Zero-Bias Tunneling Anomalies—Temperature, Voltage, and Magnetic Field Dependence

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The change of the "zero-bias tunneling anomaly" in Ta-I-Al, Sn-I-Sn, and silicon p-n junctions in magnetic fields of 0–40 kG has been measured from 4.2 to 1°K (I = insulator). The strongest magnetic field dependence was observed in Sn-I-Sn junctions, where the conductance peak is depressed and splits into two peaks when the field increases from 0 to 40 kG at 1.5°K. The results have been compared with the theoretical model proposed by Appelbaum and Anderson, who calculated the interaction between the tunneling electrons and magnetic impurities at and near the boundary of the insulating layer. The data indicate that the second-order term in the theory is sufficient to fit the magnetic field dependence, and the third-order term fits the conductance peak at zero bias. Measurements in a magnetic field thus determine the g and S values of the magnetic impurities. We have found that the number of impurities trapped inside Sn-I-Sn junctions can vary with the method of preparation. The magnitude of the zero-bias anomaly, the superconducting I-V characteristics for $V<2\Delta_0$, and the background conductance at very high bias are all affected by the number of impurities present. Giant anomalies in Cr-I-Ag and Cr-I-Pb junctions illustrate a different effect in which a very strong field-independent conductance dip is observed at zero bias. We conclude that small conductance peaks are explained by the Appelbaum-Anderson model, but the giant resistance anomalies are unexplained at present.

I. INTRODUCTION

TUNNELING between two electrodes through a thin insulating layer has been the subject of numerous investigations since interest in the field was stimulated by Fisher and Giaever[1] in 1960. In general, the dependence of the tunneling current (I) on applied bias (V) is reasonably well understood; at low voltage I is proportional to V, and at high voltages I depends exponentially on V. Deviations from this simple behavior are becoming more common as derivative techniques (measurement of dI/dV versus V or d^2I/dV^2 versus V) are applied to the study of the I-V characteristics. For example, it is well known that in semiconductor p-n tunnel diodes at low temperatures the conservation of energy and momentum for the tunneling electron involves the emission of a phonon, and important studies[2–5] of the semiconductor lattice vibrations have been carried out by measurement of the resulting structure in the I-V characteristic. This phonon emission can result in diode conductance changes of $\sim$100%. In a rather analogous way (although the momentum of the carriers is not so restricted on the two sides of the barrier) electrons tunneling between metal films have been shown to excite vibrations of impurities in the oxide layer.[6] The frequencies of these vibrations correspond to biases in the range from 100 to 500 mV and conductance changes are $\sim$1%. Below 100 mV similar effects have been ascribed to vibrations of the oxide itself[6,7] or of the surface layers of the metal films.[7] Again the conductance increases are $\sim$1%. In this paper we wish to discuss a rather different type of tunneling anomaly which is observed as a peak or dip in conductance located symmetrically about zero bias, is typically about 1 mV wide, and is approximately a 10% conductance change at 1°K.

This "zero-bias anomaly" was first observed by Hall *et al.*[8] in 1960, who observed that in tunneling in III–V semiconductor diodes at 4.2°K a rather narrow dip in conductance was located at zero bias and that this dip could be an appreciable fraction of the conductance at zero bias. In 1962 Chynoweth *et al.*[3] reported a zero-bias conductance peak in silicon p-n junctions. Further work by Logan[9] showed that this peak was typical of heavily doped diodes and that lightly doped diodes exhibited a dip in conductance rather than a peak.

The discovery of similar zero-bias anomalies in tunneling through oxide layers between normal metal electrodes was made by Wyatt,[10] in 1964. In junctions made with niobium or tantalum as one electrode, the thermally grown oxide of the transition metal as the insulator and aluminum as the second electrode, he observed a conductance peak at zero bias which was 10–20% of the total conductance, compared to the 5% effect in silicon p-n diodes. He showed that the conductance depended logarithmically on voltage (for $eV\gg kT$) and that the conductance at zero bias depended logarithmically on temperature. A logarithmic

[1] J. C. Fisher and I. Giaever, J. Appl. Phys. **32**, 172 (1961).
[2] R. N. Hall, in *Proceedings of the International Conference on Semiconductor Physics* (Academic Press Inc., New York, 1961), p. 193.
[3] A. G. Chynoweth, R. A. Logan, and D. E. Thomas, Phys. Rev. **125**, 877 (1962).
[4] R. A. Logan, J. M. Rowell, and F. A. Trumbore, Phys. Rev. **136**, A1751 (1964).
[5] R. T. Payne, Phys. Rev. **139**, A570 (1965).
[6] R. C. Jacklevic and J. Lambe, Phys. Rev. Letters **17**, 1139 (1966).
[7] J. M. Rowell and W. L. McMillan, Bull. Am. Phys. Soc. **12**, 77 (1967).
[8] R. N. Hall, J. H. Racatte, and G. Ehrenreich, Phys. Rev. Letters **4**, 456 (1960). See also Ref. 2.
[9] R. A. Logan (private communication).
[10] A. F. G. Wyatt, Phys. Rev. Letters **13**, 401 (1964).

singularity in the electron density of states at the Fermi level of the transition metal was postulated to explain these results. Anderson[11] suggested, however, that a more likely explanation was the scattering of electrons by surface states at the metal-metal-oxide interface, or by magnetic impurities in the oxide. Independently, Kim[12] calculated the effect of magnetic spin-flip scattering in the oxide and obtained a logarithmic term in conductance, but to order T^4, where T is the tunneling matrix element. As the ordinary tunneling current is to order T^2, it would appear impossible to observe a T^4 term.

Further experiments[13] led us to believe that the magnitude of the conductance peak in these metal junctions depends strongly on the tantalum (niobium) surface preparation, on the oxidation procedure, and on the second electrode, but that it is relatively independent of junction resistance (i.e., oxide thickness). It appeared that the anomalous tunneling term must, therefore, also appear to order T^2 and should arise from properties of the oxide or metal–metal-oxide interface. We also reported that this zero-bias conductance peak anomaly is rather common in other oxide junctions and is not confined to transition-metal oxides only.

In 1964 a minimum in the temperature dependence of the resistivity of dilute magnetic alloys (eg., Au–Fe, Rh–Re) was explained by Kondo.[14] He calculated the *s-d* scattering of the conduction electrons by the localized magnetic impurities and obtained a term in the resistivity proportional to $-\ln T$, an increasing contribution at low temperatures. This treatment of the scattering problem was later extended to tunneling by Appelbaum,[15] who assumed that, in junctions showing zero-bias anomalies, magnetic impurities were localized at the metal–metal-oxide interface. Appelbaum found a logarithmic conductance term of order T^2J (where J is an exchange scattering amplitude) and also predicted the magnetic field dependence of the zero-bias anomaly.

In this paper we present recent experimental results and make a detailed comparison with Appelbaum's theory. In particular the magnetic field dependence of the conductance peak gives strong support to this magnetic scattering model. Finally, we discuss "giant anomalies,"[13] which appear to be a separate problem not yet understood.

II. EXPERIMENT

A. Junction Preparation

Although the techniques used for the preparation of tunnel junctions are by now well known, it seems important to outline our procedures because rather large changes in the magnitude of the zero-bias anomaly can be produced by variations in method. We will discuss only Sn-*I*-Sn and transition-metal junctions. These are typical of junctions made on films and bulk material.

1. Sn-I-Sn Junctions

A sapphire substrate (2.5×0.8 cm) is cleaned by washing successively in detergent, distilled water, and acetone. Evaporation of tin wire (99.9%) is from a molybdenum or tantalum boat 10 cm below the substrate at a pressure of 10^{-6} Torr. To avoid agglomeration the tin film (2000 Å) is evaporated in approximately 6 sec, the substrate being at room temperature before evaporation. The evaporator is vented with air drawn directly from the laboratory, and the tin film is transferred to a glass tube under a heat lamp which produces a substrate temperature of approximately 110°C. A flow of air, also drawn from the laboratory, is maintained down the tube. Oxidation of the film in this way takes about 12 h. After replacing the film in the evaporator, five crossing tin films are evaporated using the same source and procedure as for the first film. The resulting junctions are typically 2×10^{-4} cm^2 in area and have resistances between 10 and 50 Ω. Oxidation in an oxygen flow instead of air results in resistances ~1 Ω. Electrical contacts to both ends of all the films are made by soldering fine gold wires directly to the films using indium. The mounted junctions are immersed directly into liquid nitrogen as soon as possible and into liquid helium without any attempt to minimize thermal shocks.

2. Transition-Metal Junctions—Typically Tantalum

The main difficulty in preparing junctions on bulk material is in obtaining a contamination-free surface.[16] A tantalum single-crystal slice or polycrystalline sheet is first mechanically polished, then chemically etched in a mixture of hydrofluoric and nitric acids, and finally rinsed with distilled water and alcohol. After this, and before any intentional oxidation of the surface, we find that the tantalum always has an insulating layer of unknown material which produces junctions of very high resistance ($\gtrsim$1 MΩ). In order to remove this surface layer, three methods are used.

(i) The tantalum is heated to 200°C in a 10^{-6} Torr oil-pump vacuum system. This appears to remove part of the surface layer so that lower resistance junctions can be made, but the tantalum becomes contaminated near the surface. This is apparent from the *I-V* characteristics of the junctions with the tantalum superconducting, as has been discussed by Townsend and Sutton.[16] One observes a large temperature-independent current flowing for $V<\Delta$ and often not even a hint of the tantalum gap, although by using a Pb counter

[11] P. W. Anderson (private communication).
[12] D. J. Kim, Phys. Letters **18**, 215 (1965).
[13] J. M. Rowell and L. Y. L. Shen, Phys. Rev. Letters **17**, 15 (1966).
[14] J. Kondo, Progr. Theoret, Phys. (Kyoto) **32**, 37 (1964).
[15] J. Appelbaum, Phys. Rev. Letters **17**, 91 (1966); Phys. Rev. **154**, 633 (1967).
[16] P. Townsend and J. Sutton, Phys. Rev. **128**, 591 (1962).

TABLE I. The effect of junction preparations on the magnitude of zero-bias conductance peak.

Junction	Treatment	Peak magnitude (%)
Ta-I-Al	Argon sputter	10–20
Ta-I-Ag	Argon sputter	<0.2
Ta-I-Pb	Argon sputter	10–20
Ta-I-Pb	1700°C in 2×10^{-8} Torr	<0.2
Nb-I-Al	2000°C in 10^{-9} Torr	14
Nb-I-Ag	2000°C in 10^{-9} Torr	14
Mg-I-Pb	Film	20
Silicon p-n	$n>5\times10^{19}$	5
Sn-I-Sn	Film	0.2–7
Al-I-Sn	Film	$<10^{-2}$

electrode one may be convinced that a tunnel junction has been made.

(ii) The etched Ta is placed in a 10^{-9} Torr ion-pump system and heated close to its melting point for 24 h. After cooling, the system is vented to air and the oxidation of the tantalum is accomplished by leaving in air at room temperature for 24 h. This method produces junctions with the best superconducting gap characteristics and very small zero-bias anomalies in the normal state.

(iii) A sputtering technique is also used to clean the etched metal. The Ta slice is placed on a tantalum cathode in a stainless-steel can.[17] A discharge for $\frac{1}{2}$ h in 0.2 Torr of argon at 1500 V bombards the tantalum with argon and efficiently removes the surface layers. The oxide in this case is produced (after cooling and removal from the sputtering can) by heating the Ta to 50°C in an oxygen stream for about 12 h. Junctions produced in this way are not ideal for superconducting studies, having I-V characteristics better than the junctions produced by method (i) though not as good as those of (ii), but they have large reproducible zero-bias anomalies.

After preparing the Ta and its insulating layer by one of the methods outlined above the surface is insulated by collodion except for a narrow stripe down the center of the sample. A second electrode of Ag, for example, is evaporated as crossing stripes in an oil diffusion pump vacuum system at 10^{-6} Torr. Contact to the Ag films is made with indium solder. Gallium contact areas are rubbed onto the tantalum ultrasonically and indium solder again used to attach leads.

B. Derivative Measurements

The I-V characteristic for the junction is traced on an X-Y recorder and, as mentioned above, this measurement with the junction superconducting can be very useful in estimating the state of the tantalum surface.

The first derivative dV/dI (from which the conductance $G=dI/dV$ is obtained) is measured by applying a 500-cps constant-current modulation to the dc voltage drive. The resulting voltage signal on the junction is measured with a lock-in amplifier and displayed versus dc bias on the recorder. When the zero-bias anomaly is small and measurements are required as a function of temperature and magnetic field, drift in the equipment can be a problem. In this case, a bridge circuit[18] gives much better stability and has been used for most of this work.

III. RESULTS AND DISCUSSION

A. Importance of the Oxide

In order to work at low temperatures (<4.2°K) and yet with the metals in the normal state, a magnetic field must be applied to the junction. In practice, we increase the field and monitor the conductance near zero bias until the last trace of a superconducting gap characteristic disappears. At this field the conductance-versus-voltage plot for tantalum is typically as shown in Fig. 1. The zero-bias anomaly is seen as the small conductance peak exactly at zero bias which increases the conductance locally by 15%. This is superposed on a background conductance which is not constant but which increases appreciably from 0 to 80 mV, as will be discussed later. The dependence of the magnitude of the zero-bias anomaly on the surface preparation, oxidation procedure, and counter electrode has already been pointed out,[13] but it seems worthwhile to discuss the few selected pairs of junctions summarized in Table I.

If tantalum junctions are made using method (iii) above, we consistently find that an aluminum electrode gives a 10–20% anomaly but silver only 0.2% at at 1°K. As mentioned above and shown in the second pair of Ta junctions in Table I, the anomaly is greatly reduced when the surface preparation of the tantalum

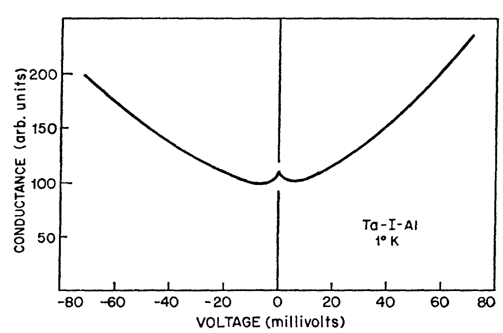

FIG. 1. Dynamic conductance versus voltage for a Ta-I-Al junction at 1°K. A field of 3 kG was used to keep the tantalum normal.

[17] H. C. Theuerer and J. J. Hauser, J. Appl. Phys. 35, 554 (1964).

[18] J. M. Rowell, in *Treatise on Superconductivity*, edited by R. D. Parks (to be published by Marcel Dekker Inc., New York).

is a high-vacuum outgas rather than an argon sputter. In the case of niobium we find no reduction of the anomaly when using silver rather than Al and even an outgas at 2000°C in 10^{-9} Torr gives a niobium surface which yields a 14% zero-bias anomaly after oxidation. The tin oxide in Sn-I-Sn junctions is clearly shown to be responsible for the zero-bias anomaly when one notices that an Al-I-Sn junction shows no anomaly, hence eliminating any properties of the tin film itself.

B. Appelbaum Magnetic Scattering Model

Tunneling between normal metals has been considered by Harrison[19] using the WKB approximation, and by Cohen, Falicov, and Phillips[20] using the tunneling Hamiltonian. They showed that the conductance is proportional to $T^2\rho^A\rho^B$, where T is the tunneling matrix element and ρ^A and ρ^B are the density of electron states of metals A and B on each side of the junction. Unfortunately for the experimentalist, T^2 contains the electron velocities normal to the barrier which cancel ρ^A and ρ^B in the conductance expression; hence, as pointed out by Harrison,[19] density-of-states effects cannot be observed in normal-metal tunneling except possibly when the change in ρ with energy is very rapid. A change that would explain the zero-bias anomaly is not likely in a normal metal near its Fermi surface. Following the suggestion of Anderson that magnetic scattering in the oxide may be important, Appelbaum[15] considered tunneling through an insulator in which a number (N_a) of noninteracting magnetic impurities are localized, particularly near the metal–metal-oxide interface. A slightly oversimplified picture of the Appelbaum model is obtained by considering the available paths an electron can take from metal A to metal B, as shown in Fig. 2. First, the electron can tunnel from A to B without any interaction with the impurity. This conductance would be proportional to T^2. Second, the electron can scatter from the impurity without spin exchange; this conductance would be a $T_a{}^2$ term, using Appelbaum's notation. As both the T^2 and $T_a{}^2$ terms are independent of magnetic field, they combine into a nonmagnetic conductance $G^{(1)}$ described by $(T+T_a)^2$. A more interesting scattering is that involving spin exchange between the impurity and the electron as it tunnels from A to B; obviously, impurities anywhere in the oxide contribute to this process. This leads to a background conductance $G^{(2)}$ which is sensitive to magnetic field but independent of voltage in zero magnetic field. The electron in A as it approaches the barrier can also be scattered back into A by the exchange interaction J; as discussed by Anderson,[21] J will only be large for impurities located near the interface. The reflected electron wave interferes with the transmitted $(T_J{}^2)$ wave and produces the anomalous logarithmic term $G^{(3)}$ in the tunneling conductance. This term appears to order $T_J{}^2J$, and its magnitude has been discussed by Anderson and Appelbaum. The total conductance is the sum of the three different contributions[22]

$$G=G^{(1)}+G^{(2)}+G^{(3)}. \qquad (1)$$

All the conductance terms containing T_a, T_J, or J should be multiplied by N_a, but this will be omitted from this discussion. The striking feature of the conductance plot in zero magnetic fields is of course the anomalous $G^{(3)}$ term which for $H=0$ and $|eV|$ much different from kT can be written

$$G^{(3)}=-CT_J{}^2J\rho^A\rho^B(\rho^A+\rho^B)S(S+1) \times \ln[(|eV|+nkT/E_0], \qquad (2)$$

where C is a constant, S the spin of the localized state, and E_0 an energy cutoff. The constant n is given by

$$\ln(n)=\iint_{-\infty}^{+\infty}\ln|x-x'|\frac{df}{dx}\frac{df}{dx'}dx\,dx', \qquad (3)$$

where f is the Fermi function. Appelbaum[23] has calculated $n=1.35$.

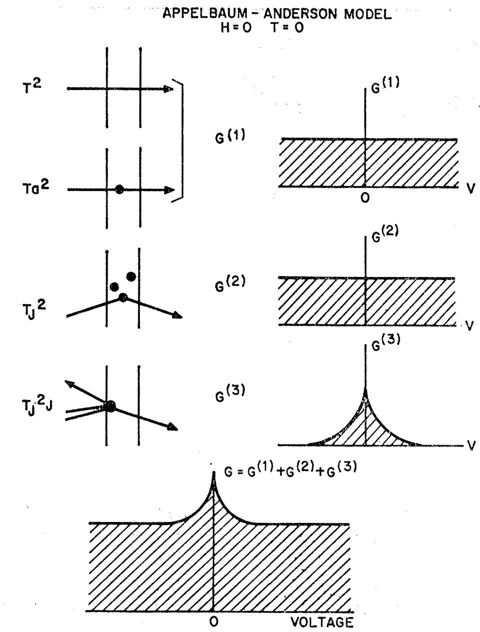

FIG. 2. Schematic drawings of the different processes that contribute to the theoretical conductance of the Appelbaum model. The magnetic impurities are represented by black dots inside the insulating barriers. The scattering of the tunneling electrons is represented by arrows on the left, the resulting conductances are shown on the right, and the total conductance is at the bottom.

[19] W. A. Harrison, Phys. Rev. **123,** 85 (1961).
[20] M. H. Cohen, L. M. Falicov, and J. C. Phillips, Phys. Rev. Letters **8,** 316 (1962).
[21] P. W. Anderson, Phys. Rev. Letters **11,** 95 (1966).
[22] This notation is close to that used by Appelbaum [Phys. Rev. **154,** 633 (1967)] and differs only in that our $G^{(1)}+G^{(2)}$ equals Appelbaum's $G^{(2)}$. Comparison of this notation with those used earlier [Refs. 10, 13, 15, and J. Appelbaum *et al.* Phys. Rev. **160,** 554 (1967)] is left as an exercise for the readers.
[23] J. Appelbaum (private communication).

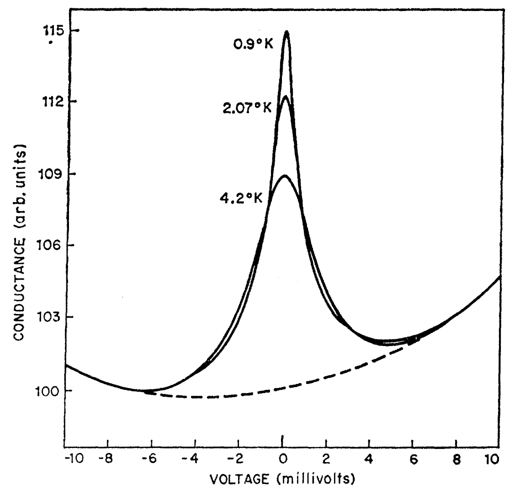

FIG. 3. The temperature dependence of a Ta-I-Al junction as shown on a G-versus-V plot. The applied magnetic field is 3 kG.

Before considering the effect of high magnetic fields on the exchange tunneling, we will discuss the observation of the $G^{(3)}$ term in low fields.

C. Low Magnetic Fields—Temperature and Voltage Dependence of the Peak

The dependence of conductance near zero bias at three temperatures is shown in Fig. 3 for a Ta-I-Al junction. The dashed line is an estimate of the conductance in the absence of the anomaly and is simply an extrapolation from the high biases of Fig. 1; it is difficult to improve on this rather arbitrary estimate of the background conductance. It was pointed out by Wyatt[10] that the conductance at zero bias depended on temperature as $-\ln T$ and that the voltage dependence of the excess anomalous conductance above the background was (for $eV \gg kT$) also logarithmic. This excess logarithmic conductance is identified with the $G^{(3)}$ term discussed above. A plot of the voltage dependence of $G^{(3)}(V)$ at 1°K and the temperature dependence of $G^{(3)}(0)$ is shown in Fig. 4. The solid line is the voltage dependence; it drops below a linear logarithmic plot at low voltages because of kT smearing. If in the expression (2) above $n=1$, the temperature dependence of $G^{(3)}(0)$ would fit on the voltage dependence of $G^{(3)}(V)$ for $eV \gg kT$. From the displacement of the temperature points, we infer in fact that $n=1.5\pm0.15$ for both Ta-I-Al and Sn-I-Sn junctions. Recent numerical calculations by Appelbaum[23] give $n=1.35$, whereas the earlier phenomenological model used by Wyatt[10] gave $n=1.1$, and the interpolation formula previously used by Appelbaum[15] had n put equal to 1.0.

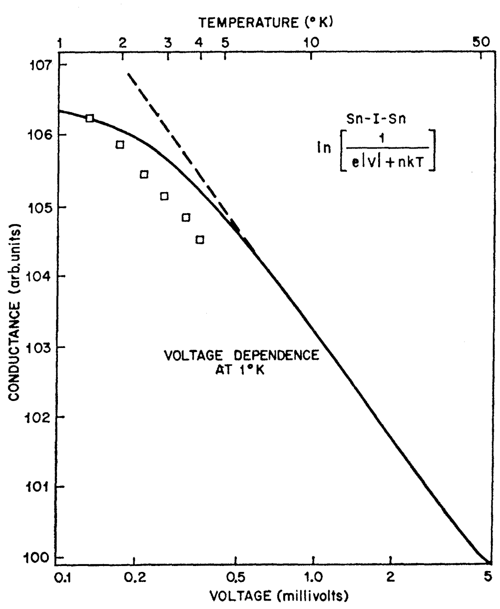

FIG. 4. The temperature dependence of $G^{(3)}(0)$ and the voltage dependence of $G^{(3)}(V)$ at 1°K for a Sn-I-Sn junction. $G(0)$ is plotted against $\ln T$ on the upper abcissa, and $G(V)$ is plotted against $\ln V$ on the lower abcissa. The value of eV is made equal to kT on this plot. A similar plot is obtained for Ta-I-Al junctions.

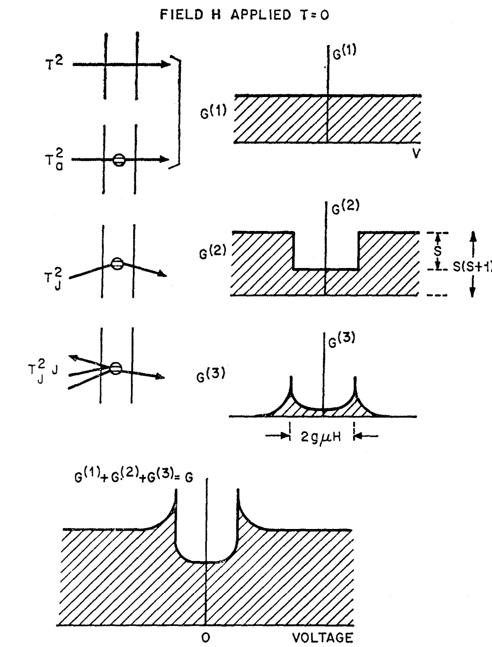

FIG. 5. Schematic drawings of the same processes of Fig. 2 under the influence of an external field. A Zeeman splitting is produced on the impurity spins which are represented by open circles on the left. The corresponding conductances are shown on the right. The total conductance is shown on the bottom.

D. High Magnetic Fields

A critical test of the theory is to investigate the predictions made by Appelbaum for the effect of magnetic field on the tunnel current. Here it is useful to consider again the simple model used in A above and shown in Fig. 5. The $(T+T_a)^2$ term ($G^{(1)}$) does not involve spin exchange and hence is expected to be independent of magnetic field. We checked for any possible magnetoresistance effects in an Al-I-Pb junction (i.e., one not displaying an anomaly) and found no change in conductance to 1 part in 10^4 for fields from 5 to 40 kG.

The T_J^2 term ($G^{(2)}$) is strongly affected by a magnetic field. This is realized rather simply by considering the splitting of the Zeeman levels of the impurity. If the tunneling electron flips the spin of the impurity, it must exchange the energy $g\mu H$ necessary to leave the impurity in an excited state. Because the tunneling electron must still arrive at an unoccupied state in metal B (i.e., above the Fermi level as we are considered $T=0$), this process can only occur for

$$|eV|\geq g\mu H.$$

Thus one expects a well (Fig. 5) in the $G^{(2)}$ term of width $2g\mu H$. If all the electrons flipped their spins and the spin of the impurity upon scattering from metal A to B, we would expect $G^{(2)}=0$ for $|eV|<g\mu H$. In fact only $S/S(S+1)$ of the electrons spin-flip; the remainder exchange spin with the impurity in a virtual intermediate state, but from metal A to metal B the spin is not changed. This has been discussed in some detail by Appelbaum[15] and by Kondo.[14] Thus the maximum depression of the $G^{(2)}$ term is for spin-$\frac{1}{2}$ impurities, where $G^{(2)}$ in a large field will be $\frac{1}{3}$ of $G^{(2)}$ in zero field for $|eV|<g\mu H$.

The effect of field on the $G^{(3)}$ term is harder to visualize physically. Appelbaum has shown that the logarithmic peak will be split into two peaks separated by $2g\mu H$. Thus, if $G=G^{(1)}+G^{(2)}+G^{(3)}$ were measured at zero temperature, we would expect the logarithmic peak in zero field to change to a well of width $2g\mu H$ with side peaks as the field is applied, as shown in Fig. 5.

Measurements of the magnetic field effect were made in a superconducting solenoid which sometimes gave 40 kG parallel to the junction interface. Unfortunately, the junction and solenoid were immersed in the same helium bath and only 1.4°K could be reached by pumping.

The results for three different types of junction are shown in Fig. 6. Consider the Sn-I-Sn junction first. The effect of field (~14 kG) is first to round the peak rather as if the temperature was being raised. At 19 kG a dip in conductance has appeared near zero bias and at 37 kG the conductance at zero bias is reduced to approximately the estimated "background" value. The effect of 37 kG on the Ta-I-Al junction is comparable to that of 19 kG on the Sn-I-Sn junction. The Si p-n junction is complicated by the very asymmetrical background diode conductance, but the depression of the conductance near zero bias is in fact very similar to that in the metal-oxide junctions.

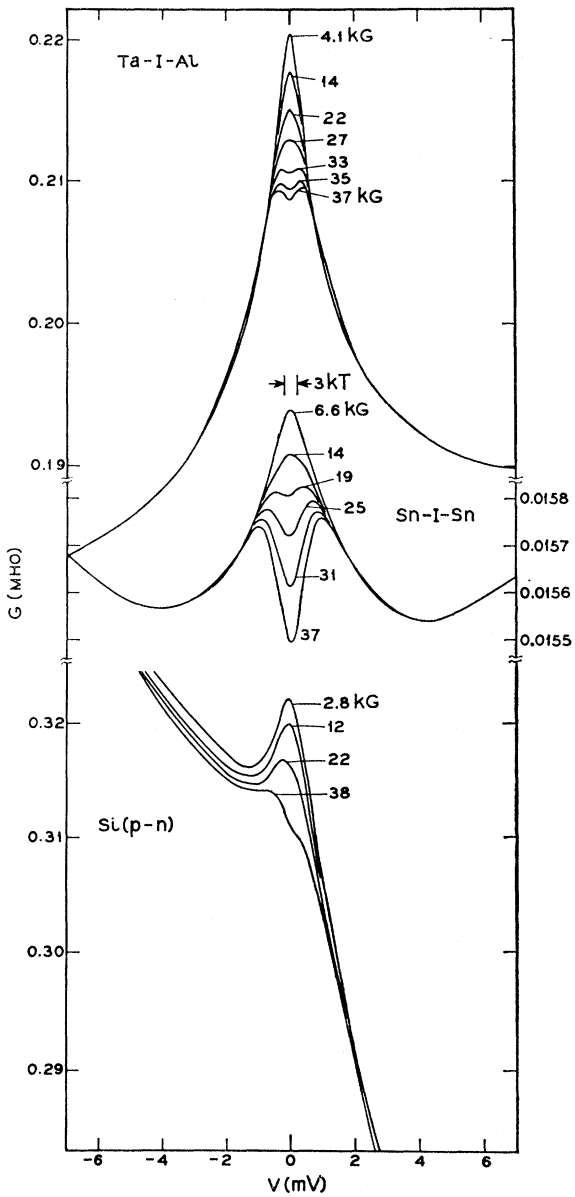

FIG. 6. Conductance-versus-voltage plots for Ta-I-Al (upper trace), Sn-I-Sn and silicon p-n junctions (lower trace) at 1.5°K. The magnitudes of the applied magnetic fields are indicated. Above the Sn-I-Sn trace the voltage corresponding to $3kT$ is shown.

Initially, one might suspect that the twin peak behavior, exhibited particularly by the Sn-I-Sn junction, is due to the splitting of the $G^{(3)}$ peak as discussed above. In fact, however, except for a slight increase in conductance for $V>1.5$ mV, the conductance has simply been reduced by an amount which is largest at zero bias and decreases to higher biases, leading us to suspect that the field effect is dominated by the reduction in $G^{(2)}$ discussed above. We have analyzed our field data in terms of the $G^{(2)}$ term alone. Small deviations from

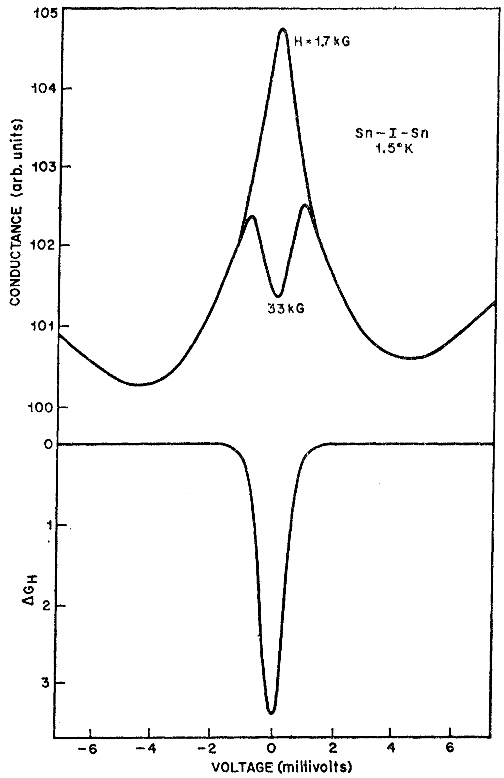

FIG. 7. Conductance-versus-voltage plot for a Sn-I-Sn junction (upper trace) in two fields (1.7 and 33 kG) and the differences ΔG_H between the two curves (lower trace).

the fits are possibly due to the magnetic field dependence of $G^{(3)}$.

Analysis of the data proceeds as follows, considering now the Sn-I-Sn junction of Fig. 7. The field-induced change in conductance as a function of voltage is found by taking the conductance difference between the 1.7-kG trace and that at 33 kG. This conductance difference ΔG_H is, as shown in Fig. 7, a simple dip suggestive of the hole in $G^{(2)}$ mentioned above. The effect of kT smearing is serious in this experiment; if $g=1$, we have $g\mu H=0.26$ mV for a field of 45 kG and kT at 1.5°K is 0.13 mV. As the smearing of a tunneling characteristic is $\sim$3.5 kT,[24] we expect that the well in $G^{(2)}$ will in fact be smeared out to a dip.

The expression given by Appelbaum[15] for the $G^{(2)}$ term is oversimplified in that $kT=0$ has been assumed in the metal films, but $T\neq 0$ for the spins in the oxide. The complete expression for $G^{(2)}$ at finite temperature has been calculated[25] and is

$$G^{(2)}=CT_J{}^2\rho^A\rho^B\left[S(S+1)-\tfrac{1}{2}\langle M\rangle \times\left\{h\left(\frac{\Delta+eV}{kT}\right)+h\left(\frac{\Delta-eV}{kT}\right)\right\}\right], \quad (4)$$

where

$$h(x)=\frac{-1+e^{2x}-2xe^{x}}{1-2e^{x}+e^{2x}},$$

$\langle M\rangle$ is the average magnetization of the spins,[26] and $\Delta=g\mu H$ is the Zeeman energy.

Comparison between ΔG_H measured experimentally and $G^{(2)}$ is shown in Fig. 8 for various temperatures and fields. For this comparison the magnitude of the depression has, in both experiment and calculation, been normalized to 1 at zero bias. The voltage dependence of $\Delta G^{(2)}$ arises only from the term

$$\left\{h\left(\frac{\Delta+eV}{kT}\right)+h\left(\frac{\Delta-eV}{kT}\right)\right\}.$$

It can be seen that the only unknown parameter in this expression is the g value for the impurity appearing

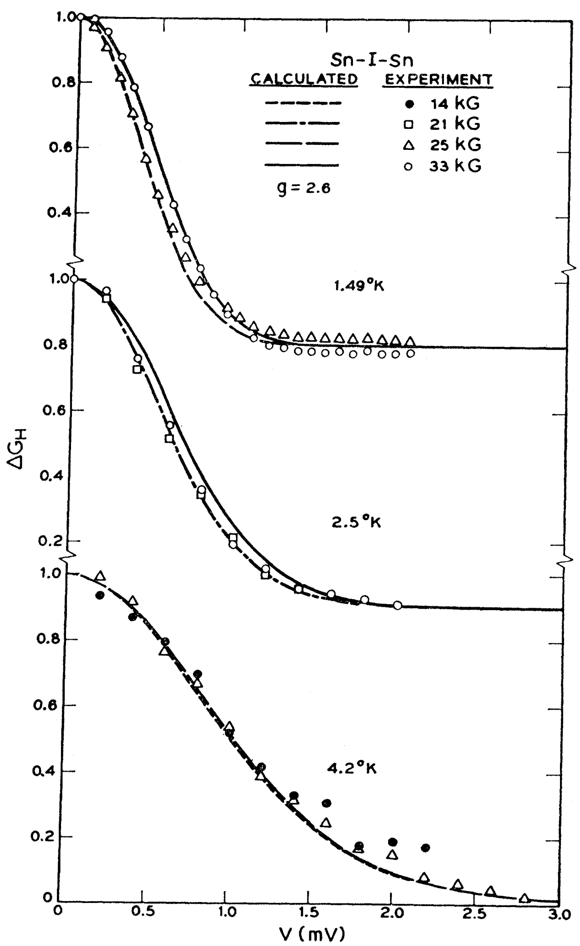

FIG. 8. Comparison between experimental and theoretical voltage dependences of ΔG_H at different temperatures and fields. The only unknown parameter used here is the value of g.

[24] S. Bermon and D. M. Ginsberg, Phys. Rev. **135**, A306 (1964).

[25] L. Y. L. Shen (unpublished).

[26] Applebaum uses $\langle M\rangle=(-1)\times$magnetization if magnetization is taken from C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1960).

in $\Delta = g\mu H$. Figure 8 shows that the width of the dip ΔG_H is determined largely by kT at the higher temperatures and the effect of increasing field is most obvious at the lowest temperature. The best agreement between experiment and theory for all fields and temperatures has been obtained for $g=2.6$, the value used in Fig. 8. A similar analysis of the tantalum data gives $g=1.1$. It appears that the magnetic field dependence of the zero-bias anomaly is dominated by changes in the $G^{(2)}$ term. The only evidence from Fig. 6 for the magnetic field dependence of the $G^{(3)}$ term is the slight increase in conductance for $V>0.75$ and 1.5 mV for the Ta-I-Al and Sn-I-Sn junctions, respectively. The effect of field on $G^{(2)}$ is always to decrease conductance.

The value of S can next be found by considering the magnitude of the conductance change ΔG_H measured at $V=0$ as a function of field. Equation (4) then reduces to

$$G(0) = CT_J{}^2\rho^A\rho^B[S(S+1) - \langle M\rangle h(\Delta/kT)].$$

The g factor in Δ is known from the discussion above, and $\langle M\rangle$ can be evaluated as a function of H/T for an impurity with spin S.[27] A family of plots for

$$\Delta G_H(0) = G^{(2)}(V=0, H=0) - G^{(2)}(V=0, H)$$

is shown in Fig. 9 for a junction with $g=2.6$ at 1.49°K.

In this plot we have shown ΔG_H in units of S for three different S values. Again, as the absolute magnitude of the $G^{(2)}$ term is not known, we have to fit the data to the shape of $\Delta G_H(0)$ versus Δ, taking a normalization at one field. This is done in Fig. 10, where first the plots of Fig. 9 have been normalized by taking $\Delta G_H(0)/S$ as the vertical scale. The tantalum point at highest field ($\Delta=0.25$) has been fit to the $S=\frac{1}{2}$ plot, and points at lower fields fall on this same line. The Sn dependence is placed on $S=\frac{1}{2}$ at $\Delta=0.37$, and one can see that agreement with the calculated behavior is very poor, particularly at high fields. The most prob-

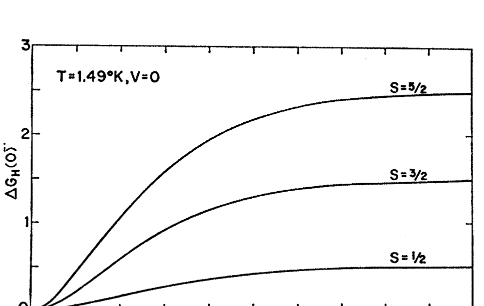

FIG. 9. A plot for the change in the $G^{(2)}$ term $[\Delta G_H(0)]$ with magnetic field from Eq. (4). Curves are shown for different values of S.

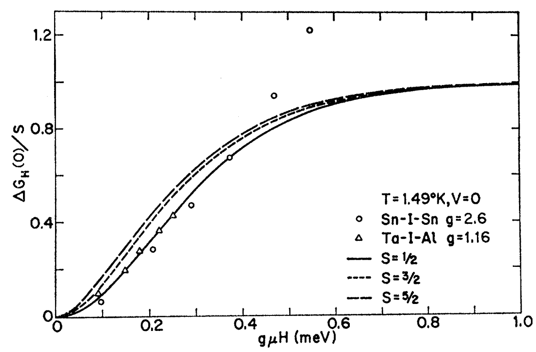

FIG. 10. The changes in $\Delta G_H(0)$ from Fig. 9 are normalized with respect to the spin value and comparison made between theory and experiment for Sn-I-Sn and Ta-I-Al junctions at 1.49°K.

able explanation of this is that the change in the $G^{(3)}$ term with field (which we have neglected) is becoming appreciable at high fields. Another possibility is that $\langle M\rangle$ is not represented in this case by the simple formula of Ref. 27.

At low fields ($\Delta \ll kT$), and when $V=0$, Eq. (4) reduces to

$$G^{(2)}(0) = CT_J{}^2\rho^A\rho^B[S(S+1) - \tfrac{1}{3}\langle M\rangle(\Delta/kT)].$$

As $\langle M\rangle$ is also linear in H/T in this limit, $G^{(2)}$ should be proportional to H^2/T^2. A plot in this low-field region of $G(0)$ versus H^2/T^2 is shown in Fig. 11. If the impurity g factor is 1, $(g\mu H/kT)^2 < 0.18$ implies that

$$H^2/T^2 < 40\ kG^2/°K^2.$$

So one would expect the linear relationship to hold for H^2/T^2 less than ~ 40 in the figure. Such a linear dependence holds quite well and the slope of $G(0)$ versus H^2/T^2 appears to be independent of temperature. This slope is given by $CT_J{}^2\rho^A\rho^B(g^2\mu^2/9k^2)$, and, as the nonmagnetic tunneling through the junction is given by $C(T+T_a)^2\rho^A\rho^B$, we can deduce that $(T+T_a)^2/T_J{}^2 = 2.2g^2 - 1$ for Sn-I-Sn junctions and $2.4g^2 - 1$ for Ta-I-Al junctions.

The experimental evidence outlined above leaves little doubt that the Appelbaum-Anderson theory accounts adequately for the zero-bias anomaly when it is a conductance peak which is rather small compared to the total conductance. The implied existence of localized magnetic moments in the tantalum oxide layer strongly suggests that free Ta atoms with their unfilled d shell exist within the oxide. Since free Sn atoms do not have d electrons, the magnetic moment inside the tin oxide could be due to paramagnetic defects. Our most recent measurements suggest that the impurity is picked up from the vacuum system. The type of impurity has not yet been identified.

E. Background Conductance

From Fig. 1 it can be seen that between 0 and 80 mV the conductance of the Ta-I-Al junction approx-

[27] F. Seitz, *Theory of Solids* (McGraw-Hill Book Co., Inc., New York, 1940), p. 581.

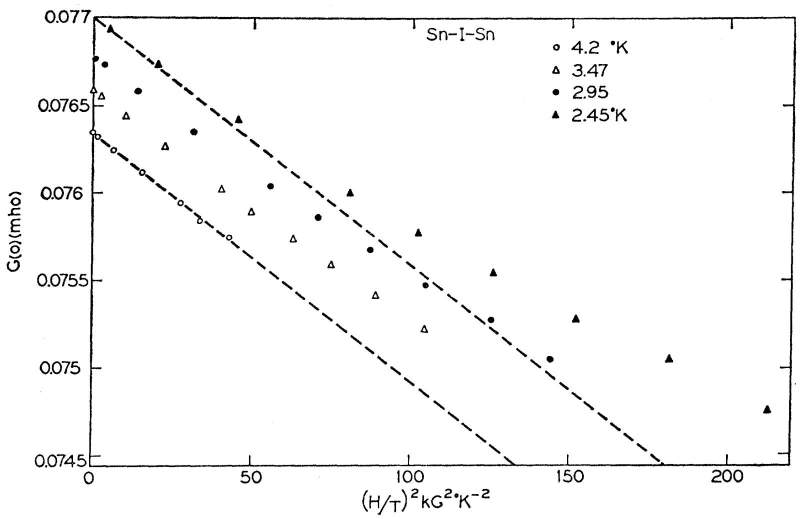

FIG. 11. Conductance measured at zero bias versus H^2/T^2 plot at different temperature for a Sn-I-Sn junction. The two dashed lines are parallel.

imately doubles. To see if this rather rapid increase in conductance with voltage is unusual, we compared a number of tunnel junctions by plotting conductance versus voltage from 0 to +140 mV; the results are shown in Fig. 12. The smallest conductance change is for aluminum oxide junctions (Sn, In, Pb counter electrode), where the change in conductance from 0 to 140 mV is only ~15% in the Al positive bias direction and practically zero or even negative in the Al negative direction.[28] Sn-I-Sn junctions have a 20–30% conductance change over the same bias range, whereas Ta-I-Al junctions change by a factor of 6. It does appear then that the tantalum junctions are also anomalous in this respect, but whether this rapid conductance change is due to a bias-dependent magnetic scattering or simply due to the peculiar shape of the tunneling potential barrier produced by the presence of the impurities remains to be seen. A Cr-I-Ag junction, which will be discussed in the next section, is also shown in Fig. 12 for comparison.

It was also observed that in tantalum junctions, if the zero-bias anomaly was large and the background conductance change very rapid, the characteristics of the junction in the superconducting state were very poor. By this we mean that even at 1°K the current flowing for $V<(\Delta_{\mathrm{Ta}}+\Delta_{\mathrm{Al}})$ was an appreciable fraction of that flowing for $V>(\Delta_{\mathrm{Ta}}+\Delta_{\mathrm{Al}})$. In a "good junction" this current is simply due to thermally excited quasiparticles, and, as $\Delta_{\mathrm{Ta}}\sim 7kT$, when $T=1$°K this number should be very small. A large current in the gap region implies either a nontunneling path through the junction (e.g., metallic short) or gaplessness of the tantalum, i.e., a finite density of allowed quasiparticle states even at the Fermi level, as could be produced by pair-breaking mechanisms such as current flow, magnetic field,[29] or magnetic impurities in or adjacent to the superconductor.[30] We have found that the magnitude of the zero-bias anomaly in Sn-I-Sn junctions varies between 0.2% and 7% depending, presumably, on the number of impurities trapped inside the tin oxide. Although we have not yet managed to vary this number in a predictable way, these variations allow us to study the connection, if any, between the zero-bias anomaly and other properties of the junction at a fixed temperature of 0.9°K.

We have, therefore, analyzed the Sn-I-Sn data to see if the superconducting gap characteristic, zero-bias anomaly, and background conductance change are correlated.

The superconducting gap characteristic of a Sn-I-Sn junction which had a 0.9% zero-bias anomaly is shown in Fig. 13. We have taken the ratio of the current flowing at 0.2 mV to that at 1.4 mV as a measure of the

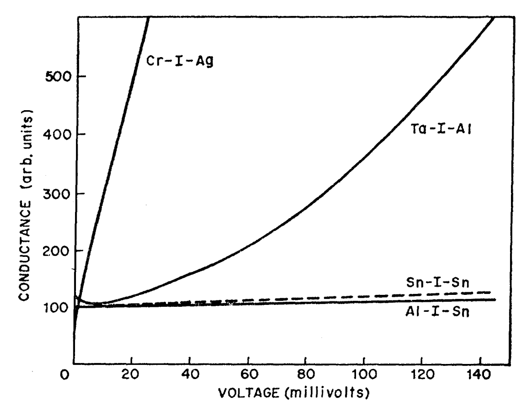

FIG. 12. Conductances versus voltage plot of several normal metal junctions which exhibit different zero-bias behaviors. The temperature is 1°K.

[28] J. M. Rowell (to be published).
[29] K. Maki and P. Fulde, Phys. Rev. 140, A1586 (1965).
[30] F. Reif and M. A. Woolf, Phys. Rev. Letters 9, 315 (1962); M. A. Woolf and F. Reif, Phys. Rev. 137, A557 (1965).

excess current flowing within the gap. This ratio is plotted against the magnitude of the zero-bias anomaly for a number of junctions in Fig. 14, and although the points are scattered there is no doubt of the approximate proportionality of the two parameters. Thus it appears that the magnetic impurities not only interact with the tunneling electrons, but also affect the superconducting properties of the surfaces of the tin films. Since the magnitude of the zero-bias anomaly is proportional to the concentration of impurities on the surface, Fig. 14 implies that the excess current flowing within the gap is also proportional to the concentration of impurities.

We also observed that, when the zero-bias anomaly is large, the normal-state background conductance in-

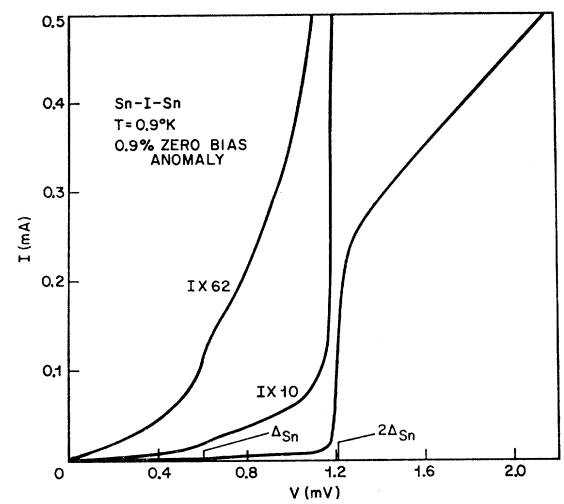

FIG. 13. I–V characteristics for a typical Sn-Sn junction. The position of Δ_{Sn} is marked on the diagram. The current scales have been expanded as shown.

crease at high biases is also large. This effect could be due to either a change in barrier height produced by the larger number of magnetic impurities or to a magnetic scattering term at high biases. The former explanation seems more probable inasmuch as the conductance in this basis range is not magnetic-field-sensitive. The effect is illustrated in Fig. 15. We have taken the conductance difference as a function of voltage between junctions with 7.45, 2.9, and 1.2% zero-bias anomalies and a junction with the smallest anomaly (0.2%) we have ever observed. This excess conductanec appears to be proportional to V^2, a reasonable result if the barrier height is changed. According to Simmons *et al.*,[31] the next higher order correction to the conductance due to finite barrier height and thickness is portional to V^2. In Fig. 15 the V^2 term is sufficient to account for the change in background conductance up

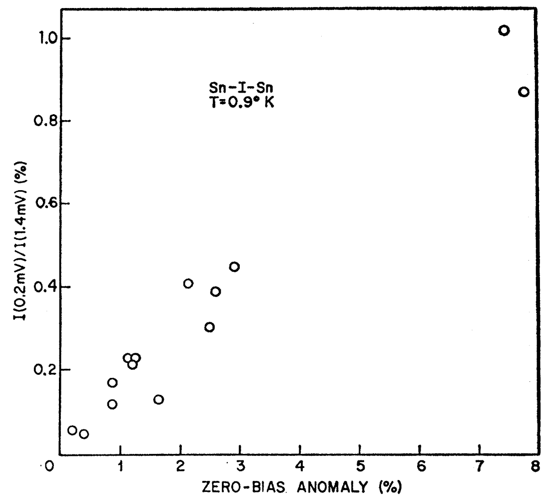

FIG. 14. A plot of superconducting background (defined in the text) versus the magnitude of the zero-bias anomaly.

to 150 mV. It indicates that the presence of magnetic impurities is lowering the tunneling barrier within the framework of WKB approximation. The increasing slopes of the lines in Fig. 15 merely indicate that the barrier height decreases as the size of the zero-bias

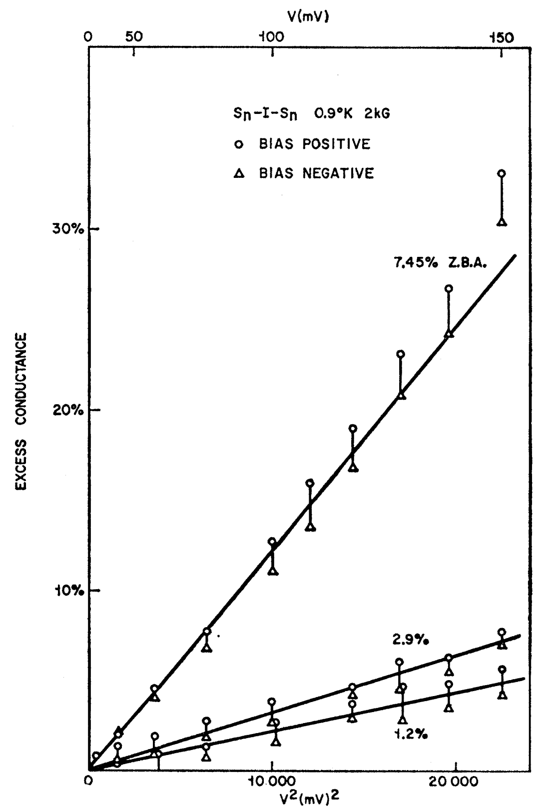

FIG. 15. Excess conductance above the lowest background junction (0.2% zero-bias anomaly) plotted versus V^2 for two directions of bias. The polarity refers to the tin film on which the oxide is grown.

[31] J. G. Simmons and G. J. Unterkofler, J. Appl. Phys. 341, 828 (1963); J. G. Simmons, *ibid.* 34, 238 (1963).

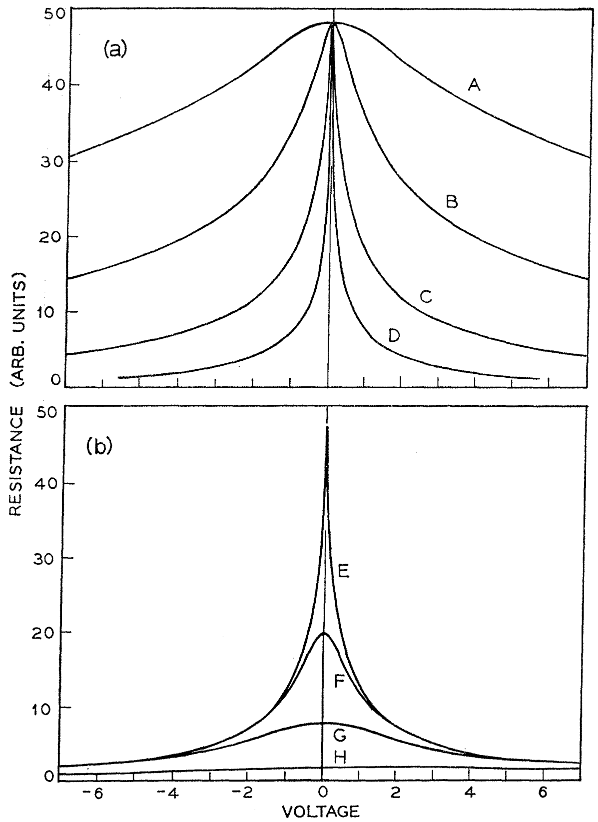

FIG. 16. (a) The dynamic resistance versus voltage for a Cr-I-Ag junction at 0.9°K. The voltage scales are $A=0.2$ mV/div, $B=1.0$ mV/div, $C=5$ mV/div, $D=20$ mV/division. (b) The dynamic resistance versus voltage for a Cr-I-Ag junction at various temperatures, $E=0.9$, $F=20.4$, $G=77$, and $H=290$°K. The voltage scale is 10 mV/division.

anomaly increases. This is consistent with the picture that ionized states inside the barrier can distort the potential barrier itself, but the details would depend on the position of the impurities. The effective potential change does not necessarily vary linearly with the zero-bias anomaly which is more sensitive to the impurity concentration on the metal-barrier interface.

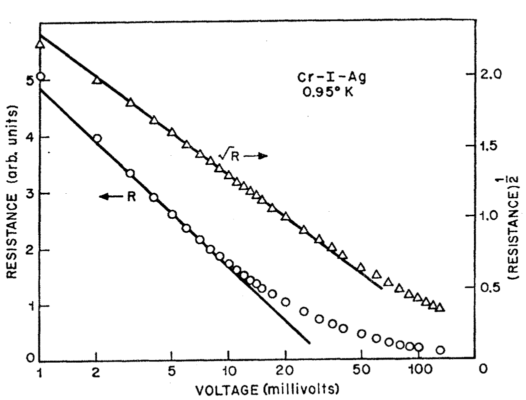

FIG. 17. Resistance and (resistance)$^{1/2}$ versus lnV at 0.95°K fora Cr-I-Ag junction.

F. Chromium Oxide Junctions—"Giant Anomalies"

When it appeared likely that the zero-bias anomalies in tantalum junctions could be explained by magnetic scattering, it seemed worthwhile to try tunneling through oxides which were known to be magnetic. The chromium–chromium oxide–silver system was chosen and junctions made by evaporating chromium films at 10^{-6} Torr and oxidizing for about 3 h at 110°C in air. The variation of resistance with voltage and temperature is shown in Fig. 16; the resistance (dV/dI) plot is shown because of the obvious logarithmic nature of the anomaly. It can be seen that the resistance of the junction falls by a factor of two when only 3 mV bias is applied, an enormous effect compared to the conductance-peak anomalies discussed above. The data were first plotted as a logarithmic anomaly, but it was recently pointed out to us by Anderson[32] that a much better fit to the data is a $(\ln V)^2$ dependence of R.

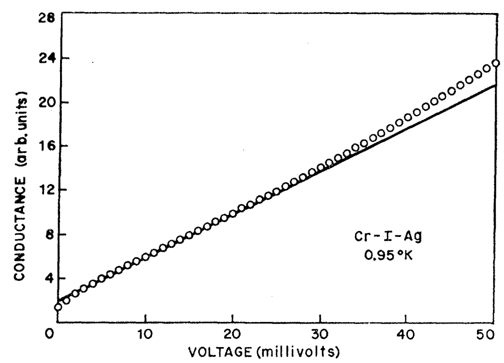

FIG. 18. Conductance versus voltage at 0.95°K for the Cr-I-Ag junction of Fig. 17.

This is shown in Fig. 17 where both R and $\sqrt{R}$ versus $\ln V$ are shown for comparison. However, just as convincing a plot can be made of conductance versus voltage as pointed out by Kondo[33] and shown in Fig. 18.

It is certainly difficult at present to explain the chromium result, as the data indicates that the whole of the current flow through the junction is anomalous, i.e., this resistance-voltage dependence is not exhibited by any of the common tunnel junctions or predicted by tunneling theory. A similar, although weaker, effect has been observed in V-I-Ag junctions; the vanadium oxide is probably antiferromagnetic,[34] as is chromium oxide. Attempts have been made to explain the results in terms of very strong coupling between magnetic impurities and the tunneling electrons, but this does not seem too likely in view of the further results to be discussed below.

In order to check that the chromium oxide was indeed

[32] P. W. Anderson (private communication).
[33] J. Kondo (private communication).
[34] K. Kosuge, T. Takada, and S. Kachi, J. Phys. Soc. Japan **18**, 318 (1963).

making an insulating layer, we replaced the Ag electrode by Pb and measured the I-V characteristics shown in Fig. 19. The fact that the current at biases $\ll\Delta$ is 1000 times smaller than the normal-state current indicates that at most only 1 part in 10^3 of the current is flowing by a nontunneling path. Of course, it is possible that for voltage >2 mV a nontunneling mechanism becomes dominant, but this seems unlikely. A more important conclusion to be drawn from Fig. 19 is that there is no effect of the antiferromagnetic oxide on the Pb gap in that no "gaplessness" seems to be induced.

An even more surprising result was obtained on measuring the resistance of the Cr-I-Pb junction as a function of bias with the lead both in the superconducting and normal states. At energies from 2 to 10 MeV above Δ_{Pb} one expects to observe the phonon-induced structures in the density of quasiparticle states in the Pb. Except for the slight effect of kT smearing one has

$$\frac{N_s(E)}{N(0)}=\left(\frac{dI}{dV}\right)_s \Big/ \left(\frac{dI}{dV}\right)_n$$

$$=\left(\frac{dV}{dI}\right)_n \Big/ \left(\frac{dV}{dI}\right)_s,$$

where $N_s(E)$ and $N(0)$ are the densities of states in the superconducting and normal states. We compare this result from a Cr-I-Pb junction with that from Pb-I-Pb or Al-I-Pb junctions[35] in Fig. 20 and the drastic reduction in the size and sharpness of the "phonon structures" is apparent. This suggests that the effect of the chromium oxide on the lead film is rather subtle,

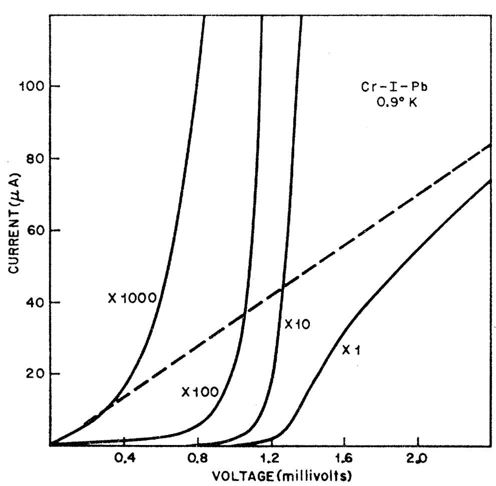

FIG. 19. Current versus voltage for a Cr-I-Pb junction at 0.9°K with no applied magnetic field. The dashed line is the characteristic with Pb in the normal state. The current scales have been expanded by decades as shown.

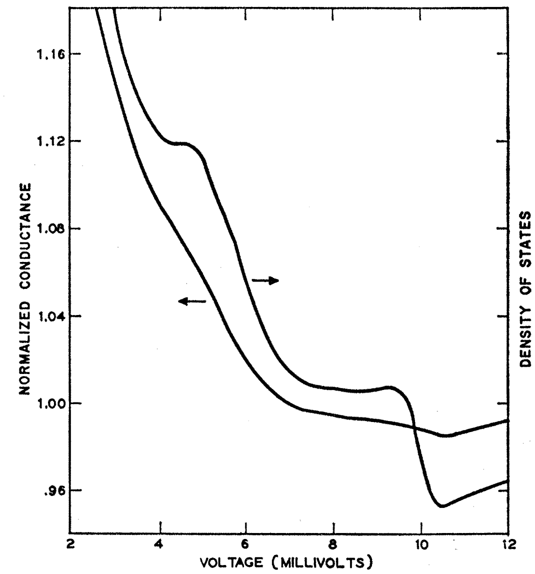

FIG. 20. The normalized derivative of a Cr-I-Pb junction at 0.9°K compared with the density of states calculated from measurements of a Pb-I-Pb junction at 0.9°K.

having little effect for energies $<\Delta$, but affecting the gap parameter very strongly in the region $E\sim\Theta_D$.

Measurement of a Cr-I-Ag junction in a magnetic field parallel to the film surface led us to conclude that there is no change in conductance to 3 parts in 10^3 at 1.5°K in fields from 0–40 kG. Vanadium junctions were similarly insensitive to field.

IV. CONCLUSION

The small zero-bias conductance peaks, typified by Ta-I-Al junctions, seem to be well explained by the Appelbaum-Anderson theory, and it seems reasonable that the conductance peaks in heavily doped silicon p-n junctions also occur because of magnetic scattering. The origin of the giant anomalies in Cr-I-Ag junctions remains a mystery at present. The question of whether the conductance dips in III–V p-n diodes are similar to either of the types of behavior discussed in this paper remains open. Vul *et al.*[36] have recently pointed out some of the technical difficulties which arise in studying III–V diodes, but when these are avoided they observe a small logarithmic dip at zero bias. The lack of any field dependence suggests, however, that magnetic scattering is not taking place.

ACKNOWLEDGMENTS

We wish to thank P. W. Anderson, J. Appelbaum, J. Kondo, and W. L. McMillan for many valuable discussions, and W. L. Feldmann for considerable technical assistance.

[35] W. L. McMillan and J. M. Rowell, Phys. Rev. Letters **14**, 108 (1965).

[36] B. M. Vul, E. I. Zavaritskaya, and N. V. Zavaritskii, Fiz. Tverd. Tela **8**, 888 (1966). [English transl.: Soviet Phys.—Solid State **8**, 710 (1966)].