Phonon Emission and Self-Energy Effects in Normal-Metal Tunneling

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We discuss the dependence of conductance on voltage for metal-insulator-metal junctions for the bias range from 0–1 V. The dependence is roughly parabolic but the minimum conductance need not occur at $V=0$. Small deviations from this parabolic conductance behavior are described. These are due to interactions of the tunneling electrons with impurities in the oxide, the oxide itself, or the surface layers of the metal electrodes. These emission processes are studied by calculating the even conductance and its derivative. This derivative, at low voltages, is a crude measure of the phonon density in the normal-metal electrode. We show that self-energy effects in the normal metal can be conveniently displayed by calculating the odd conductance. Such experimental effects are presented for normal Pb, and are in good agreement with the self-energy calculated from superconducting tunneling.

I. INTRODUCTION

THE possibility that a tunnel current may flow between metals separated by an insulating layer was first considered by Frenkel[1] in 1930. Interest in this phenomenon increased markedly following the investigations carried out in 1960 by Fisher and Giaever[2] when they showed that the insulating layer could be made fairly simply by the thermal oxidation of freshly evaporated Al films. In order to show that the current flow was indeed due to tunneling, Giaever[3] substituted a superconducting film (Pb) on one side of the insulator and observed dramatic changes in the characteristic of the current I versus voltage V below the transition temperature. This result not only convincingly proved the existence of the tunneling mechanism but also fascinated further investigators to such an extent that tunneling between normal metals in the low-voltage region ($\lesssim 1$ V) was largely forgotten. In the high-voltage range ($eV>\varphi$, the barrier height, typically 2 V), where the current increases exponentially with voltage, work continued in an attempt to deduce barrier parameters from the I-V characteristic.[4]

Interest in normal-metal tunneling has increased during the past two years owing to the discovery of new phenomena as derivative techniques (measurement of $\partial I/\partial V$ and $\partial^2 I/\partial V^2$ versus V), widely exploited in superconductor tunneling, have been applied more critically to normal-metal junction characteristics. For example, the "zero-bias tunneling anomaly," previously observed in semiconductor diodes,[5] was found by Wyatt[6] to occur in junctions using transition-metal oxides as the insulating layer. More recently, Jaklevic and Lambe[7] showed that the tunneling electrons interact with vibrational modes of impurity molecules trapped in the insulating oxide layer. The excitation of such a mode gives rise to an increase in conductance (dI/dV) and thus the frequency of the modes can be determined from the tunneling characteristic. We observed not only such impurity vibrations but also realized that the tunneling electron excited phonons of the oxide layer itself and of the surfaces of the metal films adjacent to the oxide.[8] Later Duke *et al.*[9] invoked these barrier excitations as a possible explanation of the conductance dip near zero bias in III-V diodes.[5] As we investigated such interactions in a number of thin-film junctions using different metals and various oxides, we realized that very little was known about normal-metal tunneling; in fact, even the over-all shape of conductance versus voltage for $-1\text{ V}<V<+1\text{ V}$ had not been reported in the literature.[10] In this paper we will first present our measurements of the gross features of tunneling behavior in this low-voltage region. The small structures, due to excitation processes, which are superimposed on this behavior, will be presented for a variety of junctions. We will reach two interesting conclusions; first, that the conductance can be roughly described by $G=\alpha+2\beta V+3\gamma V^2$, a parabolic dependence but with the parabola offset from $V=0$. Second, we show how an analysis of the data into "odd" and "even" conductances is a way to separate effects due to direct emission processes (even terms) and self-energy corrections (odd terms).

II. EXPERIMENTAL

All the tunnel junctions to be discussed below were prepared by the conventional techniques[2,11] of thin-film

[1] J. Frenkel, Phys. Rev. 36, 1604 (1930).
[2] J. C. Fisher and I. Giaever, J. Appl. Phys. 32, 172 (1961).
[3] I. Giaever, Phys. Rev. Letters 5, 147 (1966).
[4] Thomas E. Hartman and Jay S. Chivian, Phys. Rev. 134, A1094 (1964).
[5] R. N. Hall, J. H. Racette, and H. Ehrenreich, Phys. Rev. Letters 4, 456 (1960); R. N. Hall, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Academic Press Inc., New York, 1961), p. 193; A. G. Chynoweth, R. A. Logan, and D. E. Thomas, Phys. Rev. 125, 877 (1962); R. A. Logan and J. M. Rowell, Phys. Rev. Letters 13, 404 (1964).
[6] A. F. G. Wyatt, Phys. Rev. Letters 13, 401 (1964).
[7] R. C. Jaklevic and J. Lambe, Phys. Rev. Letters 17, 1139 (1966); J. Lambe and R. C. Jaklevic, Phys. Rev. 165, 821 (1968).
[8] J. M. Rowell and W. L. McMillan, Bull. Am. Phys. Soc. 12, 77 (1967).
[9] C. B. Duke, S. D. Silverstein, and A. J. Bennett, Phys. Rev. Letters 19, 315 (1967).
[10] We have found that such conductance plots were shown by Matthew Kuhn [thesis, University of Waterloo, Waterloo, Canada, 1966 (unpublished)].
[11] J. M. Rowell and L. Kopf, Phys. Rev. 137, 907 (1965).

evaporation to produce the metal electrodes and thermal oxidation to produce the tunneling barrier. Aluminum oxide was prepared by exposure of the freshly evaporated aluminum film to laboratory air for $\sim$1 min, lead oxide by heating the lead film to $\sim$50°C in dry oxygen, and tin oxide by heating the tin film to $\sim$100°C in air or oxygen.

In order to discuss the measurements confidently, one must confirm that tunneling is the dominant transport mechanism in the junctions. As all the junctions involve two films which can be made superconducting, this can be done conclusively for low voltages. For example, in an Al-I-Sn junction at 0.95°K, the tunneling current for $V \ll \Delta$ is proportional to the number of thermally excited quasiparticles, $I_{SS} \sim I_{NN} e^{-\Delta_{\mathrm{Sn}}/kT}$, where I_{NN} is the current at the same voltage with both films normal. As $\Delta_{\mathrm{Sn}} \simeq 1.76kT_c (T_c = 3.7°\mathrm{K})$, $I_{SS} \sim 10^{-3} I_{NN}$. Thus, one simply measures the ratio of the currents at low voltages at 0.95 and 4.2°K. If this ratio were 10^{-2} instead of the expected 10^{-3} we would say that 1% of the current in the junction is not a tunneling current. This may not appear serious, but if this current is carried by a metallic bridge, it may lead to completely spurious structures in the derivative curves where we are interested in changes which are often <1%. In this paper we will only discuss those junctions in which, as far as we could tell, tunneling was the only current mechanism.

As the measurements of interest in this paper were obtained with both films of the junction in the normal state, it was necessary to either apply a magnetic field to the junction or work above the transition temperature T_c. As thermal smearing of the tunneling characteristic is $\sim 3kT$(1 meV at 4.2°K), we generally applied a magnetic field to the junction held at 1°K. This had the disadvantage of introducing some noise into the derivative measurement which we believe is because of vibration of the junction relative to the field.

When the changes in conductance of the junction were relatively large (>15%) we used the conventional method of measuring derivatives of the tunneling characteristic. We modulated the slowly varying dc voltage with an ac signal (constant current, 500 cps) and detected the generated ac voltage (typically <60 μV rms) with a phase-sensitive detector. This detector output is essentially dV/dI, which could be recorded on an X-Y recorder or on punched paper tape. The conductance (dI/dV), which is the measurement of interest, was taken from tables or calculated by computer if a large number of data points was involved. In most of the measurements of normal-state tunneling, especially at low voltages (<50 mV), the changes in conductance are rather small and increases in conductance $\ll$1% are significant, as will be shown below. Often we wanted to study these conductance changes in detail for both bias directions, and drift in the direct measurement of dV/dI could lead to large errors. To avoid this we used a bridge circuit designed by

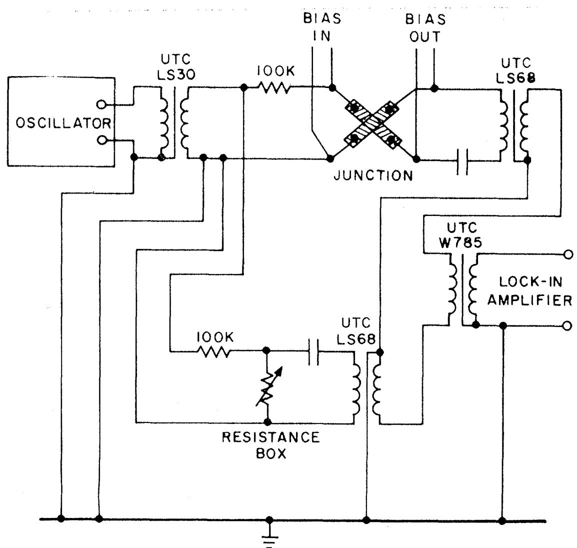

FIG. 1. Schematic of ac bridge circuit used to measure very small resistance changes. The bridge is operated at 500 cps.

Thomas and shown in Fig. 1. Rearrangement of the components shows that this is essentially an ac Wheatstone bridge with the 100-kΩ resistors as fixed arms. The linearity and resolution of the bridge were checked initially using two resistance boxes. Our linearity requirements confine the use of the bridge to ±15% changes in resistance. The resolution approaches 1 part in 10^5, with modulation signals <100 μV rms, but was reduced in the experiments described here by the noise from the magnetic field. The drift over a period of 1 h was comparable to the resolution.

In a typical measurement (say that of Fig. 8) the junction (immersed in liquid helium) was cooled to $\sim$0.95°K, which is the limit of the pumping system. A transverse magnetic field was applied and increased until the resistance-versus-voltage plot near zero bias showed no evidence of the superconducting energy gap. In some junctions (especially those using Al films) our maximum field of 4.5 kG was not sufficient to quench a small trace of the gap characteristic which presumably arises from the edges of the film. These junctions were either measured at 2°K (where this gap disappears) or rejected. Having satisfied ourselves that the junction was completely normal the bridge was balanced at the point of maximum resistance, which was found by inspection of a resistance-versus-voltage plot taken on the X-Y recorder. The off-balance signal of the bridge is proportional to the resistance change in the junction produced by varying the bias. This signal, as the dc output from the lock-in amplifier, was integrated using a digital voltmeter with 10-sec time constant. The time constant of the lock-in amplifier was kept short, 10 or 30 msec. The dc voltage on the junction was swept very slowly from −27.5 to +27.5 mV, and the count of the digital voltmeter punched onto paper tape every

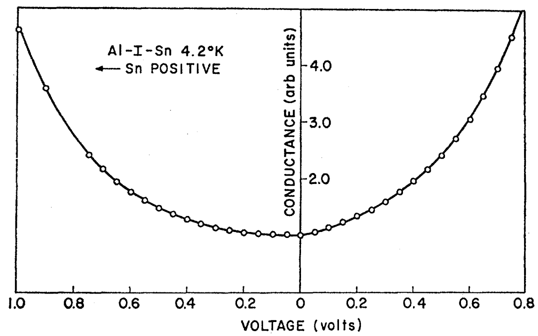

FIG. 2. Conductance versus voltage for an Al-I-Sn junction at 4.2°K. The open circles are measured points and the solid line is drawn through them. Note that the conductance changes by a factor of 5.

10 sec. Thus, approximately 220 readings of junction resistance were recorded (in about 37 min) across the 55-mV voltage range. Voltage calibration was obtained by noting the voltage and corresponding count at approximately 5-mV intervals. The voltage sweep rate has, of course, to be accurately constant and this is achieved by driving a potentiometer with a synchronous motor fed from an oscillator and power amplifier. Changing the oscillator frequency is a convenient way of adjusting the sweep rate. The advantage of the digital voltmeter is that it provides a true 10-sec integration of noise and is relatively insensitive to transient signals (because the lock-in amplifier is used with short time constant). The resistance readings, punched on the paper tape, were read onto IBM cards, and a computer calculation of the following parameters was made: (1) the conductance for the positive $[G(+V)]$ and negative $[G(-V)]$ biases, (2) the odd conductance $G^0(V)=\frac{1}{2}[G(+V)-G(-V)]$, (3) the even conductance $G^E(V)=\frac{1}{2}[G(+V)+G(-V)]$, and (4) the derivative of the even conductance $dG^E(V)/dV$, called the "barrier phonon density of states." This derivative corresponds roughly to d^2I/dV^2, which could be measured directly from the junction, but we found it more convenient to generate it from the first-derivative measurement. The technique used was to calculate the slope of $G^E(V)$ versus V at each datum point by averaging the slope with a straight line through $2n$ neighboring points. Usually $n=1$ was sufficient to give good signal-to-noise ratio; $n=3$ was the maximum ever used. In Fig. 9 the voltage grid was 250 μV, so averaging over the $2n+1$ points with $n=1$ corresponds to finding d^2I/dV^2 with a 750-μV sensing signal. The success of this "generated" second derivative is obviously due to the good signal-to-noise ratio obtained in the first-derivative measurement, which in turn is largely a result of using the 10-sec integration time at each datum point. An alternative approach to obtain detailed first derivatives would be to use a multichannel pulse-height analyzer, sweep the voltage relatively rapidly, and average the resistance at each datum point over many sweeps. (This alternative was rejected, as the recording system is also used for superconducting studies,[12] and would lead to problems in normalization of the superconducting conductance to the normal conductance.)

III. TUNNELING BEHAVIOR FOR -1 V$<V<$1 V

The work of Giaever[2] showed that for a tunnel junction with average barrier height $\bar{\varphi}$, the I-V characteristic could be easily understood in two limiting voltage ranges. In the high-voltage range ($eV>\bar{\varphi}$) the electrons tunnel through a progressively thinner barrier as V increases, and I increases exponentially with voltage. At low voltages ($eV\ll\bar{\varphi}$) the barrier shape is assumed to be independent of applied bias and the tunneling characteristic is Ohmic ($I\propto V$). While this description of the low-voltage behavior is adequate to analyze I-V measurements, we would like to stress here (and substantiate later), that if measurements of conductance ($G=dI/dV$) are made to an accuracy of $>1\%$, then the "Ohmic region" *does not exist* in any tunnel junction except over surprisingly small voltage ranges (possibly 10 mV). In addition, these ranges of approximately constant conductance need not occur exactly at $V=0$. Having disposed of an Ohmic low-voltage region, we must therefore consider in more detail what might be called the "intermediate-voltage range" ($eV<\frac{1}{2}\bar{\varphi}$, say—typically 1 V). A simple approach,[13] which seems to be an adequate description of the experimental data in this region, is to assume that the current can be expanded in powers of V and that progressively higher orders in V become important as the voltage increases. Thus, we write

$$I=\alpha V+\beta V^2+\gamma V^3+\delta V^4+\cdots \tag{1}$$

or

$$G=\alpha+2\beta V+3\gamma V^2+4\delta V^3+\cdots. \tag{2}$$

A dependence of the form $I=\alpha V+\gamma V^3$ was deduced by Knauss and Breslow[14] simply from I-V measurements. It was pointed out by Simmons[15] that these low-order terms could be obtained quite simply from the usual tunneling expressions.[16] However, Simmons makes the simplification that the barrier can be approximated by a symmetrical rectangular potential $\bar{\varphi}$. Thus he obtains the even conductance terms, $G=\alpha+3\gamma V^2+\cdots$. It has been shown[17,18] that if a more realistic asymmetrical potential barrier is assumed then the odd terms, $G=2\beta V+4\delta V^3+\cdots$, are nonzero and become larger as the barrier asymmetry increases. Thus, in the intermediate range, the conductance appears roughly as a

[12] W. L. McMillan and J. M. Rowell, *Treatise on Superconductivity*, edited by R. Parks (Marcel Dekker, New York, 1969).
[13] J. M. Rowell, in *Tunneling Phenomena in Solids*, edited by E. Burstein and S. Lundqvist (Plenum Press, Inc., New York, 1969).
[14] H. P. Knauss and R. A. Breslow, Proc. IRE **50**, 1834 (1962).
[15] John G. Simmons, J. Appl. Phys. 34, 238 (1963).
[16] John G. Simmons, J. Appl. Phys. 34, 1793 (1963); 34, 2581 (1963).
[17] R. Stratton, J. Phys. Chem. Solids **23**, 1177 (1962).
[18] T. E. Hartman, J. Appl. Phys. **35**, 3283 (1964).

parabola ($G=\alpha+3\gamma V^2$), which is offset from zero bias by a voltage $\beta/3\gamma$. It is our experience that many tunnel junctions (Al-I-Pb, Al-I-Sn, Al-I-In, and Pb-I-Pb) exhibit this type of parabolic behavior, and the parabola is always offset from zero voltage, implying asymmetrical barriers. Very recently, detailed calculations of conductance versus voltage have been made[19] for trapezoidal barriers and the results agree very well with the experimental "offset parabolas" if rather large junction asymmetries are used.

We present in Fig. 2 the measurement of conductance versus voltage for an Al-I-Sn junction at 4.2°K. The parabolic dependence is apparent, as is the offset from zero bias. We find that in Al-I-Pb and Al-I-In junctions as well, the offset is always in the Al negative-bias direction. There is a slight departure from the smooth conductance variation at low voltages due to the excitation processes which will be discussed below.

IV. EXCITATION OF IMPURITY MOLECULES

Having established what we believe are the gross features of tunneling in the intermediate-voltage range, we can now study deviations from this behavior. In most cases these deviations are observed as rather abrupt increases in conductance at voltages corresponding to the excitation energies of vibrational modes in the oxide. These modes may be due to impurities in the oxide, the oxide itself, or the films adjacent to the oxide. The excitation of impurities has been studied in great detail by Jaklevic and Lambe,[7] who introduced organic contaminants into "clean" oxides produced by glow-discharge oxidation. The technique has been extended to impurities on a semiconductor surface-barrier junction by Thompson[20]; the elimination of unwanted impurities on a semiconductor would again appear to be a difficult problem unless the surface is cleaved in vacuum. As pointed out by Jaklevic and Lambe, organic contaminants (and water molecules) are always present in oxide junctions made in the conventional way. The results are usually shown in d^2I/dV^2-versus-V plots; it is helpful also to see the conductance behavior in order to appreciate the order of magnitude of the excitation effects compared to the over-all tunneling behavior of Fig. 2. We show in Fig. 3 a detailed conductance measurement for an Al-I-Sn junction, which was prepared in an oil-diffusion-pump evaporation station (evaporation pressure $\sim 10^{-6}$ Torr) and oxidized by exposure of the Al film to laboratory air for ~ 1 min. It can be seen that the conductance up to 400 mV is in fact dominated by the excitation processes and the only evidence for the general behavior discussed above is the *decrease* in conductance out to 270 mV. The arrows in Fig. 3 mark the positions of the most pronounced maxima in d^2I/dV^2 obtained by Lambe and Jaklevic

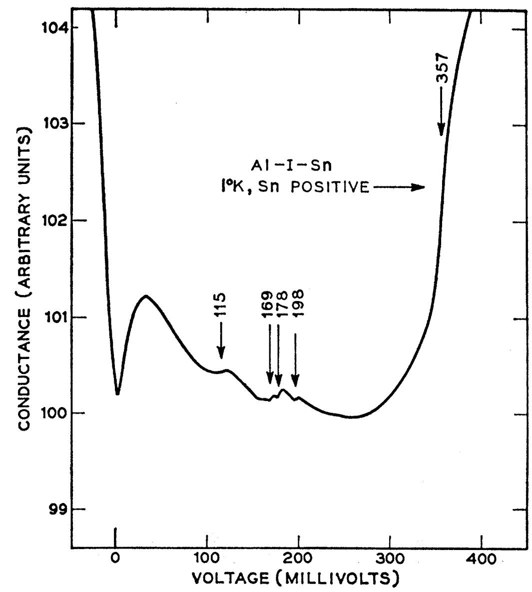

FIG. 3. Conductance versus voltage for an Al-I-Sn junction at 1°K with magnetic field applied to quench superconductivity. Only the Sn positive bias is shown. The arrows mark the position of second-derivative peaks in an Al-I-Pb junction (see Fig. 14 of Ref. 7). Note that in contrast to Fig. 2, the conductance changes by only 4%.

for an Al-I-Pb junction made by exposure to air (Fig. 14 of Ref. 7). The agreement between the positions of the arrows and points of maximum positive slope of the conductance in Fig. 3 is remarkable. This suggests that both laboratories are equally and identically polluted. One naturally suspects that this impurity is the diffusion-pump oil, but Lambe and Jaklevic have pointed out that solvents used in the laboratory are a more likely cause. They, in fact, showed that relatively "clean" oxides could be produced in a conventional diffusion-pump system as long as a glow discharge in pure oxygen, rather than thermal oxidation, was used to produce the oxide. The junction of Fig. 3 shows that the excitation of the C—H stretching mode at 360 mV gives rise to a 2% increase in conductance. This is the largest effect we have observed; generally these increases are $<1\%$ and are not so striking on a conductance plot as those of Fig. 2. We have shown the result only for the Al negative bias because (see Fig. 2) the over-all conductance rises much faster for the Al positive bias and the small excitation increases are correspondingly harder to observe. However, these excitations do occur symmetrically about $V=0$.

V. EXCITATION OF OXIDE PHONONS

The energies of the impurity vibrations described above cover the range 100–450 mV, and harmonics have been observed to approximately 1 V. At energies <100 mV we have observed similar conductance increases which we ascribed to excitations of the oxide

[19] W. F. Brinkman, R. C. Dynes, and J. M. Rowell (to be published).

[20] William A. Thompson, Phys. Rev. Letters **20**, 1085 (1968).

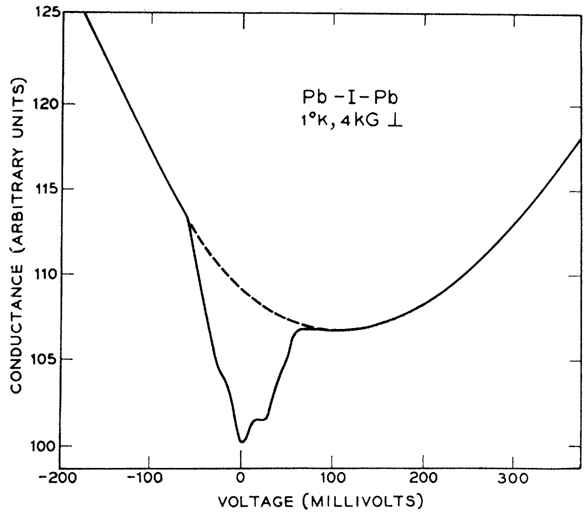

FIG. 4. Conductance versus voltage for a Pb-I-Pb junction at 1°K. A magnetic field was applied to produce the normal state.

itself.[8] Whether one considers these vibrations to be "phonons" (in an oxide 15 Å thick?) or vibrations of the oxide molecules themselves seem unimportant. These oxide vibrations were first observed in Pb-I-Pb junctions,[8,21] where they are particularly well defined, and later in aluminum oxide junctions, where, for reasons which are not understood, the effects are relatively weak.[22] Recently, Giaever[23] has identified such barrier emission processes in thermally grown zinc, magnesium, and cadmium oxides, in evaporated insulators of zinc and cadmium sulphides, and in amorphous germanium.

The conductance-versus-voltage plot for a Pb-I-Pb junction is shown in Fig. 4. The distinction between the parabolic conductance for $V>65$ mV and the excitation region <65 mV is particularly striking in this figure. In fact, the logical way to regard this behavior is as a sum of two conductances—the barrier dependence (shown as the dashed line), and the excitation conductance, which increases with a complex series of steps from $V=0$ to 65 mV and is then a constant contribution for higher voltages. The conductance for $V>65$ mV is in fact described very well by a parabola offset to $\sim$100 mV, but it is the lower-voltage range which is of greater interest here. This is shown in detail in Fig. 5, and it is apparent that there are two voltage ranges where the conductance increases most rapidly: that from 0 to 18 mV, where the conductance increase is $\sim$2.5%, and that from 30 to 60 mV, where the increase is 7%.

Because of the asymmetry of the background conductance about $V=0$ [arising from the $2\beta V$ term in Eq. (2)], it is difficult to decide from Fig. 4 whether the excitation processes are exactly symmetrical about $V=0$. A convenient analysis of the data can be carried out by calculating the even and odd conductances (G^E and G^0). These are defined as $G^E=\frac{1}{2}[G(+V)+G(-V)]$ and $G^0=\frac{1}{2}[G(+V)-G(-V)]$, where $G(+V)$ is the conductance at positive voltage V and $G(-V)$ the conductance at the same negative voltage. In this analysis, all symmetrical processes should appear only in G^E, whereas any asymmetrical processes (for example, an increase in conductance occurring only for one bias direction) will also appear in G^E but more obviously in G^0. At first sight the only asymmetrical term we expect is $2\beta V+4\delta V^3+\cdots$ odd terms from Eq. (2). Thus, the calculation of G^E is a convenient way to move the parabolic $3\gamma V^2$ term back to $V=0$ and display excitation processes which we expect to be symmetrical. This even conductance, calculated directly from the data of Fig. 5, is shown in Fig. 6. It has been shown by McMillan[12,24] and by Scalapino and Marcus[25] that the spectral density of excitations in the barrier region is proportional to dG^E/dV, which is roughly d^2I/dV^2 of the original characteristic. [To be strictly correct, dG^E/dV contains the terms $6\gamma V+\cdots$ from Eq. (2). This gives a linear background which should not be regarded as due to excitations but simply as a barrier-shape term.] This derivative, generated from the G^E plot of Fig. 6, is shown in Fig. 7. (Perhaps we should again stress that this "second derivative" is not measured directly but is calculated by taking the slope of Fig. 6 at each datum point and calculating the slope by averaging over the two neighboring points, as outlined in Sec. II. This calculation, and that of G^E and G^0, is done by computer, as the "raw data" of Fig. 5 includes

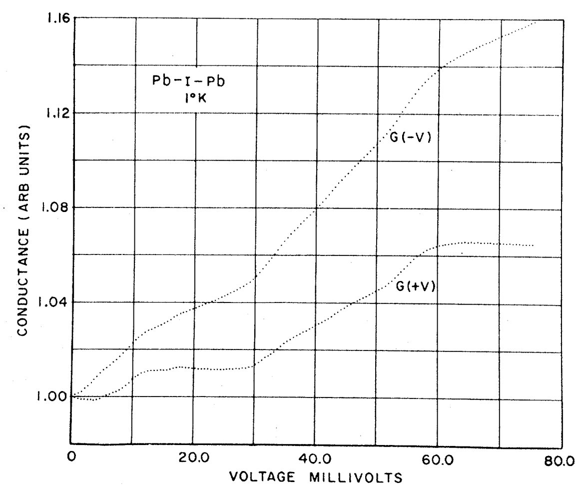

FIG. 5. Detailed measurement of conductance versus voltage for a Pb-I-Pb junction in the normal states at 1°K. $G(-V)$ and $G(+V)$ are for opposite polarities of the bias.

[21] Similar structures were reported by S. M. Marcus, Phys. Letters 23, 28 (1966), but were not interpreted as excitation effects.
[22] J. Lambe and R. C. Jaklevic (private communication).
[23] I. Giaever and H. R. Zeller, Phys. Rev. Letters 21, 1385 (1968).
[24] W. L. McMillan (unpublished).
[25] D. J. Scalapino and S. M. Marcus, Phys. Rev. Letters 18, 459 (1967).

300 derivative measurements over the energy range −75 to +75 mV.) This "barrier phonon density" of Fig. 7 shows very clearly a series of peaks in the energy range 30–60 mV. These, we believe, are due to excitations of the lead oxide. An exact comparison with optical spectra is not possible, as the composition of our insulating layer is unknown. It is probably a mixture of the various oxides, for which optical measurements[26] show a series of absorption lines from 56–73 mV (measurements were not made at energies less than 51 meV). These are somewhat higher than our tunneling peaks, but the general agreement seems reasonable.

A second series of peaks occurs for $V<20$ mV; we believe that most of these are due to excitation of phonons in the surface layers of the metal. This will be discussed in more detail below.

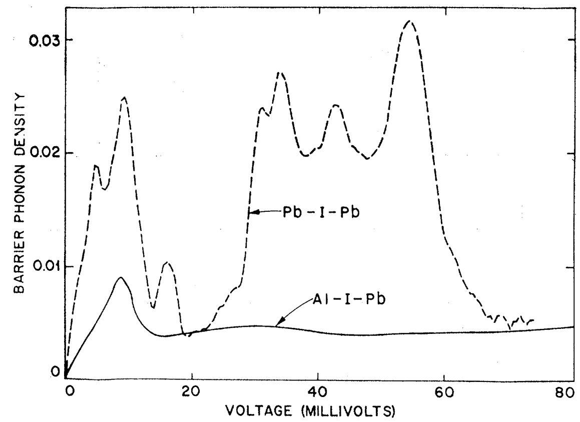

FIG. 7. The voltage dependence of the "barrier phonon density" (derivative of the even conductance) for Pb-*I*-Pb and Al-*I*-Pb junctions. The Pb-*I*-Pb plot (dashed line) was generated from the even conductance of Fig. 6. Units of the vertical scale are $(mV)^{-1}$.

VI. EXCITATION OF THE METAL FILMS

It is well known that in tunneling in semiconductor *p-n* junctions the emission of phonons in the junction region can be observed easily even in the *I-V* characteristic.[5] This is particularly so in the case of the indirect semiconductors, where the tunneling electron must emit a phonon in order to conserve momentum as it tunnels from the conduction to valence bands. As the insulating barrier is simply the depletion region of the semiconductor used, the energy of the phonon can be found from the dispersion curves at the momentum difference between valence and conduction bands. Such arguments do not apply directly to metal-film tunnel junctions, and the emission processes outlined in this paper are of course orders of magnitude weaker than those in semiconductor junctions. However, it is true that the electron injected into a metal by tunneling relaxes from this excited state to the Fermi level by phonon emission (and electron-electron interactions). If this process occurs in the bulk of the metal it will not affect the tunneling probability; if it occurs near the surface (and we cannot claim that the metal-oxide interface is an abrupt one), we might hope that such phonon emission, typical of the surfaces of the metal films, would be observed in the conductance-versus-voltage characteristic. That this seems to be occurring is evident from Fig. 7, where we note that the peaks at 5 and 9 mV are very close to the transverse and longitudinal phonon peaks in bulk lead, which are known from both superconducting tunneling[12,27] and neutron scattering.[28] One could claim, however, that the low-energy peaks of Fig. 7 are also due to oxide interactions. This is easily checked by changing the oxide but not the Pb film, i.e., by making an Al-*I*-Pb junction. This is compared to the Pb-*I*-Pb junctions in Fig. 7, where three features are worth noting:

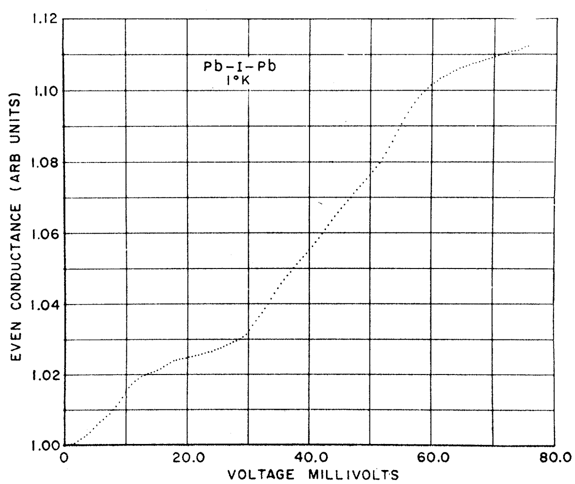

FIG. 6. The even conductance versus voltage calculated for the Pb-*I*-Pb junction of Fig. 5.

(1) The peaks from 30–60 mV in Pb-*I*-Pb are not present in the Al-*I*-Pb junction, supporting our claim that these are due to lead oxide.

(2) The low-energy peaks (<10 mV) are present in both junctions and must be due to the Pb film.

(3) The single peak at 16 mV is present only in the Pb-*I*-Pb junction. We must suppose that this is a low-frequency mode of the lead oxide molecules (possibly the vibration of the heavy lead atom as opposed to that of the light oxygen atoms at higher frequencies).

The low-energy range has been studied in more detail by measuring the conductance from −27.5 to

[26] F. Vratny, M. Dilling, F. Gugliotta, and C. N. R. Rao, J. Sci. Ind. Res. (India) **20B**, 590 (1961).

[27] J. M. Rowell, P. W. Anderson, and D. E. Thomas, Phys. Rev. Letters **10**, 334 (1963); W. L. McMillan and J. M. Rowell, *ibid.* **14**, 108 (1965).

[28] B. N. Brockhouse, E. D. Hallmann, and S. C. Ng, in *Magnetic and Inelastic Scattering of Neutrons by Metals*, edited by T. J. Rowland and P. A. Beck (Gordon and Breach, Science Publishers, Inc., New York, 1969); R. Stedman, L. Almqvist, and G. Nilsson, Phys. Rev. **162**, 549 (1967).

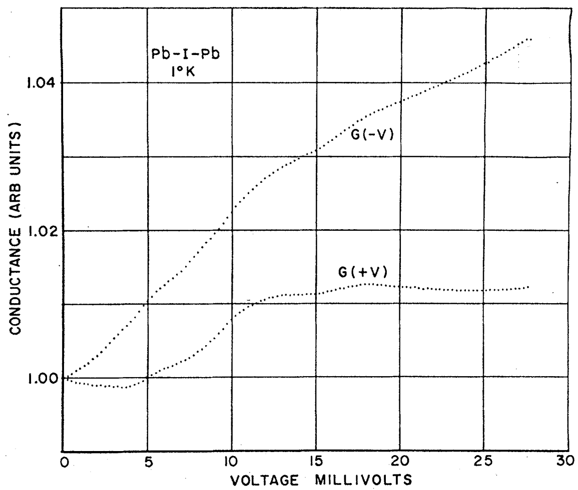

FIG. 8. Dependence of conductance on voltage for two polarities of the bias for a Pb-I-Pb junction at 1°K. A field was applied to quench superconductivity. The figure was photographed from computer output (see text) and is not smoothed.

+27.5 mV, as shown in Fig. 8. The symmetry of the increases in conductance about $V=0$ is readily observed in this figure. The even conductance was calculated as before and is shown in Fig. 9. Its derivative, the barrier phonon density of states, is shown in Fig. 10. For comparison, we also show the same measurement for an Al-I-Pb junction and the $\alpha^2(\omega)F(\omega)$ [(coupling constant)$^2\times$phonon density] obtained from superconductor tunneling.[12,27] The peaks obtained from the normal tunneling appear to be slightly higher in energy than the phonon peaks in $\alpha^2(\omega)F(\omega)$. The superconducting measurement is essentially a determination of bulk properties of the Pb film; the normal-metal result reflects the properties of the surface. It is known that the interatomic forces in Pb are quite long range, and the disturbance of the surface may in fact extend a number of atomic layers into the film. Both the normal-metal barrier phonon densities in Fig. 9 show a peak at 2 mV. This could possibly be due to a hint of the superconducting energy gap remaining in the tunneling characteristic or could be a surface mode of vibration of the film. The surface of the film is not free as in a single film, however, but is adjacent (and probably diffused into) the lead oxide. At first sight, the normal-metal spectra of Fig. 9 bear a striking resemblance to the phonon spectrum calculated by Dickey and Paskin[29] for small, thin, disklike particles of metal. However, their calculations were made for a particle with free surfaces, and the low-energy mode they obtain is associated with the edge of the particle. The edges of our junctions are a negligible fraction of the total junction area, but if the films have a very rough surface such edge modes might be enhanced. It is also interesting to note that the main phonon peaks calculated for the free particles are at slightly lower energies than in the bulk. The normal-metal peaks of Fig. 9 move to slightly higher energies than the bulk, and one can speculate

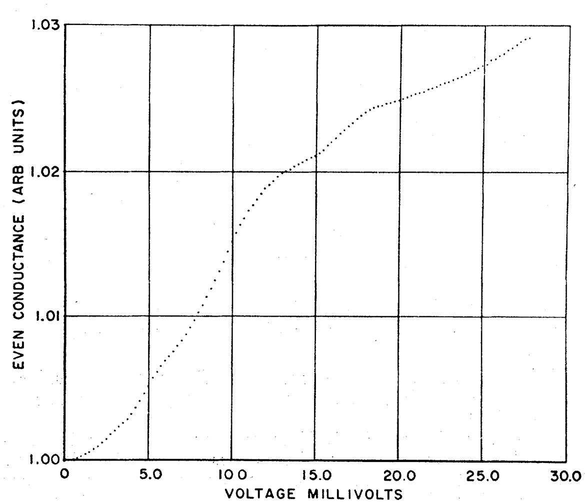

FIG. 9. The even conductance versus voltage for the Pb-I-Pb junction of Fig. 8.

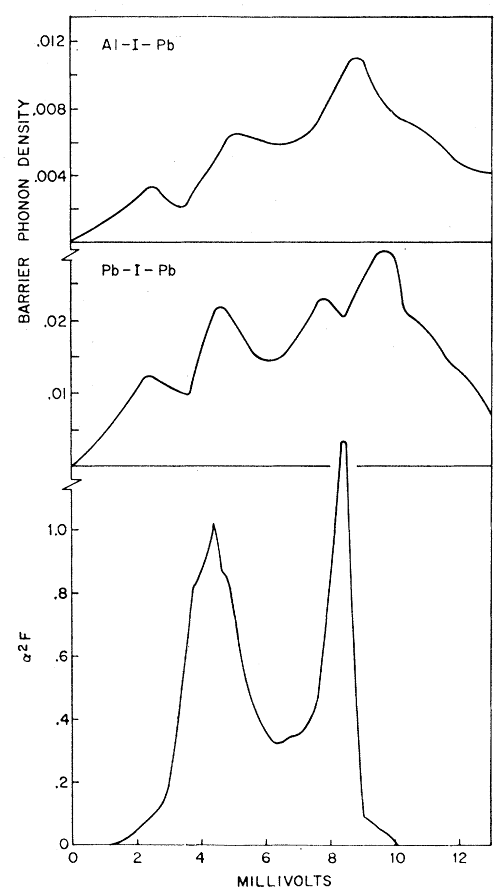

FIG. 10. The upper two plots are the barrier phonon density for Al-I-Pb and Pb-I-Pb junctions. The Pb-I-Pb result is the derivative of Fig. 9. The units of the vertical scale are $(\text{mV})^{-1}$. The lower plot is (coupling constant)$^2\times$phonon density for Pb from superconducting tunneling. The scale for $\alpha^2(\omega)F(\omega)$ is dimensionless.

[29] J. M. Dickey and Arthur Paskin, Phys. Rev. Letters **21**, 1441 (1968).

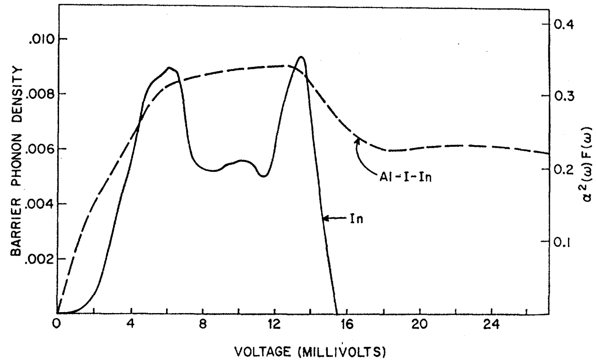

FIG. 11. Barrier phonon density versus voltage for an Al-I-In junction compared with $\alpha^2(\omega)F(\omega)$ for In from superconducting tunneling. Units of the left scale are $(\text{mV})^{-1}$.

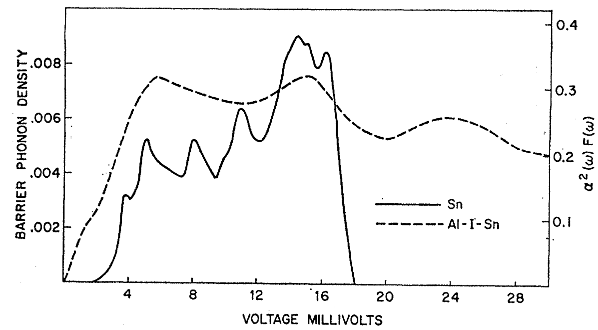

FIG. 12. Barrier phonon density versus voltage for an Al-I-Sn junction compared with $\alpha^2(\omega)F(\omega)$ for Sn from superconducting tunneling. Units of the left scale are $(\text{mV})^{-1}$.

whether a surface adjacent to a stiffer material (oxide) rather than softer material (vacuum) would show such an effect.[30]

We have extended this measurement of G^E, G^0, and dG^E/dV to a number of other junctions. We will not present the conductance data, as it is similar to the low-energy range of Fig. 8 except for shifts in the positions of the broad conductance increases. The barrier phonon density dG^E/dV contains the significant information and is shown in Fig. 11 for an Al-I-In junction and Fig. 12 for an Al-I-Sn junction. In both cases we have also plotted $\alpha^2F(\omega)$ determined from superconductor tunneling.[12] Although dG^E/dV is a much less detailed probe of the phonon density (partly due to the fact that normal-metal tunneling is always smeared by $\sim 3kT$) the agreement in the position of peaks in dG^E/dV and regions of high phonon density in $\alpha^2F(\omega)$ convinces us that the phonons of the metal films are indeed coupled into the tunneling process.

We can also measure a second type of junction involving tin films, namely, Sn-I-Sn. The derivative of the even conductance is shown in Fig. 13 and compared to that for an Al-I-Sn junction. Both seem to show a peak at $\sim$25 meV, which is well above the maximum frequency of phonons in bulk tin. One possible explanation is that this is due to a 2-phonon process but this does not seem to occur for any other metals. The derivative for the Sn-I-Sn junction has a negative peak at $\sim$1 mV. This is due to a small conductance-peak zero-bias anomaly ($\sim$0.2%), which we always observe in this type of junction.[31] The Al-I-Sn junction (and other aluinmum junctions) has weak structure from 30–40 mV, which corresponds to the energy of the longitudinal phonon peak in Al.[32]

Measurements of metal phonon densities using the derivative of the even conductance are not confined to materials which become superconducting. We show in Fig. 14 results for an Al-I-Bi junction at 2°K. The bismuth film was evaporated onto a substrate at room temperature in a vacuum $\sim 10^{-6}$ Torr. The majority of our Al-I-Bi junctions and those of others[33] show a strong dip in conductance at low voltages, with a minimum conductance at $V=0$. This dip is strong enough to obscure the phonon emission processes. The origin of this dip is not understood (it might arise from a charge depletion layer at the Bi surface), but its strength varies from sample to sample, and the junction of Fig. 14 had a relatively slowly changing conductance at low voltages. The derivative dG^E/dV shows clearly two peaks at 3.5

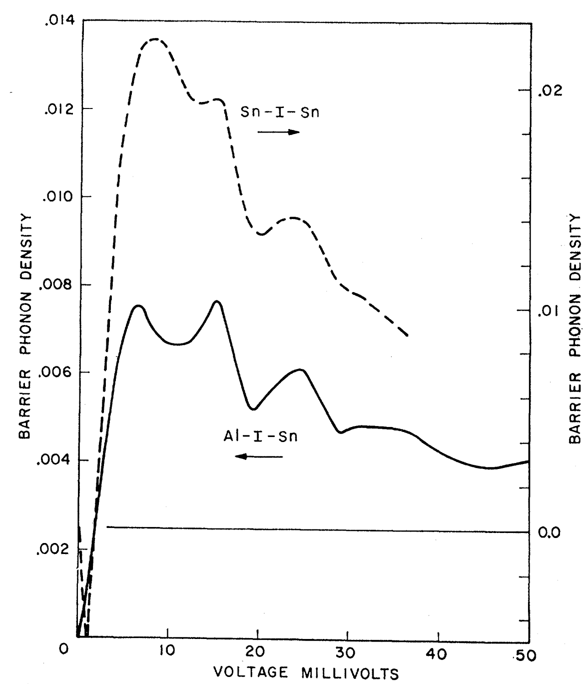

FIG. 13. Comparison of the barrier phonon density versus voltage obtained for Al-I-Sn with that for a Sn-I-Sn junction. Units of the vertical scales are $(\text{mV})^{-1}$, and the zeros are offset.

[30] We are indebted to the authors of Ref. 29 for a very interesting discussion of their work and its relevance to our data.

[31] J. M. Rowell and L. Y. L. Shen, Phys. Rev. Letters **17**, 15 (1966); L. Y. L. Shen and J. M. Rowell, Phys. Rev. **165**, 566 (1968).

[32] G. Gilat and R. M. Nicklow, Phys. Rev. **143**, 487 (1966).

[33] J. J. Hauser and L. R. Testardi, Phys. Rev. Letters **20**, 12 (1968); Y. Sawatari and M. Arai, J. Appl. Phys. (Japan) **7**, 560 (1968); L. Esaki, L. L. Chang, P. J. Stiles, D. F. O'Kane, and N. Wiser, Phys. Rev. **167**, 687 (1968).

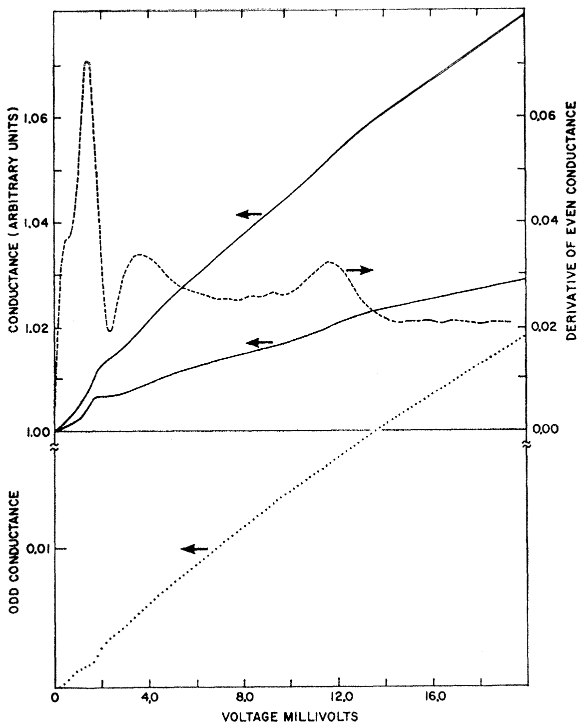

FIG. 14. Conductance (solid line), barrier phonon density (dashed line), and odd conductance (dotted) versus voltage for an Al-*I*-Bi junction at 2°K. Units of the right vertical scale are $(\mathrm{mV})^{-1}$.

and 12 mV, which correlate reasonably well with regions of high transverse and longitudinal phonon density in Bi deduced from neutron scattering experiments.[34] It is very interesting to note that the energy of this longitudinal phonon peak found from neutron scattering and normal-metal tunneling is appreciably higher than that which can be deduced at 9 meV from superconducting tunneling measurements of amorphous bismuth condensed at low temperatures.[35,36] This seems to suggest that the phonon spectrum of the amorphous phase is appreciably different from that of the bulk semimetal.

We also notice in Fig. 14 that the low-energy peak (~2 meV), which was resolved in Pb [there also seems to be structure at this energy in In (Fig. 11) and Sn (Fig. 12), but it is a shoulder in dG^E/dV rather than a peak], is very marked in Bi. This was present even at 4.2°K and cannot be due to traces of superconductivity in the Al or Bi films (unless the Bi was contaminated with a small amount of Pb, but this seems unlikely). It is also possible that this peak is associated with the dip in conductance at zero bias, which is usually strong in Al-*I*-Bi junctions. The odd conductance is also shown in Fig. 14 and also shows structure near 2 mV, with a very weak kink at 10 meV. This plot of the odd conductance should be a very sensitive way of locating band-edge structure in bismuth, and we conclude that this is not being observed in our polycrystalline films at low energies.

The magnitudes of the phonon emission peaks in the various metals (Figs. 10–12 and 14) is of interest. First, we note that, as should be expected, the peaks are approximately twice as large for symmetrical junctions (Pb-*I*-Pb and Sn-*I*-Sn) as they are for asymmetrical junctions (Al-*I*-Pb and Al-*I*-Sn). Confining ourselves to the junctions using aluminum, if we subtract the magnitude of dG^E/dV at energies ~50% greater than the longitudinal peak from its maximum value at the longitudinal peak, we obtain for the strength of the emission processes in Bi ~0.013 mV^{-1}, in Pb ~0.007 mV^{-1}, in In ~0.0032 mV^{-1}, and in Sn ~0.0027 mV^{-1}. It is clear that these magnitudes scale roughly with the electron-phonon coupling strength for the superconducting materials. One would also expect the strength to scale with the skin depth of the metal, in that this is a measure of the volume of electrode that can be affected by the electric field set up by an electron as it tunnels. This factor probably accounts for the strong effect in bismuth.

VII. ODD TERM G^0

As we pointed out earlier, the odd term G^0 is a convenient way to study processes which are asymmetrical

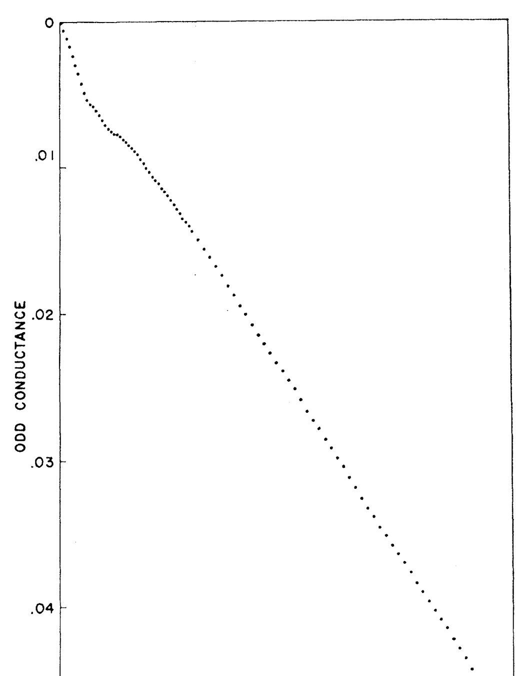

FIG. 15. Odd conductance versus voltage for a Pb-*I*-Pb junction in the normal state at 1°K. (From the data of Fig. 5.)

[34] J. L. Yarnell, J. L. Warren, R. G. Wenzel, and S. H. Koenig, IBM J. Res. Develop. **8**, 234 (1964).

[35] N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **5**, 434 (1967) [English trans.: Soviet Phys.—JETP Letters **5**, 352 (1967)].

[36] J. T. Chen, T. T. Chen, J. D. Leslie, and H. J. T. Smith, Phys. Letters **25A**, 679 (1967).

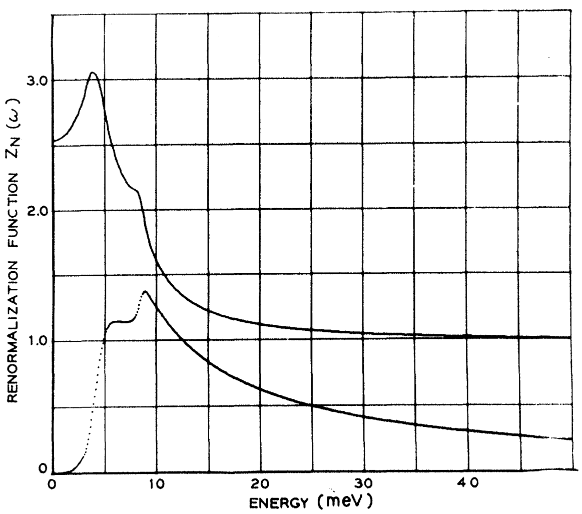

FIG. 16. Energy dependence of the renormalization function $Z_N(\omega)$ for Pb as calculated from superconducting tunneling. The upper and lower plots are the real and imaginary parts, respectively. The self-energy is $[\mathrm{Re}Z_N(\omega)-1]E$.

in conductance about $V=0$. We also expected only the small odd terms from the barrier background conductance to contribute to this term. The odd conductance, calculated from the data of Fig. 5, is shown in Fig. 15. The first encouraging feature is that the excitation processes from 30–60 mV are completely absent from this plot, showing they are exactly symmetrical about $V=0$. However, there is a weak structure in the odd term which extends over the range of energy corresponding to high phonon density in Pb (0–10 mV).

As we have mentioned before,[8] we believe this arises from a weak reflection of the self-energy of the electrons in Pb in the tunneling characteristic. Such a mechanism has been considered independently by Hermann and Schmid.[37] Summarizing their calculation, they point out that there are two assumptions normally made in calculations of tunneling currents which should be reexamined. The most serious of these appears to be that the tunneling matrix element does not depend on momentum $|T(p_1,p_2')|^2=T^2$. (p_1 is the momentum of an electron in metal 1, p_2' that in metal 2.) They show that for electrons near the Fermi level,

$$|T(p_1,p_2')|^2=|T|^2\{1+\alpha[(\epsilon_p+\epsilon_{p'})/\mu]\}, \qquad (3)$$

where $\epsilon_{p'}$ is the free-electron energy in metal 2, μ is the Fermi energy, and

$$\alpha=\tfrac{1}{2}dp_F/\hbar(\mu/\bar{\varphi})^{1/2}\sim 30,$$

p_F being the Fermi momentum.

The second assumption is that the self-energy is also independent of momentum, $\Sigma(p,E)=\Sigma(E)$. They consider that the momentum-dependent part of Σ will also be of order ϵ_p/μ but will not involve such a large coefficient as $\alpha\sim 30$. Calculating the tunneling conductance at $T=0$ with $\Sigma(E)$ independent of momentum but with $|T(p_1,p_2')|^2$ given by (3), they obtain

$$G=G_0[1-\alpha\Sigma_1'(eV)/\mu-\alpha\Sigma_2'(-eV)/\mu], \qquad (4)$$

where G_0 is the conductance neglecting the momentum dependence of $|T|^2$ and $\Sigma_1'(eV)$ is the real part of the self-energy for the electron in metal 1. The bias dependence of G_0 is ignored. To evaluate (4) for normal-metal tunneling, we can use the self-energy determined from superconducting tunneling.[12] We have

$$\Sigma=[Z_N(E)-1]E, \qquad (5)$$

where $Z_N(E)$ is the renormalization function which is shown in Fig. 16 for Pb. The self-energy Σ is an odd function of energy about the Fermi level. If we measured a tunnel junction M-I-Pb with M a metal with negligible self-energy effects (very weak electron-phonon coupling—Al, say), then we would have

$$G^+(V)=G_0[1-\alpha\Sigma_{\mathrm{Pb}}'(eV)/\mu],$$
$$G^-(V)=G_0[1-\alpha\Sigma_{\mathrm{Pb}}'(-eV)/\mu],$$

and the odd conductance

$$G^0(V)=\tfrac{1}{2}[G^+(V)-G^-(V)]=(G_0\alpha/\mu)\Sigma_{\mathrm{Pb}}'(eV). \qquad (6)$$

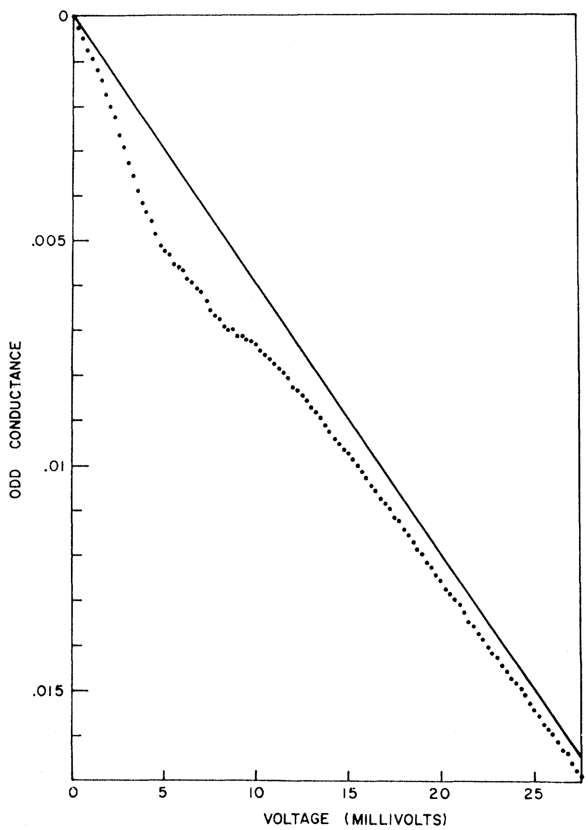

FIG. 17. Odd conductance versus voltage for a Pb-I-Pb junction at 1°K (points). (From the data of Fig. 8.) The straight line is an estimate of the odd conductance in the absence of self-energy effects.

[37] Helmut Hermann and Albert Schmid, Z. Physik 211, 313 (1968).

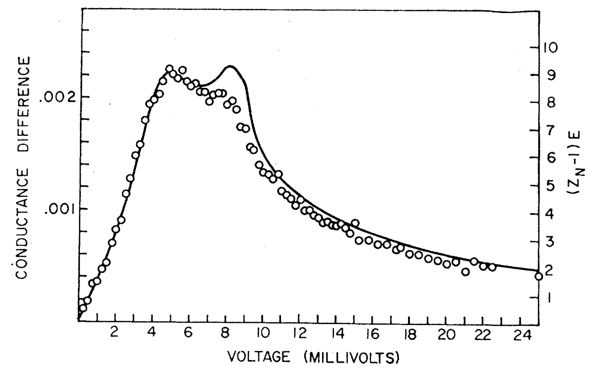

FIG. 18. Comparison of self-energy effects in normal-metal tunneling with the self-energy of Pb found from superconducting tunneling. The circles are the difference between the odd conductance and the straight line of Fig. 17. The solid line is the energy dependence of the self-energy in Pb.

Thus, within the approximation mentioned above, the odd conductance reflects directly the energy dependence of the self-energy.

As pointed out by Hermann and Schmid, for a Pb-I-Pb junction the self-energy effects should disappear as $\alpha\Sigma_1'(eV)=-\alpha\Sigma_2'(-eV)$. However, we have shown (Fig. 4) that Pb-I-Pb junctions have G-versus-V plots, which are asymmetrical about $V=0$. This leads[24] to a modification of the expression (4) to

$$G=G_0[1-\alpha_1\Sigma_1'(eV)/\mu-\alpha_2\Sigma_2'(-eV)/\mu], \quad (7)$$

with $\alpha_1\neq\alpha_2$. Thus, the odd conductance is

$$\begin{aligned} G^0(V)&=(G_0/\mu)(\alpha_2-\alpha_1)[\Sigma'(eV)] \\ &=(G_0/\mu)(\alpha_2-\alpha_1)\{[Z_N(E)-1]E\}. \quad (8) \end{aligned}$$

Returning to Fig. 15, we can see that it is only the deviations from a linear odd conductance which can be explained by self-energy corrections, the much larger linear term being a contribution from the asymmetrical barrier shape. This low-energy region is shown in more detail in Fig. 17, where the straight line represents an estimate of the odd term in the absence of self-energy effects. The difference in measured conductance from this straight line should be proportional to $[Z_N(E)-1]E$. This difference in conductance is compared with the calculated self-energy in Fig. 18. The agreement is obviously better than one has any right to expect. In particular, the superconducting measurement essentially determines $Z_N(E)$ for the bulk material, whereas the normal tunneling is affected by only the first few layers of atoms at the oxide-lead interface. The agreement of Fig. 18 is "adjustable" to some extent by the choice of the straight line in Fig. 17. To estimate $\alpha_2-\alpha_1$ we note that at 6 mV we have $G^0(V)/G_0=0.0021$, $\mu\sim10$ V, $[Z_N(E)-1]E=8.6$ meV, which gives $\alpha_2-\alpha_1\sim2.5$. In view of this rather small effective value for α, the neglect of the momentum-dependent part of Σ should possibly be reexamined. Our measurements of Al-I-Pb junctions give an odd term of similar shape, with $G^0(V)/G_0=0.007$ at 6 mV, or $\alpha\sim1$, again appreciably smaller than estimated by Hermann and Schmid.

VIII. SUMMARY

In this paper we have outlined the conductance-versus-voltage behavior for junctions which may be regarded as typical of those prepared by thermal oxidation. We have purposely avoided any discussion of junctions which exhibit zero-bias anomalies[6,31] or those where intentional doping is added to the oxide layer.[38]

We have shown that the ideal behavior in the intermediate-voltage range appears to be a roughly parabolic dependence of G on V, with the parabola offset from $V=0$. This in itself is an uninteresting result but when one considers the effort expended recently on "anomalous" tunneling[6,7,31,33,38] it is surprising that it has been possible to ignore any understanding of the "nonanomalous" conductance for so long. It appears to us that the appearance of this parabolic dependence is reasonable evidence for the presence of tunneling up to reasonably large voltages, especially when combined with a check of the superconducting energy gap near $V=0$. It also implies that junctions showing very different behavior, for example, $G\propto|V|$ for chromium oxide and doped junctions,[31,38] must be first suspected of having a large nontunneling current. The superconducting density of states can be used to establish the predominance of tunneling, at least for low voltages, but at higher voltages (30 mV–1 V) the claim to be observing tunneling is based on weak inference rather than proof.

We have reported that rather small ($\sim1\%$) deviations from the parabolic conductance behavior are the result of interactions of the tunneling electron with impurities in the oxide, the oxide itself, or the surface layers of the metal films adjacent to the oxide. These emission processes can be studied conveniently by calculating the even conductance and its derivative. This derivative, at low voltages, is a crude measurement of the phonon density on the normal metal, but the value of this determination is overshadowed by the superconducting technique,[12,27] which is a much more sensitive probe of normal-metal properties. Our most important result is that the odd conductance is independent of emission processes but does reflect self-energy effects in the normal metal. This offers fascinating possibilities when applied to metals where the electron has strong interactions with excitations other than phonons.

ACKNOWLEDGMENTS

We would like to thank W. F. Brinkman, R. C. Dynes, and L. Y. L. Shen for many helpful discussions.

[38] F. Mezei, Phys. Letters **25A**, 534 (1967); A. F. G. Wyatt and D. J. Lythall, *ibid.* **25A**, 541 (1967); D. J. Lythall and A. F. G. Wyatt, Phys. Rev. Letters **20**, 1361 (1968); I. Giaever and H. R. Zeller, *ibid.* **20**, 1504 (1968).