MOLECULAR VIBRATION SPECTRA BY ELECTRON TUNNELING

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The conductance of metal–metal oxide–metal tunneling junctions has been observed to increase at certain characteristic bias voltages. These voltages are identified with vibrational frequencies of molecules contained in the barrier.

In an experimental study of a number of metal-oxide-metal tunneling junctions a new phenomenon has been identified. Tunneling electrons are found to interact with vibrational states of molecules included at a metal-oxide interface. There are increases in the conductance G of the junction occurring at various characteristic voltages V. These voltages correspond to vibrational frequencies ν of molecules contained in the junction, i.e., $eV=h\nu$. These increases represent changes in G of about 1% and correspond to the onset of new tunneling channels paralleling the bulk of the tunneling current. The characteristic voltages occur when molecular impurities are introduced in the junction, usually after formation of the oxide insulating barrier and before deposition of the top metal film. Coverage is estimated to be of the order of one monolayer.

The majority of the junctions were Al–Al oxide–Pb. These were made entirely in an oil-free ultrahigh-vacuum system (10^{-9} Torr ultimate pressure) so equipped that air was not admitted to the system until all steps in fabrication were completed. These steps include an initial pumpdown and degassing of evaporation sources, a $\frac{1}{2}$-h cleanup in a high-purity O_2 discharge (5×10^{-2} Torr, 500 V), second pumpdown, and evaporation of the 2000-Å Al film. This film was oxidized to approximately 30 Å in the gas discharge with a one-volt potential.[1] At this point, when desired, the oxide was exposed to the vapor of an organic material. After a short pumpdown the Pb overlay cross strip was deposited (~1 μ thickness) and the junctions were removed. Nominal resistance ranged from 10 to 10^4 Ω. Measurements were made with the sample in a liquid-helium Dewar so that temperatures from 0.9 to 300°K were possible. The derivative $\Delta G/\Delta V$ was measured by a second-harmonic detection system operated at a fundamental frequency of 50 kc/sec. Modulation amplitudes of 5 mV were used. Voltage was scanned up to 1 V. The effects discussed here occur in the region of 0.050 to 0.5 V corresponding roughly to the infrared (IR) region from 25 to 2.5 μ.

In Fig. 1 a number of recording traces of $\Delta G/\Delta V$ are reproduced. These were taken at 4.2°K. Each peak represents an increase of conductance of the Al–Al oxide–Pb junction. Not shown is the low-voltage region below 50 mV, where structure due to the Pb superconducting density of states was prominent. Curve A is for a junction fabricated without any deliberate addition of molecular impurities. This "clean" spectrum shows prominent peaks due to OH bending and stretching modes, respectively, as identified by comparison with IR spectra.[2] These possibly arise from OH groups present either chemically in the oxide, or as

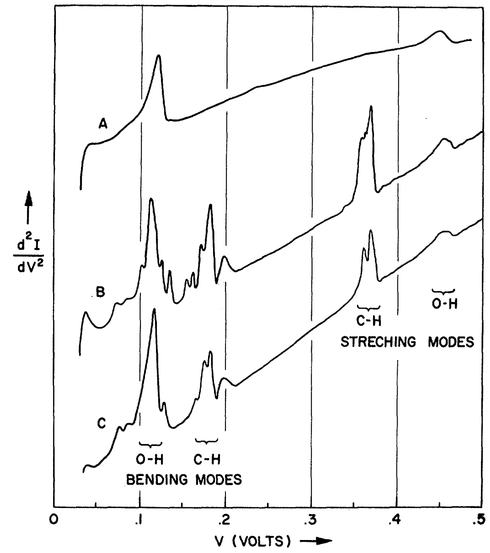

FIG. 1. Recorder traces of d^2I/dV^2 versus applied voltage for three Al–Al oxide–Pb junctions taken at 4.2°K. The zero of the vertical scale is shifted for each curve, and all three are normalized to the same arbitrary units. The largest peaks represent increases of 1% in G. Also indicated are intervals associated with the energy of IR-active molecular vibrational modes. Curve A is obtained from a "clean" junction. Curves B and C are obtained from junctions exposed to propionic acid [$CH_3(CH_2)COOH$] and acetic acid (CH_3COOH), respectively. The peak positions are independent of voltage polarity.

absorbed residual water vapor. Spectra *B* and *C* are observed when propionic acid and acetic acid, respectively, are admitted to the vacuum system. Prominent structure occurs in the C-H bending and stretching mode regions. OH vibrations are also characteristic of these spectra. Samples exposed to room air for even a few minutes produced spectra indicating contamination by other organic molecules as evidenced by typical C-H vibrational spectra. The effects of organic impurities are always seen unless care is taken to eliminate them. Other tunneling structures studied were Ta–Ta oxide–Pb, Al–Al oxide–Sn, Al–Al oxide–Al. All gave similar results. Resolution is apparently limited by temperature broadening of the Fermi edge in the metals. The lines are considerably broadened at 77°K, but have been seen up to dry-ice temperature.

We believe these observations indicate inelastic electron-molecule interactions in the tunneling. These become allowed as soon as tunneling electrons have sufficient excess energy to cause molecular excitations. Subsequent increase in voltage provides an increasing number of such candidates. This provides a mechanism for increased conduction, which occurs as each voltage threshold is reached. This may be similar to what has been observed in phonon interactions in certain p-n junctions.[3] We cannot, of course, rule out more complex mechanisms which may actually modify tunneling density of states such as are observed in strong coupling superconductors.

Vibrational spectra due to the host oxide should appear below 100 mV and indeed new structure was observed in this region. We have not made definite identifications, however. Removal of OH impurities will probably be necessary before such identification can be done reliably.

This measurement has implications for several aspects of tunneling studies as well as other related subjects. One aspect of significance is the measurement of electron coupling to surface layers on metals. This is of importance in connection with proposed mechanisms of surface superconductivity.[4] In this connection one would like to relate the tunneling scattering process which we measure to the more general problem of surface scattering. It may be possible to relate these following procedures outlined for elastic scattering.[5] This would then yield a microscopic probe of inelastic surface scattering.

It should also be noted that the technique has application in the study of various surface phenomena such as adsorption and catalysis. It also clearly has implications for metal tunneling junction technology.

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QUESTION OF SINGLET STATES OF PARAMAGNETIC IMPURITIES IN METALS*

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After Kondo's discovery of a singularity in the electron scattering cross section of a paramagnetic impurity in metals,[1] this problem was examined by Abrikosov, using arbitrary-order perturbation theory,[2] and by the present author, using scattering theory.[3] Both these treatments led to the conclusion that for antiferromagnetic exchange coupling between the conduction electrons and the impurity spin, inadmissible complex poles of the scattering amplitude will arise below a certain critical temperature T_C. Subsequently Suhl and Wong[4] showed that this difficulty could be avoided by proper analytic continuation of the scattering solution from $T > T_C$ to $T < T_C$. However, there is no guarantee that the continued solution is the one of lowest free energy.

Recently Yosida[5] suggested a variational sin-