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Inelastic Electron Tunneling in Al-Al-Oxide–Metal Systems*

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A systematic study of inelastic electron tunneling in Al-Al-oxide–metal thin-film junctions in the bias range 30–500 mV has been made. Most measurements were performed on twin junctions made by evaporating two different metal films across the same oxidized Al base film. The experimental results of this paper can be divided into three groups. The first of these is a reidentification of some vibrational bands that appear in the tunneling spectra of Al-oxide systems. A prominent peak that appears between 115 and 120 mV in these spectra has been identified as being due to a vibrational mode of an alumina hydrate. In addition, a new OH mode has been found at about 75 mV in these systems. The experimental results that constitute the second group are the effects on the tunneling spectra of Al-Al-oxide systems due to the metal used as the top electrode. By studying the twin junctions described above, it has been found that the intensity of vibrational bands due to molecular impurities relative to the intensity of vibrational bands due to oxide modes is correlated with the ionic radius of the metal used as the top electrode. This correlation is interpreted as being caused by a size-dependent penetration of the top electrode into the oxide layer of the junction. The last group of experimental results involves changes in tunneling spectra of Al-Pb junctions produced by applying a DC potential across the samples at room temperature. These changes are interpreted as being due to the movement of dissolved gases in the Pb electrode of the junctions.

I. INTRODUCTION

THE tunneling of electrons between two metals separated by a thin insulating layer has been an active subject of research since 1960 when a series of pioneering studies were begun by Giaever.[1] In contrast to the initial period following these studies, in which tunneling phenomena in superconducting systems were studied almost exclusively, tunneling between normal metals has received considerable attention in the last few years. One of the significant findings which has emerged from these studies of normal-metal tunneling is the detection of inelastic interactions between tunneling electrons and localized impurities in the insulating layer of the systems. The onset of inelastic interactions in the barrier region of a tunnel junction opens up a new channel for tunneling, resulting in an increase in the conductance of the junction.

The initial studies of inelastic tunneling[2] detected the vibrational excitation of molecular impurities in the oxide layer of Al-Al-oxide–Pb junctions; further experiments on this system by the same group[3] have demonstrated very convincingly that the vibrational spectrum of these impurities is faithfully reflected in the d^2I/dV^2-versus-V characteristics of the junctions. A simple model[4] considering only the electrostatic interaction between the tunneling electrons and dipole impurities in the insulating layer has been used to predict the correct order of magnitude for the conductance increases that are seen at the threshold for these excitations. Other recent experimental studies have reported the detection of rotational excitation of molecular impurities[5] and the excitation of phonons[6] and surface plasmons[7] in the tunneling barrier of junctions.

This paper describes the results of a systematic experimental study of inelastic tunneling in Al-Al-oxide–metal thin-film tunnel junctions. After a description of the experimental procedures used in these experiments, the main results of the study are presented in Secs. III A–III C. First are presented the results of a detailed examination of the vibrational bands appearing in the tunneling spectra of these junctions. A consequence of this study is to make an important change in the assignment of a prominent peak appearing in all Al-Al-oxide systems. In addition to this reidentification, an OH vibrational mode not previously reported has been found. The effects of using different metals as the top electrode of Al-Al-oxide junctions are next described and a model which accounts for these effects is presented. Finally, the results of an original type of experiment studying the effects of applying a small dc potential across certain junctions at room temperature are given. The application of such a potential produces changes in the tunneling spectra of these junctions

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[1] I. Giaever, Phys. Rev. Letters **5**, 147 (1960).

[2] R. C. Jaklevic and J. Lambe, Phys. Rev. Letters **17**, 1139 (1966).

[3] J. Lambe and R. C. Jaklevic, Phys. Rev. **165**, 821 (1968).

[4] D. J. Scalapino and S. M. Marcus, Phys. Rev. Letters **18**, 459 (1967).

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

[6] I. Giaever and H. Zeller, Phys. Rev. Letters **21**, 1385 (1968).

[7] D. C. Tsui, Phys. Rev. Letters **22**, 293 (1969).

which may be interpreted in terms of the movement of gases dissolved in the electrodes of the system.

II. EXPERIMENTAL TECHNIQUES

A. Junction Fabrication

The tunnel junctions studied in these experiments were of the usual thin-film type made by evaporating a film strip of a metal on a glass substrate, growing an oxide layer on this film, and evaporating a second metallic film strip over the oxidized base film. The preparation of the junctions was carried out in a vacuum system pumped by a mercury diffusion pump, with a liquid-nitrogen trap between the diffusion pump and the vacuum chamber and a zeolite trap in the foreline, between the mechanical pump and the rest of the system. The vacuum chamber was enclosed in an 18-in.-diam bell jar and was pumped to a vacuum of about 3×10^{-6} Torr for the evaporation of the metallic films. The evaporator was constructed so that up to four different metals could be evaporated in succession, without breaking the vacuum. In addition to the evaporation apparatus, the vacuum chamber was equipped with an aluminum electrode to which voltages up to -500 V dc with respect to the rest of the system could be applied. This electrode was used to create a discharge in O_2 gas introduced to the vacuum chamber, for use in growing oxides on the base film of tunnel junctions and to promote the cleanup of residual impurities in the chamber after initial pumpdown.

Cleaned sections of Pyrex microscope slides were used as substrates for the junctions to which copper leads were attached with indium solder. In most junctions, the base film was 99.99% Al which was evaporated from a stranded tungsten filament to a thickness of several thousand Å. This film was then oxidized, either by exposing it to the atmosphere for a few minutes or by a gas-discharge technique using pure oxygen. It was found that oxide films grown in the atmosphere were not thick or compact enough to consistently produce tunnel junctions of usable resistance with most metallic overlayers. In addition, films grown in this way contain a large number of uncontrolled impurities due to atmospheric pollution. Because of the above difficulties, a gaseous anodization technique described by Miles and Smith[8] was used for most junctions. By using this method, relatively clean oxide layers of controllable thickness were produced. The technique consists of allowing pure oxygen (commercial quality) into the vacuum chamber to a pressure of 50×10^{-3} Torr after the evaporation of the base film and then setting up a discharge between the Al cathode in the chamber and the rest of the system. During the period in which the discharge was maintained, the mask was moved aside and the film to be oxidized was held about 2 in. from the cathode, being shielded from it by a metallic foil. The thickness of an oxide film grown by this process depends on the period of time the discharge is maintained. It was found for Al films that exposure for about 10 min produced an oxide layer which was of a proper thickness to produce usable tunnel junctions, presumably about 20 Å. Oxides grown in this way have a considerable number of OH impurities but very few impurities of any other type. The impurities in these oxides are the consequence of residual impurities present in the vacuum system during the oxide growth; the predominance of OH groups among these is consistent with mass spectrographic studies of residual gases in this type of system which indicate that water vapor is the principal constituent at low pressures.[9]

To dope an oxide with a specified impurity, either the oxide was exposed to the desired impurity after its formation or the impurity was added to the vacuum chamber during the growth of the oxide. Exposing grown oxides to room air was sometimes done to deposit hydrocarbon impurities on it, thus causing large vibrational bands of these impurities to appear in the tunneling spectra, making electrode effects on the spectra easier to analyze. The only impurities added to the system during the formation of the oxide were H_2O and D_2O. These were introduced by breaking a glass capillary tube filled with the liquid in the vacuum chamber after the evaporation of the base metal film, pumping the system back down to about 20×10^{-3} Torr and then admitting about 50×10^{-3} Torr of O_2 and carrying out the usual gaseous anodization procedure.

After the base film was oxidized and doped, the vacuum chamber was again evacuated to a pressure of about 3×10^{-6} Torr and overlayer metallic films of at least 99.99% pure materials were evaporated from appropriate filaments to complete the junctions. To investigate the effects on the tunneling spectra made by the metal used as the second electrode, twin junctions were made by evaporating two different metallic films at different locations on the same oxidized base film. By doing this it was hoped that only electrode effects would be responsible for differences in the spectra, the base film and the oxide being the same for both junctions. There is some evidence, given in Sec. III B, that outgassing of the sources before their evaporation contributes some impurities to the oxide, so that the oxide layer of the junction evaporated last contains a slightly larger number of impurities than the junction evaporated first.

In addition to the Al-Al-oxide–metal junctions which made up the bulk of the samples studies, a few Mg-Mg-oxide–metal junctions were examined. These were prepared in the same way as Al-based junctions, except that it was necessary to continue the discharge for a longer time, usually from 15 to 20 min., to obtain an oxide layer thick enough to produce usable junctions.

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[8] J. L. Miles and P. H. Smith, J. Electrochem. Soc. **110**, 1240 (1963).

[9] H. L. Caswell, IBM J. Res. Develop. **6**, 130 (1960).

Apparently the Mg-oxide films grown this way are not as compact as the corresponding Al-oxide films, making the fabrication of Mg-Mg–oxide junctions with resistances larger than $\sim 1\ \Omega$ difficult when metals of small atomic radius are used as the second electrode.

B. Measurement of Tunneling Characteristics

The specific property of the tunnel junctions that is desired in this study is the derivative of the dynamic conductance $\sigma(V)$ of the junction with respect to voltage as a function of the dc bias V across the junction. It is this quantity d^2I/dV^2 which has been shown to be proportional to the vibrational spectrum of the barrier impurities. To obtain this relation, the dynamic resistance dV/dI and its current derivative d^2V/dI^2 were measured as a function of bias voltage; these two quantities together are sufficient to determine the desired relation between d^2I/dV^2 and V.

The measurement of dV/dI and d^2V/dI^2 was made using a bridge circuit designed by Adler and Jackson.[10] A modulation frequency of 1000 Hz with an amplitude of about 125 μV across the junction was used in all measurements of dV/dI. For the measurement of d^2V/dI^2, the sample was modulated by a 500-Hz signal, usually with an amplitude of about 2 mV at the junction, with the lock-in amplifier detecting at a frequency of 1000 Hz. To resolve narrow linewidths appearing in some samples, it was necessary to use smaller modulation amplitudes, the smallest being about 0.5 mV.

The measurements described above were all done with the tunnel junctions immersed in liquid helium at atmospheric pressure, a temperature of about 4.2°K.

The conversion of the above measurements to a curve of d^2I/dV^2 versus V was done with the aid of a digital computer. A set of uncalibrated ordinate values representing dV/dI and d^2V/dI^2 at discrete voltages which spanned the bias range of interest was compiled; generally, values at 5-mV intervals from 20 to 500 mV were used. A direct calibration of the dV/dI curve made by replacing the junction with a precision decade resistor enabled the absolute value of $\sigma = dI/dV$ to be immediately computed for this set of points. An uncalibrated set of values for d^2I/dV^2 was then found by using the identity $d^2I/dV^2 = -\sigma^3 d^2V/dI^2$; these values are uncalibrated because the values of d^2V/dI^2 are uncalibrated. The calibration of this quantity was performed by graphically measuring the slope of the dV/dI curve $[(d/dV)(dV/dI)]$ at a number of points and using the identity $d^2I/dV^2 = -\sigma^2[(d/dV)(dV/dI)]$ to obtain the absolute value of d^2I/dV^2 at these points. The ratio of the calibrated to the uncalibrated values of d^2I/dV^2 should then be a constant η which can be used to compute the absolute value of d^2I/dV^2 for all voltages; i.e., $(d^2I/dV^2)_{\text{abs}} = \eta(d^2I/dV^2)_{\text{uncal}}$. In practice, it was found that this ratio had a weak voltage dependence, so that rather than using an average of the above values for η, a linear function of voltage, $\eta(V) = A + BV$, calculated by a least-squares fit of this set of conversion factors to a straight line, was used to convert the uncalibrated set of d^2I/dV^2 to their calibrated values. The absolute values of d^2I/dV^2 in $(\Omega\ \text{mV})^{-1}$ were then plotted by hand to give the curves shown in this paper.

When one of the electrodes of a junction is superconducting, criteria are available to test whether the conduction process being studied is tunneling. It is generally agreed that when the density of states of the superconductor is present in the differential conductance of the junction and that the conductance is very small at zero bias, that the dominant conduction process is tunneling. These density of states effects are very large compared to the inelastic processes studied in the present experiments so that the above properties were easily identified in all Al-Pb junctions analyzed (the Pb was superconducting at 4.2°K). The other metals used to make junctions were not superconductors or were studied at temperatures above their transition temperatures, so that no criteria other than the observation of inelastic tunneling structure were available to verify that most of the current being measured was due to tunneling. The conductance increases due to barrier excitations are, however, only 1% effects and appear only for tunneling current, so that the observation of these increases in itself provides sensitive confirmation that most of the current being measured is due to tunneling. Most of the conclusions reached in the following sections are not based on a direct comparison of conductance increases in the spectra of different junctions, but on properties normalized so that they are independent of differences in the junctions due to nontunneling current.

III. EXPERIMENTAL RESULTS

A. Identification of Vibrational Bands in Tunneling Spectra

Most vibrational bands appearing in the tunneling spectra of Al-Al-oxide–metal junctions are easily identified by comparison with molecular infrared (IR) absorption spectra. In particular, the presence of hydrocarbon impurities may be detected by the appearance of a strong CH stretching band at about 360 mV and a series of CH bending bands from about 160 to 210 mV. The identification of some of the vibrational bands that appear at lower biases, however, is not so easily accomplished and requires a more detailed analysis.

Figure 1 shows the tunneling spectrum of an Al-Al-oxide–Pb junction whose oxide was prepared in an oxygen discharge so that any impurities contained in the oxide are the result of residual impurities in the vacuum system during the growth of the oxide. The structure in this spectrum consists basically of two large peaks at about 118 and 450 mV. In addition, there

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[10] J. G. Adler and J. E. Jackson, Rev. Sci. Instr. 37, 1049 (1966).

are much smaller peaks at the characteristic CH frequencies, indicating a small number of hydrocarbon impurities, and the first harmonic of the 118-mV peak at about 235 mV. The peak at 450 mV can be associated with a stretching mode of nearly free OH groups and indicates that these groups are present in considerable number in the vacuum system during the oxidation process, probably in the form of water vapor, even though only pure oxygen was introduced into the system. The peaks at 118 and 450 mV were first observed by Jaklevic and Lambe,[2,3] who concluded that these peaks arose either because of the introduction of OH during oxide formation or because of the absorption of water vapor on the oxide. Our results given in this section agree with their general conclusion and enable us to establish that the 118-mV peak is due to the OH vibration in alumina hydrate, rather than to a free-OH bending mode, while the 450-mV peak arises from stretching modes of free-OH groups. Structure below 50 mV is dominated by phonon effects at the metal electrodes.

The tunneling spectrum of an Al-Al-oxide–Al junction made in an oxygen discharge is shown in Fig. 2. The only structure present in this spectrum is the large peak at about 118 mV and its first harmonic, and a smaller peak between 35 and 40 mV. The conductance increase associated with the 118-mV peak in the Al-Al junction is about 1.2%, more than twice the size of the corresponding peak in Al-Pb, yet there is no detectable peak at 450 mV implying that these two peaks (118 and 450 mV) do not correspond to a different vibrational mode of the same chemical bond. Spectra similar to Fig. 2 are obtained for all Al-Al-oxide–Al or Mg junctions, even when twin Pb junctions made on the same oxidized Al base film show definite free-OH stretch modes at 450 mV.

A most important clue to the identity of the 118-mV peak comes from the examination of IR absorption studies of alumina films. Dorsey[11] has studied alumina films formed by anodizing pure Al sheet in different types of acidic electrolytes, through their absorption of reflected IR radiation. In most electrolytes alumina is slightly soluble and two types of oxide film may form. The first layer, closest to the metal, is called the barrier layer and is very compact, with good dielectric properties. The second type, which may be formed on top of the barrier layer, is a porous layer, with poorer dielectric properties, made by the simultaneous building up of the oxide in some parts of the film and dissolution of it in other parts. With some anodizing electrolytes, such as orthoboric acid, only a barrier layer is formed. The type of alumina formed with these electrolytes might reasonably be assumed to be similar to the film formed in the gaseous anodization process used in tunnel junction fabrication, except that the acidically anodized films may be more completely hydrated. This assumption leads to very fruitful results when the absorption studies of Dorsey on barrier layer films are examined. The reflectance spectrum of this type of alumina has only one absorption band in the energy range 4–500 meV: at 118 meV (955 cm^{-1}), exactly the location of the prominent peak seen in Al-Al and clean Al-Pb tunnel junctions. The similarity between the tunneling spectrum of Al-Al junctions and the IR spectrum of barrier-layer alumina is very striking; both have basically only one peak, at 118 mV. This strongly supports the hypothesis that in Al-Al junctions the tunneling spectrum is displaying the vibrational modes of the insulating oxide itself, and these modes only. In Al-Pb junctions, the oxide modes are again present, but in addition vibrational modes of molecular impurities not associated with the oxide structure appear.

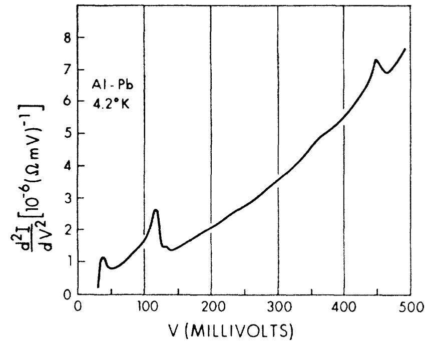

FIG. 1. Tunneling spectrum of the Al-Al-oxide–Pb junction in which the Al-oxide layer was grown by a discharge technique using pure O_2 gas. Impurities contained in the oxide are due to residual impurities present in the vacuum system during the growth of the oxide.

By comparison with IR spectra of known mineral forms, Dorsey identifies the 118-mV peak as an OH bending mode of an alumina hydrate (or aluminum hydroxide), specifically a trihydrate. The existence of only this bending band presents an anomaly, because alumina hydrates normally have an OH stretching band near 420 mV. Dorsey[12] proposes that the absence

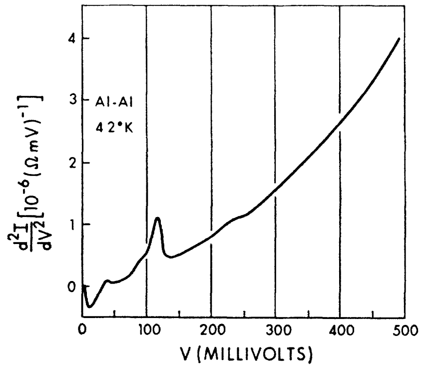

FIG. 2. Tunneling spectrum of an Al-Al-oxide–Al junction; oxide grown in O_2 discharge.

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[11] G. A. Dorsey, Jr., J. Electrochem. Soc. **113**, 169 (1966).

[12] G. A. Dorsey, Jr., J. Electrochem. Soc. **113**, 284 (1966).

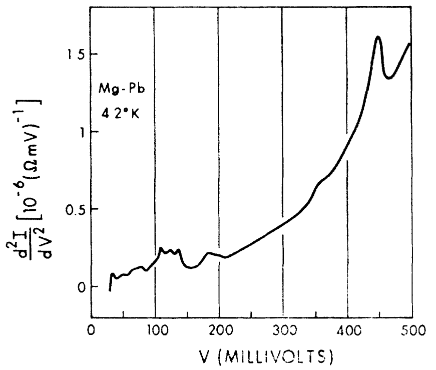

FIG. 3. Tunneling spectrum of a Mg-Mg-oxide–Pb junction; oxide layer grown in O_2 discharge.

of a stretching band in these aluminas is due to the existence of strong hydrogen bonding present within the alumina, which reduces the intensity of such a band by broadening it. The dynamics of the bending vibration seen in these spectra are discussed later in this section. The identification of the 118-mV peak in tunneling spectra as an OH bending mode of aluminum hydroxide has been substantiated by a number of independent results, as described below.

The assignment of the 118-mV peak to an alumina hydrate mode implies that it depends on the detailed structure of the oxide and that a junction whose oxide layer is different should have a tunneling spectrum that differs from the spectra of Al-oxide junctions in the 118-mV region. The tunneling spectrum of a Mg-Mg-oxide–Pb junction made in an oxygen discharge is shown in Fig. 3. It is clearly seen from this figure that the region 100–150 mV of the spectrum no longer consists of one large peak as it does in Al-Al-oxide junctions, but instead has a more complex form containing three smaller peaks of nearly equal size. The remainder of the spectrum is similar to Al junctions. This is convincing evidence that the large peak at 118 mV in Al-Al-oxide–metal junctions is characteristic of the oxide, while the peaks at higher voltages are not.

The identification of the 118-mV peak as an OH mode can be verified by studying the shift in the energy of the peak when a different isotope of H is introduced to the oxide. The experiment done to investigate the isotope shift of OH modes in tunneling spectra was to add heavy water D_2O to the oxygen discharge during the formation of the oxide layer of an Al-Al-oxide–Pb junction, a technique used successfully by Lambe and Jaklevic.[3] With the substitution of D for H, any vibrational mode associated with H atoms should shift downward in voltage by a factor of approximately $\sqrt{2}$. The tunneling spectra of two Al-Pb junctions are shown in Fig. 4. In the junction of Fig. 4(a), H_2O has been added to the oxygen discharge during the formation of its oxide; in the junction of 4(b), D_2O has been added. The assignment of vibrational bands appearing in Fig. 4 is explained as follows.

Figure 4(a) is similar to a "clean" Al-Pb junction in which no H_2O has been purposely added (Fig. 1), except that the OH stretch peak at 450 mV is larger and the shoulder on the low-voltage side of the 118-mV peak is more prominent. If a smoothly rising background due to the 118-mV peak is assumed in this voltage region, this shoulder represents a small peak at about 75 mV. The spectrum of the deuterated junction shown in Fig. 4(b) appears complex but can be completely explained by using the above scheme to label OH peaks at 450 and 118 mV, plus an assignment of the 75-mV shoulder. Even though D_2O was added to the system, OH bands are still very strong, as evidenced by the large peaks remaining at 450 and 118 mV. This is probably due to the fact that chemical reactions involving deuterium generally proceed more slowly and less completely than those involving hydrogen,[13] so that even when more D_2O than H_2O is present in the system, the D atoms are less likely to be incorporated into the oxide structure. The tunneling spectrum of Fig. 4(b) does contain OD bands at frequencies equal to $\sim 1/\sqrt{2}$ times the OH frequencies for every OH mode in Fig. 4(a). In particular, the OD bending band of alumina hydrate and its first harmonic are clearly present, verifying that the identification of the 118-mV peak as an OH mode is correct. In addition to these, a new peak appears at 53 mV, which can be explained by identifying the 75-mV shoulder in Fig. 4(a) as an OH mode and the 53-mV ($=1/\sqrt{2}\times 75$) peak as an OD mode. With this last determination the spectrum is completely explained.

It should be noted that the shift of the 118-mV to 83-mV band on deuteration, shown in Fig. 4, is not

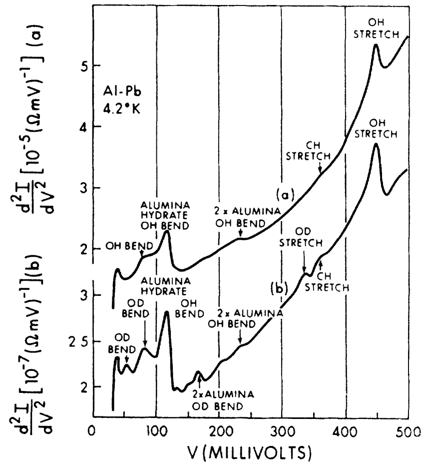

FIG. 4. Tunneling spectra of Al-Al-oxide–Pb junctions in which H_2O (a) and D_2O (b) was present in O_2 discharge used to grow the oxide films.

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[13] T. Moeller, *Inorganic Chemistry* (John Wiley & Sons, Inc., New York, 1952), p. 390.

consistent with results Dorsey[12] has obtained for alumina films made with deuterated electrolytes. Dorsey observes a downward shift of less than 1% in this band when deuterated solutions are used. The meaning of such a result is difficult to interpret; if the 118-mV band is actually an OH bending mode as he proposes, it should experience a shift of $1/\sqrt{2}$ on deuteration, not a small shift of less than 1%. Because reactions involving deuterium proceed more slowly and less completely than those involving hydrogen, a deuterated compound, when exposed to hydrogen, may experience substitution of D atoms by the more chemically active hydrogen on the surface of exposure. In his description of these results, Dorsey nowhere mentions any precautions taken to prevent this substitution when the reflection spectrum of the deuterated alumina is measured in room air. A possible explanation of this discrepancy is that near the surface of his alumina films, hydrogen present in water vapor has replaced most of the D atoms and the frequency shift he observes is due to the small effect of changing the mass of the remainder, interior portion, of the molecule to which the OH groups are attached.

The detailed dynamics of the OH bending modes appearing in Al-oxide junctions remains to be considered. Insight into this problem can be gained by considering the structure of the insulating oxide region of these junctions in the light of vibrational analyses of compounds with similar structures. Dorsey[12] proposes that the structure of barrier-layer alumina films is described by the stereographic diagram shown in Fig. 5(a). The hydrogen bonding mentioned earlier refers to the simultaneous attraction of the H atoms to two electronegative O atoms, thereby acting as a bridge or bond between them. The simplest situation involving hydrogen bonding consists of the connnecting of two molecules together to form what is called a dimer. Compounds with dimeric structure which have OH bending frequencies close to the 118-mV band of aluminum hydroxide are found in carboxylic acids. These acids have the configuration shown in Fig. 5(b). The similar environment of the H atoms in these two compounds explains how their modes of vibration may be similar if there are no vibrations with frequencies close to these in the remainder of either molecule.

An analysis of the vibrational band that appears at about 116 meV in most carboxylic acids has been performed by Hadži and Sheppard.[14] The conclusion of this analysis is that the 116-mV band is due to a vibrational mode associated with the hydrogen bonds themselves; a mode corresponding principally to the motion of the H atom of the OH group perpendicular to the plane of the dimer. When no hydrogen bonding is present, this type of vibration corresponds to a restricted rotation, or torsional motion, of the OH bond about the C-O linkage. In hydrogen peroxide, this vibration results in a broad band at about 79 meV.[15] The higher energy of vibration in acid dimers is almost certainly due to hydrogen bonding which further hinders the rotation and the reduced breadth to the more strictly defined position of the OH bond in the plane of the dimer. It seems reasonable, considering the similarities in energy of the vibrational bands and of the environment of the H atoms in these compounds, that the 118-mV band in the tunneling spectra of Al-Al-oxide–metal junctions is also due to the out-of-plane deformation vibration of the H atoms.

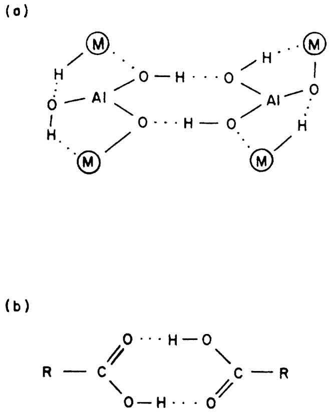

FIG. 5. (a) Stereographic diagram of barrier-layer alumina film. This diagram representing a unit section of a long polymer and *M* represents an identical unit within the same chain. (b) Diagram of a carboxylic acid, where *R* represents the remainder of the individual acid molecule. (A hydrogen bond is represented by ··· in both diagrams.)

A possible explanation for the OH mode appearing at 75 mV is that it is due to the torsional motion of OH groups about Al-O linkages at the surface of the oxide. Under these conditions, there is no hydrogen bonding affecting the motion and it would be analogous to the 79-mV vibration in H_2O_2.

B. Electrode Effects

Electrode effects on the tunneling spectra of Al-Al-oxide–metal junctions have been investigated by systematic variation of the upper electrode using comparison techniques. The systems studied in these experiments were twin junctions whose construction is described in Sec. II. In these systems, the base electrode and oxide layer of each junction should be nearly identical so that differences in the tunneling characteristics of the two should depend largely on properties of the top electrodes.

The particular system studied in these experiments were made with Pb always serving as one of the overlayer electrodes, the second overlayer M_x being varied. For each metal M_x, separate twin junctions were made in which the M_x film was evaporated before and after the Pb film. The metals used for M_x were Au, Ag, In,

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[14] D. Hadži and N. Sheppard, Proc. Roy. Soc. (London) **A216**, 247 (1953).

[15] R. C. Taylor, J. Chem. Phys. **18**, 898 (1950).

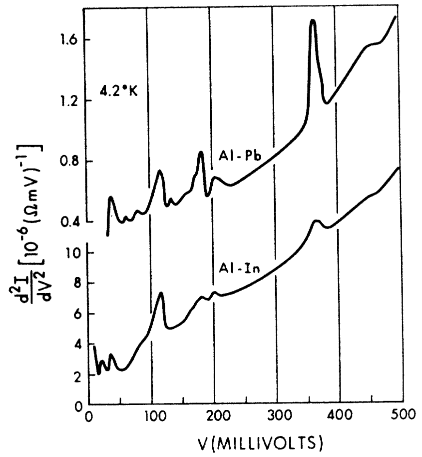

FIG. 6. Tunneling spectra of Al-(Pb and In) twin junctions. The Al oxide was exposed to room air before the evaporation of the top electrodes.

Sn, Al, Mg, and Pb. The tunneling spectra of both pairs of an Al-Al-oxide–(Pb and In) junction are shown in Fig. 6. In each junction of this pair, the spectra are plotted so that the size of the peak between 115 and 120 mV associated with the oxide structure is of about equal size in both junctions. The impurity bands in the In junction appearing at higher biases, however, are considerably smaller in size than the corresponding bands in the Pb junction. This variation in the relative size of the impurity bands relative to the oxide band is generally observed to be the main effect of using different metals as the top electrode of a tunnel junction. For Au overlayers, the impurity bands are considerably larger than in Pb and for each succeeding metal in the series Au, Ag, Pb, In, Sn, Mg, and Al they are smaller; in Mg and Al the impurity bands are not detectable at all.

If a single property of the overlayer electrode is determining the differences present in the characteristics of the junctions, the variation in tunneling characteristics should be correlated with variation of this property. A property of the metals which displays this correlation is the ionic radius of M_x as given by Pauling.[16] This radius decreases monotonically in the sequence Au, Ag, Pb, In, Sn, Mg, and Al; the same order that is seen in the size of the impurity bands relative to the oxide band in the tunneling spectra of junctions whose top electrodes are composed of these metals. To display this correlation in a quantitative manner, it is necessary to define a parameter which measures the relative size of the impurity and oxide bands in such a way that the spectra of different twin junctions can be compared. The parameter decided upon for this purpose is obtained by dividing the relative size of the two types of vibrational bands in the M_x junction by the same relative size in the twin Pb junction. The results of all M_x junctions are then standardized to Pb and can be compared directly.

The over-all strength associated with an individual vibrational band of a tunneling spectrum is proportional to the increase in conductance associated with this band. This increase can be found by measuring the area under the peak due to this vibration in the curve of d^2I/dV^2 versus V. To measure this area, the background change in conductance not associated with the inelastic processes must be subtracted off. This background is not adequately predicted by any existing model; in the present analysis, therefore, the background d^2I/dV^2 is approximated by a smooth curve through the relative minima of the characteristic. The sum of the increases associated with all impurity peaks at biases greater than 125 mV is then divided by the increase associated with the oxide peak that appears between 115 and 120 mV. This normalized size of the impurity bands is finally divided by the same quantity for the Pb twin to obtain the parameter used to characterize the tunneling spectrum of M_x. A graph of this parameter plotted against the ionic radius of M_x for all metals studied is shown in Fig. 7. The correlation mentioned above is clearly displayed in this graph.

Results for each metal M_x are shown in Fig. 7 for junctions in which M_x was evaporated before and after the Pb. The main difference produced by interchanging the order of evaporation of the overlayer electrodes is to increase the relative size of the impurity bands in the junction whose top electrode is evaporated last. This effect can be readily explained as being due to outgassing of the heated sources from which the top electrodes are evaporated before the laying down of the films. The oxide of the second junction evaporated receives outgassed impurities from both sources, whereas the junction evaporated first receives them only from one source. The spectra of twin Pb junctions illustrate this effect; the junction evaporated last has impurity bands about 10 to 20% larger than the one evaporated first. It appears from the data in Fig. 7 that Pb in particular contributes a large number of impurities through outgassing.

The correlation between ionic radius of M_x and relative size of the impurity bands in tunneling spectra suggests that the controlling mechanism which accounts for the spectral variations may be the penetration or diffusion of the M_x atoms into the oxide film. A similar type of correlation between atomic radius and junction resistance has been explained by this mechanism.[17]

A simple model of a tunnel junction demonstrates how a size-dependent penetration will produce the results of this section. In this hypothesized model the oxide grown on the Al base film consists basically of an alumina hydrate with the structure shown in Fig. 5(a). Free molecular impurities to which the oxide is exposed either during the oxidation process or after its

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[16] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, N. Y., 1960), p. 514.

[17] R. M. Handy, Phys. Rev. **126**, 1968 (1962).

completion are assumed to be present largely on the surface of this oxide. By the suggestion mentioned above, as the top electrode is evaporated onto this oxide, the penetration of the metal into the oxide is dependent on the ionic radius of the metal. For a metal of large radius like Au or Pb, there is very little penetration, so that the M_x-oxide interface is very close to the initial surface of the oxide. In this case, most of the molecular impurities on the oxide surface are present in the tunneling region of the junction so they contribute to inelastic tunneling. For a metal of small radius like Al or Mg, there is considerable penetration of the metal into the oxide so that the M_x-oxide interface for tunneling is in the interior of the original oxide film. In such a case, the surface impurities are not in the tunneling region of the junction and only oxide vibrations contribute to inelastic tunneling.

The composition of the oxide of Al base systems as an alumina hydrate is established by the results of Sec. III A. Residual water vapor present in the vacuum chamber during the formation of the oxide is apparently sufficient to supply the hydrogen needed in this structure. That molecular impurities reside mainly on the surface of the oxide is not well established by independent methods. The fact that the overlayer electrode has such a large effect on tunneling spectra, however, is an indication that impurities near this surface are most important, because it is only this region that is affected by the top electrode. The penetration of atoms of the top electrode into the oxide is probably a complex phenomenon depending on more than just the ionic radius of the metal. It would be expected that this penetration would depend on the space taken up by the M_x atom in the oxide, a quantity measured by its ionic radius. The above model, which explains the correlation exhibited in this section, is thus seen to reply on reasonable, but unproven assumptions about the detailed structure of the metal-oxide interface region of a junction. Further study on this type of interface will probably be necessary to prove the validity of this model.

C. Alterations Produced in Completed Junctions

An additional type of result found in these experiments involves changes in the tunneling spectra of Al-Pb junctions produced by applying a dc potential across the junctions at room temperature. These experiments were suggested by a technique described by Miles and Smith[8] for growing an oxide film between two metals. This technique, which they call "solid state anodization," consists of evaporating a film of either Pb or Sn containing a large amount of dissolved oxygen over an Al film which has been oxidized for a short time. After the evaporation of the top film, a small dc potential is applied between the metallic electrodes, the Al being held positive. When this is done, a current passes between the films which decays with time, indicating a growth of the oxide layer between the two metals. This growth occurs only when the Al is positive and only occurs at high temperatures; no oxide growth is observed when the junction is cooled to 243°K. They interpret this growth to be caused by movement, in the presence of the external field, of oxygen dissolved in the top electrode and of Al dissolved in the Al oxide to the oxide-top metal interface. When the oxygen reaches the interface, it combines with exposed Al atoms, increasing the thickness of the Al oxide.

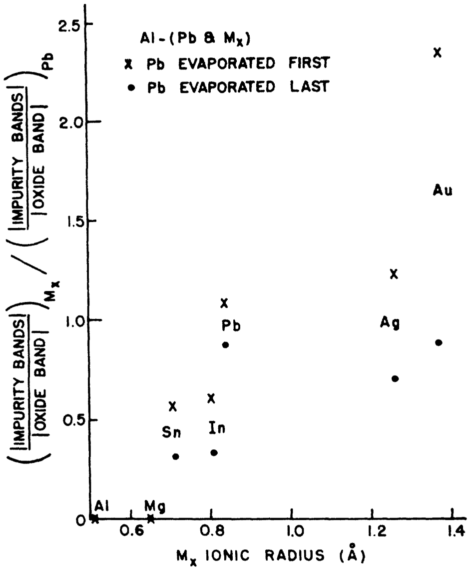

FIG. 7. Graph showing the correlation between size of the impurity bands of tunneling spectra and the ionic radius of the top electrode. Each point represents the results of an Al-(Pb and M_x) twin junction pair.

The movement of gases dissolved in an electrode of a tunnel junction to the oxide region should be detectable by changes it produces in the tunneling spectrum of the junction. To study these effects, the following operations were performed on a number of Al-Pb junctions. A junction was prepared in the usual way and a series of measurements, described in Sec. II, were made with the junction at 4.2°K. The junction was then warmed to room temperature and a dc potential was applied across it for a short time. The junction was then cooled again to 4.2°K and another series of measurements made. Maintaining the Pb electrode at +1.5 V with respect to the Al for 30 sec produced the visible changes in the tunneling spectrum shown in Sec. III A. When the potential was such that the Pb was held at −1.5 V, it was necessary to maintain the potential for a longer period, generally 2 or 3 min, to produce visible changes in the tunneling spectrum of the junction.

Warming an Al-Pb junction to room temperature after a series of measurements at 4.2°K usually increased the resistance of the junction by a factor of 2 or 3. Applying a potential which made the Pb positive made no further change in the resistance. Making the

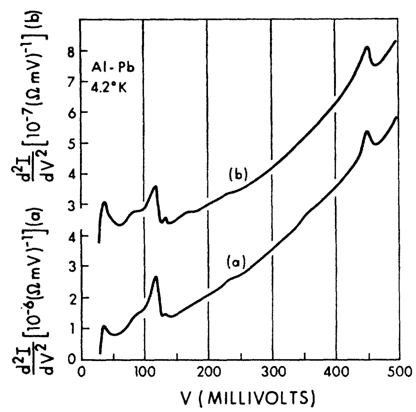

FIG. 8. (a) Tunneling spectrum of an Al-Pb junction. (b) Tunneling spectrum of the same junction after a potential of 1.5 V (Pb positive) was maintained across the junction for 30 sec at room temperature.

Pb negative increased the resistance only very slightly; a large increase in resistance like that reported by Miles and Smith was not generally seen. The reason for this may be either that the Pb did not contain enough dissolved oxygen or that the field in the Pb was not large enough to cause movement of large quantities of oxygen because nearly all of the potential drop was across the insulating layer of the junctions. The result of holding the Pb film positive for a short time is shown in Fig. 8; holding the Pb negative, in a different junction, results in the change illustrated in Fig. 9. A simple interpretation of these results is given below.

When the Pb is held positive relative to the Al, H^+ dissolved in the Pb will move toward the Pb-oxide interface in the presence of the electric field. Dissolved O^{--} in the Pb and Al^{+++} in the oxide will move away from this interface, inhibiting any growth of the Al oxide. The result is an increase in the H concentration at the interface, evidenced by an increase in the size of the free-OH vibrational band at 450 mV relative to the oxide band at 118 mV. When the Pb is held negative, H^+ dissolved in the Pb will move away from the Pb-oxide interface, whereas O^{--} in the Pb and Al^{+++} in the oxide will tend to move toward the interface, promoting a growth of the oxide. The result is a decrease in the free-OH band relative to the oxide band for this polarity.

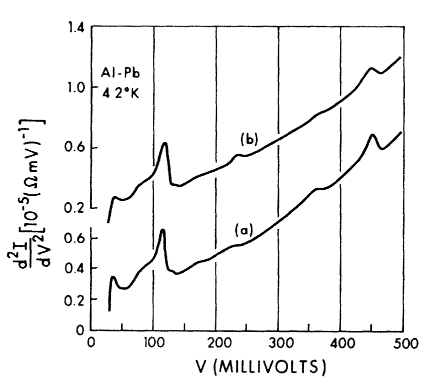

FIG. 9. (a) Tunneling spectrum of an Al-Pb junction. (b) Tunneling spectrum of the same Al-Pb junction after a potential of 1.5 V (Pb negative) was applied across the junction for 4 min at room temperature.

The simple analysis given above is based on the model Miles and Smith have suggested to explain their solid-state-anodization results. In reality, such processes are not well understood and are probably quite complex. The simple oxidation of a metal, in fact, is still the subject of considerable controversy.[18] The changes seen in the tunneling spectra do indicate that the insulating region of the junctions is being altered by this potential. The movement of hydrogen in the Pb from or to the Pb-oxide interface in the presence of these potentials would explain the basic results of these experiments and verify that it is free molecules at the interface that are largely responsible for the vibrational bands appearing at energies greater than 125 mV. In a larger context, inelastic tunneling may be a sensitive probe of such phenomena as the movement of dissolved gases through metals and solid-state oxidation processes. The above experiments demonstrate that such effects are probably observable in tunneling spectra and point the way to further studies in this area.

IV. SUMMARY

The experimental results described in this paper can be divided conveniently into three groups. The first of these is the new interpretation of vibrational bands appearing in tunneling spectra. Of particular significance is the identification of the large peak that appears between 115 and 120 mV in Al-oxide systems as being due to the OH vibration of alumina hydrate. Thus the insulating layer grown on an Al film is actually a hydroxide. We have also observed a new OH mode in Al-oxide junctions at about 75 mV.

The experimental results that constitute the second group are the electrode effects. Large effects in tunneling spectra were found to be made by the metal used as the top electrode of Al-Al-oxide junctions and a strong correlation of these effects with the ionic radius of the top electrode was established. This correlation of tunneling characteristics with atomic size is consistent with a similar type of correlation found between atomic radius and junction resistance. This correlation indicates that the penetration of the overlayer metal into the oxide layer plays a primary role in determining the current-voltage characteristics of the junction.

The last group of experimental results is the change in tunneling spectra of Al-Pb junctions produced by applying a potential across the samples at room temperature. These results, although somewhat speculative in their interpretation, may provide a means of studying diffusion of gases through metals in the presence of an electric field by electron tunneling.

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[18] J. Benard, J. Electrochem. Soc. **114**, 139C (1967).