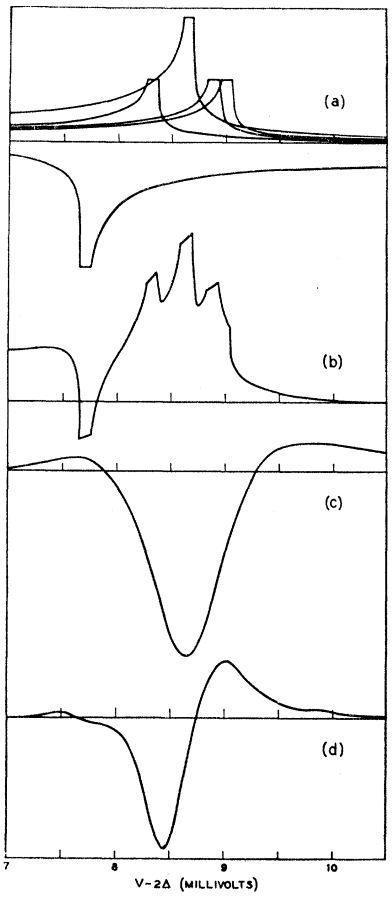

FIG. 9. (a) The shape and position of the expected singularities in d^2I/dV^2 versus V arising from critical points in the longitudinal region of the spectrum. (b) The sum of the singularities in (a), the total effect of critical points in the longitudinal region. (c) d^2I/dV^2 versus V for an Al-I-Pb junction at 1.3°K. (d) d^2I/dV^2 versus V for a Pb-I-Pb junction at 1.3°K.

[Fig. 9(c)] with the effect of the singularities 9(b) should produce the d^2I/dV^2 versus V plot for the Pb-I-Pb junction Fig. 9(d), if the relative magnitudes of the effects were known. While this is not true in complete detail, four points of agreement between curves (b) plus (c) and curve (d) suggest essential validity of the theory. (1) The maximum in curve (d) at 9 mV is consistent with addition of curves (b) and (c). (2) The square-root behavior beyond 9 mV results from the combination of singularities due to critical points. (3) The dip in (d) at 7.7 mV is located at the position of two singularities of the correct sign. (4) It

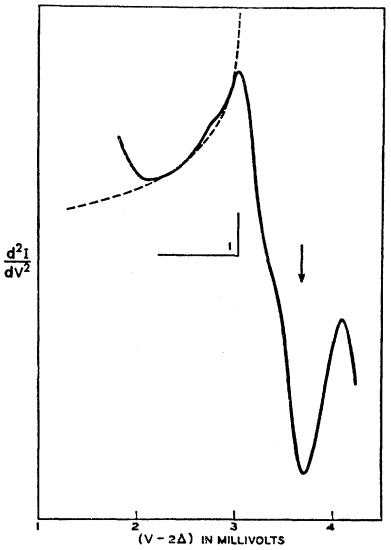

FIG. 10. The low-energy behavior of d^2I/dV^2 versus V for a Pb-I-Pb junction at 1.3°K. Origin 1 is that of the logarithmic singularity shown by the dashed line. The arrow is the critical point of lowest energy from Brockhouse *et al.*

is not necessary to find a singularity to explain the sharp dip in (d) at 8.45 mV, as we believe it is related to the broader dip in (c) at 8.6 mV sharpened (and altered slightly in position) by the addition of the singularities at 8.34 and 8.67 mV. Note that the sharp dip in (d) occurs at the position of the minimum in (b) between these singularities.

One unfortunate fact does arise from the above interpretation of the results. This is that the singularities at 8.34 and 8.67 mV are not resolved in detail. This suggests that it is desirable to obtain improved experimental traces, and to this end the lowest possible temperatures should be employed and, more important, attempts should be made to manufacture Pb-I-Pb junctions with discontinuous jumps in current at 2Δ. A substrate with a coefficient of expansion closer to that of the lead films should be chosen, and the lead films should be much thinner than that at which a double gap appears.[22] When this is done we believe structure will be displayed in considerably greater detail.

In the region from 2.5 to 6 mV, structure due to critical points from transverse branches is resolved. As can be seen from Fig. 8, at the energies of the critical points along symmetry directions structure of the correct sign is resolved but not all the observed structure is accounted for in this way. In particular, the positive structure at 3.0 mV, which can be fitted rather well by a logarithmic singularity (see Fig. 10) located at 3.05 mV, is at an energy lower than that of any critical point taken from Brockhouse *et al.* and we suggest a nonsymmetry direction critical point at this energy.

HARMONIC STRUCTURE

As pointed out by Morel and Anderson,[17] an Einstein phonon peak at energy E_E will produce structure in the density of states versus energy variation at $\Delta+E_E$,

[22] P. Towsend and J. Sutton, Phys. Rev. Letters 11, 154 (1963).

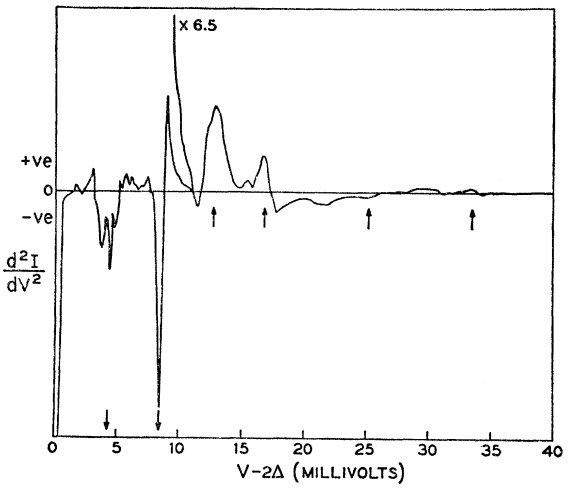

FIG. 11. d^2I/dV^2 versus V for a Pb-I-Pb junction at 1.3°K. The signal was increased at a bias of 10 mV to record the weak high-energy structure. Arrows mark fundamental, sum, and harmonic structures.

$\cdots$, $\Delta+nE_E$. We show this structure in Fig. 11, a d^2I/dV^2 versus V plot for a Pb-I-Pb junction to a bias of 42 mV. In order to resolve the weak structure at higher biases, the 500-cps measuring signal was increased in amplitude at 10 mV, giving the 6.5 times increase in derivative signal. Taking the negative peaks at 4.35 and 8.4 mV as the transverse and longitudinal structures, we observe sum effects at 12.75 mV and harmonic effects at 16.8, 25.2, and 33.6 mV. It can be seen that the sign of the second derivative structure switches with successive harmonics, for example negative at 8.4, positive at 16.8, negative at 25.2, and positive at 33.6 mV. The fine structure of the transverse and longitudinal regions is rapidly smeared in the harmonics. The apparent discontinuity in slope of d^2I/dV^2 versus V at 17.7 mV is close in energy to the harmonic of the critical point at the end of the phonon spectrum.

SINGULARITIES IN TIN

The effect of the phonon spectrum on the density-of-states variation is most easily observed in the strong-coupling superconductors, lead and mercury. Measurements on lead have been described above and these on mercury have been made by Bermon and Ginsberg.[23] Giaever has shown that two weaker coupling superconductors, tin and indium, have a density-of-states variation in good agreement with that of BCS, but the use of the second derivative technique reveals fine structure not resolved in a first derivative (density-of-states) measurement. This is shown in the d^2I/dV^2 versus V plot for a Sn-I-Sn junction in Fig. 12. It can be seen that the structure extends from 3.0 to 19.0 mV and is obviously the result of a large number of Van Hove critical points. Three main features are of interest, the first being the relatively simple structure at 8.0 mV which appears to be a negative square-root singularity with $\beta=2\gamma$ caused by a minimum in a dispersion curve (Fig. 12). As in the case of lead, the high-energy end of the structure is approximated by a square-root singularity, located at 17.7 mV, although a number of critical points probably fall close together near this

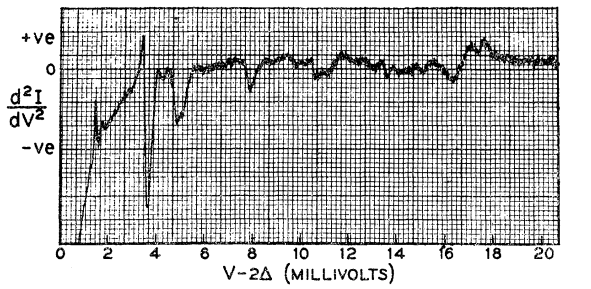

FIG. 12. Photographed recorder trace of the second derivative versus voltage plot for a Sn-I-Sn junction at 1.3°K. The 500-cps measuring signal was 100 μV rms.

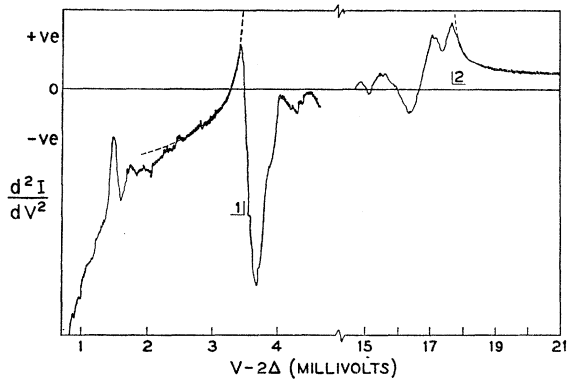

FIG. 13. d^2I/dV^2 versus V for a Sn-I-Sn junction at 1.3°K. The low-energy structure is fitted by a logarithmic singularity located at 3.5 mV, the high-energy structure by a square-root singularity at 17.7 mV. Note the break in voltage scale and scale change.

energy [Fig. 13(b)]. The low-energy end of structure is best fit by a logarithmic singularity at 3.4 mV [Fig. 13(a)]. Theoretical calculations of the white tin phonon spectrum have been made by Musgrave[24] and by Wolfram *et al.*,[25] who obtained reasonable agreement in location of high-energy critical points but do not find points as low as 3.4 mV. Recently De Wames[26] and Shpiz[27] have made further calculations and do find some agreement at these low energies in that low-lying branches are found.

We have generally found that the rise in current at 2Δ is less smeared in Sn-I-Sn than in Pb-I-Pb junctions and the d^2I/dV^2 versus V plot resolves correspondingly

[23] S. Bermon and D. M. Ginsberg, Bull Am. Phys. Soc. **8**, 232 (1963). Phys. Rev. **135**, A306 (1964).
[24] M. J. P. Musgrave, Proc. Roy. Soc. (London) **A272**, 503 (1962).
[25] T. Wolfram, G. W. Lehman and R. E. De Wames, Phys. Rev. **129**, 2483 (1963).
[26] R. E. De Wames (to be published).
[27] J. M. Shpiz (to be published).

sharper structures, especially at low energies. In a junction made with 500-Å-thick tin films (instead of 2000 Å normally used), some of the low-energy peaks were so sharp that the measurement was probably limited by the amplitude of the 500-cps signal.

SINGULARITES IN INDIUM

A measurement of the density-of-states variation with energy in indium has been made by Adler and Rogers[28] using a very sensitive technique. They resolved a dip in density-of-states at 14.5 mV and also, although they did not comment on the fact, observed that the density of states drops below that of BCS at about 6 mV. By comparison with the lead data this suggests two phonon peaks, located in this case at roughly 6 and 14 mV. Ideally we should measure d^2I/dV^2 versus V for an In-I-In junction to check these peaks in detail, but although we managed to make such junctions none survived long enough to allow a derivative to be taken. We have, however, made a satisfactory measurement using an Al-I-In junction. Contrary to our earlier publication[29] we now believe that the density of states versus energy variation in aluminum contains no structure that we can resolve with our usual 500-cps signal levels, as we have measured a number of Al-I-Al junctions at 0.8°K and found no structure attributable to phonon effects (other than the BCS variation). We therefore use aluminum as a "structureless" superconductor in an Al-I-In junction at 0.8°K so that we can probe the indium structure with the density of states gap singularity rather than with the Fermi edge of a metal with correspondingly greater thermal smearing. If an exact density-of-states measurement is required a normal metal should be used, but in a search for weak phonon effects a two-superconductor junction is preferred. The results for an Al-I-In junction are shown in Fig. 14; we resolve structure between 3 and 7 mV and suggest this energy range as the location of the transverse phonon peak. A relatively simple structure is observed from 11 to 17 mV which is presumably due to the longitudinal peak and is the structure observed by Adler and Rogers. This structure locates the end of the indium phonon spectrum as 14.8 mV.

An interesting effect was observed in measurements on these Al-I-In junctions. The indium films were evaporated onto the substrate and Al film which were held at liquid-nitrogen temperatures. The sample was then warmed to room temperature so that electrical connections could be made to the films. Following our usual practice, the junctions were then cooled to helium temperatures and derivative measurements taken later the same day. With this procedure no phonon structure was observed. However after leaving the junctions at

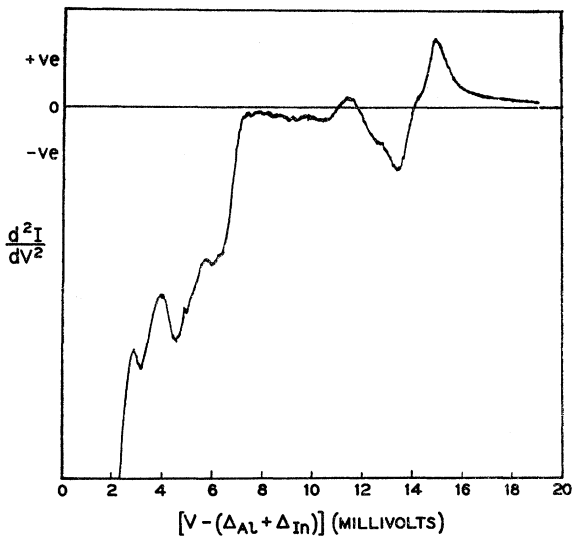

FIG. 14. Second derivative versus voltage plot for an Al-I-In junction at 0.8°K.

room temperature (stored in a desiccator) for five days, some structure was observed on remeasuring at 0.8°K, and after 15 days the structure was more pronounced. The plot of Fig. 14 is for a junction six weeks old, little change occurring after 15 days. We suggest that immediately after preparation the In films are composed of very small crystallites, and that peaks in the phonon spectrum are broadened. After annealing at room temperature the peaks become sharp enough to be observed in the tunneling characteristic, although the structure is still relatively broad compared to that in lead and tin. Even though the phonon structure is broad the current-voltage characteristic approaches the ideal with the rise in current at $\Delta_{Al}+\Delta_{In}$ taking place within a voltage range of 0.02 mV.

It is apparently not possible to make neutron scattering measurements for indium so the tunneling results give, to our knowledge, the only suggestions as to the form of the phonon spectrum in this metal.

SINGULARTIES IN THALLIUM

It is apparent that superconductors with a relatively high value of the ratio of transition temperature to Debye energy are the most promising for observation of phonon effects in the density of states versus energy variation. Using this criterion, thallium was expected to have structure comparable to that observed in tin and indium. Because of the rapid oxidation of thallium, we prepared junctions by evaporating the films onto slides with prepared contacts and the samples were immersed in liquid nitrogen immediately after removal from the evaporator.

The second derivative versus voltage plot (Fig. 15, (Curve 2) for an Al-I-Tl junction at 0.8°K (aluminum superconducting) exhibits features similar to those

[28] J. G. Adler and J. S. Rogers, Phys. Rev. Letters **10**, 217 (1963).
[29] J. M. Rowell, P. W. Anderson, and D. E. Thomas, Phys. Rev. Letters **10**, 334 (1963).

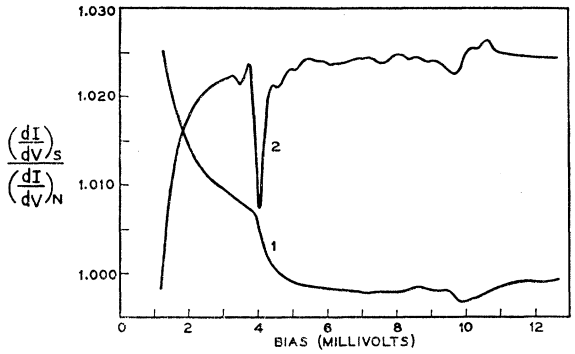

FIG. 15. Curve 1: The ratio of dI/dV for an Al-I-Tl junction at 0.8°K with the thallium superconducting to dI/dV with the thallium normal, plotted against voltage measured from Δ_{Tl}. Curve 2: The second derivative versus voltage plot for an Al-I-Tl junction at 0.8°K. The voltage is measured from $\Delta_{Al}+\Delta_{Tl}$.

discussed above for Pb, Sn, and In. For example, at 4.0 mV a sharp negative peak in second derivative is observed which we associate with the transverse peak in the phonon spectrum. The longitudinal peak appears to be from 9.0 to 10.5 mV with the end of the phonon spectrum located at 10.5 mV. The similarity of this longitudinal structure in thallium to that in tin from 16 to 18 mV is striking. We also show in Fig. 15 (curve 1) the ratio $(dI/dV)_S/(dI/dv)_N$ versus voltage or the density-of-states plot. This trace was taken at 0.8°K with more sensitive equipment than that used for lead,[30] and the aluminum was driven normal with a magnetic field. The phonon effects are weaker than in lead, but the two drops in density of states associated with the phonon peaks are unmistakable.

LOW-ENERGY STRUCTURES IN Pb AND Sn

In the second derivative plots for Pb-I-Pb and Sn-I-Sn junctions (Figs. 8 and 12) a peak is observed at low energies, as 1.75 and 1.5 mV, respectively. These could be due to Van Hove critical points, but it would be surprising to find these at such low energies in both metals. It has been noted that in the infrared experiments of Richards and Tinkham[31] an absorption is observed over a rather broad energy range, 1.4–2.1 mV for lead, 1.1–1.4 mV for tin. The low-energy tunneling peaks, although much sharper, do fall in these energy ranges and it is possible that the effects are of the same origin. However, no entirely satisfactory explanation of either effect has yet been advanced.

CONCLUSIONS

We have shown that a detailed study of the tunneling characteristics for junctions involving superconducting films can be a powerful tool for the study of both superconductivity and lattice dynamics. The measurement of the density of states in lead and the agreement with the theoretical result of Schrieffer *et al.* give powerful support to the validity of the Eliashberg formulation of the gap equation. It should be noted that such agreement is only obtained using the relationship of Schrieffer *et al.* between gap parameter and density of states measured by the tunneling technique. By using two-superconductor junctions and the second derivative technique we have resolved fine structure which is attributed to Van Hove critical points in the phonon spectrum. The theory of Scalapino and Anderson explains quite well the type and sign of the singularities observed.

The work as a whole, with good agreement between theory and experiment for each measurement, gives very strong support to the basic assumption of the BCS theory, namely that the coupling between electrons is via the exchange of phonons. Although for lead, tin, indium, and aluminum this coupling has not been questioned, there have been suggestions[32,33] lately that other mechanisms may be effective in other superconductors. The tunneling technique is an obvious tool for the study of this problem once technical difficulties are overcome.

ACKNOWLEDGMENTS

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[30] We are indebted to A. F. G. Wyatt for development of this equipment and the techniques used in preparing the thallium films.

[31] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960). P. L. Richards, Phys. Rev. Letters **7**, 412 (1961).

[32] D. C. Hamilton and M. A. Jensen, Phys. Rev. Letters **11**, 205 (1963). C. G. Kuper, M. A. Jensen, and D. C. Hamilton, Phys. Rev. **134**, A15 (1964).

[33] B. T. Matthias, Science **144**, 378 (1964).