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Inelastic Tunneling Due to Vibrational Modes of Yttrium and Chromium Oxides

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Previous measurements of the tunneling spectra (d^2I/dV^2 versus applied voltage) of metal-oxide-metal tunnel diodes have revealed the presence of structure due to the interaction of tunneling electrons with vibrational impurities contained within the oxide region. New observations with diodes of the type Y-(Y oxide)-metal and Cr-(Cr oxide)-metal reveal relatively intense structure in the range 0–100 mV which we associate with vibrational modes of the oxides themselves. Experimental evidence indicates that the structure is not due to the metal electrodes. The new spectra are comparable with infrared absorption data taken for oxide films grown at low temperatures. For both cases, the structure corresponds to an increase in conductance of slightly less than 1%, and is therefore comparable in intensity to molecular inelastic tunneling spectra. Cr oxide barriers grown at elevated temperatures (200 °C) on films produced in good vacuum (10^{-7} Torr) do not exhibit the "giant" resistance anomaly at zero bias.

INTRODUCTION

In the study of tunneling characteristics of metal-(metal oxide)-metal tunnel diodes, it has been found that tunneling electrons can lose energy upon tunneling from one metal to another, in contrast to the usual *elastic* tunneling picture.[1] These new *inelastic* tunneling processes arise because electrons can lose their energy by creating excited vibrational states within the barrier layer and thereby go to final states of lower energy. Such processes can only happen if the applied voltage $|V| \geq h\nu/e$ where ν is the vibrational frequency. Such behavior accounts for the observation that structure in the I-versus-V curves for diodes has been caused by the addition of molecular organic impurities in the oxide layer. In fact, the second derivative d^2I/dV^2 versus V yields a series of peaks resembling optical absorption spectra with the wavelength related to the voltage by $e|V| = h(c/\lambda)$. These tunneling peaks correspond to a net *increase* in the conductance of the junction and typically are about 1% for a molecular impurity. For organic vibration spectra the majority of peaks occur in the range 50–500 mV corresponding to the near-infrared spectral region (2-25-μ wavelength).

In addition to molecular impurities, there is no fundamental reason why other types of excitations should not be seen. The Al-(Al oxide)-metal system, most extensively studied for the case of molecular additions, also showed structure due to the presence of OH bonds which were found to be characteristic of the insulating barrier.[1] Structure attributable to the Al_2O_3 vibrations was not seen, however. It is possible that these results and other studies[2] indicate that the insulating barrier is not Al_2O_3, but possibly some other chemical species involving OH radicals. Giaever and Zeller[3] produced a series of diodes in whose tunneling layers were evaporated small amounts of inorganic insulators. They found intense structure which, for some cases, could be associated with known vibrational lattice modes of these materials. Other experiments have indicated that PbO lattice vibrations were observable in Pb-(Pb oxide)-Pb diodes.[4] Adler[5] has observed structure in Mg-(Mg oxide)-metal diodes which shows a correlation with experimental optical data on MgO.

Oxide vibrational spectra typically occur in the spectral range 25–200 mV or 5–50-μ wavelength and should produce structure as intense as organic molecules. This is inferred from typical absorption coefficients measured optically for these materials. By analogy with molecular tunneling, the coupling of tunneling electrons with the lattice vibrations can be visualized to take place by a direct interaction of the electrons with those modes of oxide which show optical activity. This activity can either be infrared absorption or Raman scattering.

Structure due to the phonons of the metal electrodes has also been observed,[4,6] even with the metals in the nonsuperconducting state. These are less intense (< 0.5%) than organic or oxide phonons and occupy the range 0–50 mV or 25–200 μ. However, the details of how these phonon modes couple to tunneling electrons are just now beginning to be understood.[7] It appears that at least a part of the structure observed in these diodes is caused by inelastic tunneling processes. It is important to note that none of the above effects is associated with superconductivity of the electrodes.

The present experiment is a report of the observation of structure in the tunneling spectra of Y-(Y oxide)-metal and Cr-(Cr oxide)-metal tunnel diodes. This structure is believed to be due to the oxide vibrations. Both of these metals form dependable tunnel junctions with a variety of metals as top electrodes. Yttrium is an example of a metal which will form a good tunneling oxide layer upon exposure to pure oxygen. It has been known for some time that Cr-(Cr oxide)-metal diodes can exhibit large resistance anomalies, one of whose characteristics is the very large temperature dependence of the resistance at zero bias, together with a large resistance peak centered about $V=0$.[8] It was found in these experiments, however, that if the Cr films were deposited at 10^{-7} Torr or better and oxidized at elevated temperature (200 °C) in air, this effect could be greatly reduced.[9] This made possible the observation of the structure between 25 and 100 mV.

TUNNELING MEASUREMENTS

The diodes were fabricated according to the general procedure previously described.[1] Base-metal films of Y or Cr were deposited in an oil-free vacuum of 10^{-7} Torr or less by evaporation from an electron-beam gun. Cr was also deposited from a resistance-heated tungsten boat. Although heating the substrate to 450 °C resulted in Cr films with resistivities near bulk values,[10] no difference in the tunneling data was observed.

For Cr, oxidation was accomplished by heating in air at 200 °C for 2 h or more. Attempts to produce Cr-(Cr oxide)-metal tunnel junctions by exposure to pure O_2 were not successful, even with added water vapor and temperatures up to 200 °C. Likewise, attempts to use a gas discharge method failed. For Y, the oxidation took place in one-half atmosphere of pure O_2 for 2 h. Exposure of Y to air results in rapid oxidation with unsatisfactory tunneling oxides. After oxidation, the top metal cross strip was deposited. This was usually Pb, although a variety of metals (Sn, Pb on Y; Sn, Pb, Tl on Cr) showed the same behavior insofar as the oxide vibronic structure was concerned. We experienced no success in making a diode with a Cr *top* film. This included Al-(Al oxide), Y-(X oxide), Cr-(Cr oxide), and Ta-(Ta oxide) base structures. Typical diode resistances were in the range 25–1000 Ω. Ratios of resistance measured at zero bias for room temperature compared to 4 °K were 1:2 or more for Cr-(Cr oxide)-metal and 1:2 for Y-(Y oxide)-metal. Cr-(Cr oxide)-metal diodes had a long shelf life with no observable degradation of tunneling properties and only slight increase in resistance. Y-(Y oxide)-metal diodes, on the other hand, were unstable with time and were studied immediately after removal from the vacuum system. Attempts to add organics to Y-(Y oxide)-metal diodes were unsuccessful in that no useable diodes were obtained.

Measurements were made in a ^{4}He cryostat, usually at 4 °K. With superconducting Pb or Sn as the top metal, it is possible to check the low-voltage tunneling properties of the diode. The superconducting density-of-states structures near zero bias were in quantitative agreement with theory. In addition, the Pb and Sn phonon lines due to the superconducting density of states as well as those observed with Pb normal were both visible.[6] This indicates that, at least for low voltages, the current through these oxides is due to tunneling.

OPTICAL MEASUREMENTS

In order to make a meaningful comparison of our data with optical measurements, it was decided to make a direct measurement of the optical properties of the grown oxides themselves. In order to do this, reflectance measurements were taken with a Perkin Elmer model 521 spectrometer. To obtain oxides of sufficient thickness, it was necessary to increase the temperature and time over that used for growing tunneling oxides. For Y-(Y oxide), a temperature of 200 °C in dry air was sufficient to produce an oxide of about 2500 Å in several hours. For Cr, it was difficult to achieve thicknesses above a few hundred angstroms even for temperatures of 450 °C or more.

Typically, of course, the reflectance of clean metals is near 100% in the infrared region and shows no structure. The spectra obtained from the Y-(Y oxide) samples are characteristic of "thick" oxide films, i.e., the over-all reflectance is greatly decreased from near 100%, and peaks in the absorption coefficient cause peaks in the reflectance. For Cr, on the other hand, the very thin oxide causes only a relatively small decrease of the reflectance from 100%. Absorption peaks in this case cause reflectance dips. This behavior is especially evident by inspection of the actual data.

It was found that this direct measurement of oxide infrared spectra was very successful for locating the actual absorption peaks of the oxide in order to compare with the tunneling data. The difficulty with using published transmission or reflection spectra taken with powders or other crystalline types of samples is caused by the large variation in reflectance also occurring in this spectral range.[11] In such measurements, for example, a peak in the absorption spectra can be caused by a peak in the reflectance and need not correspond to any fundamental absorption at that wavelength. Thus, the actual data is often dominated by dispersion effects. In fact, the thin film infrared data seems to be a more direct measurement of the location of absorption maxima than the more usual method of analyzing reflectance data. Optical data on crystalline Y_2O_3 and Cr_2O_3 are available.[12,13] Whenever comparison was possible, fundamental absorption peaks inferred from reflection spectra on crystals agreed with our data.

It is felt that the actual measurement of oxides in the as-grown state is more pertinent to the present experiment. It is likely that the oxides formed are Cr_2O_3 and Y_2O_3. It is known that such oxides are amorphous,[14] and hence are not necessarily comparable with the vibrational properties of crystalline samples. In fact, "low-temperature" oxide as used here designates that temperature range over which the oxide is amorphous and optically smooth. Above these temperatures, the oxidation causes formation of a microscrystalline film which can become quite diffuse optically. For Cr, the low-temperature range extends as high as 450 °C. For both metals the unoxidized metal films showed high reflectivity (~ 95% or more) and were structureless over the range of interest.

DATA AND RESULTS

Chromium

Figure 1 shows the curve of d^2I/dV^2 versus voltage for a Cr-(Cr oxide)-Pb diode at 4 °K. The superconducting energy gap structure has been removed by the application of a magnetic field, although this did not affect the structure of interest for fields as high as 17 kG. The structure from 25–100 mV is apparent and is represented by a series of peaks at about 30, 60, and 90 mV. These appear in both polarity directions, although obviously the structure is not symmetric. The large step structure at zero bias represents the resistance maximum discussed above. Although it is still quite observable, it is sufficiently narrow at 4 °K so that it does not interfere with the structure of interest. Although it is not shown in Fig. 1, it is possible to increase the resolution in the range 0–10 mV and observe the structure due to the normal phonons of the Pb electrode.[7] Although it might be expected from neutron diffraction data that the Cr metal phonons should appear at 30 mV (TA) and 45 mV (LA)[15] with the LA modes strongest, there is no evidence of them. The intensity of the tunneling structure is about 0.5%, or about the same strength as molecular vibronic structure. This is to be expected from the optical absorption strengths of such partially ionic crystals. Due to the relatively large increasing background, absolute intensity measurements are difficult to make accurately.

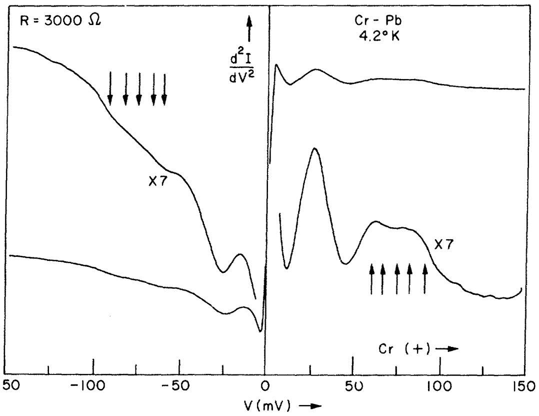

FIG. 1. Plot of (d^2I/dV^2) in arbitrary units versus applied voltage V for a Cr-(Cr oxide)-Pb tunneling diode at 4.2 °K. The arrows indicate the structure associated with the vibrational modes. Modulation amplitude was 3 mV.

At low voltages it was easy to observe the effect of the superconducting energy gap and density-of-states phonons as well as normal metal phonons. However, structure due to hydrocarbons (expected at 180 and 360 mV) was not usually observed even though the tunneling layer was exposed to room air for 1 h or longer. In one case, when an estimated monolayer of acetic acid was included in the tunneling layer, barely detectable organic peaks were observed. Under similar conditions, Al-(Al oxide)-Pb diodes would show intense organic structure. A similar lack of organic spectra where they were expected has been reported by Mikkor and Vassell[16] in Schottky barrier diodes.

Figure 2 shows the infrared reflectance data for three oxidized Cr films where the thickest oxide is several hundred angstroms. The arrows indicate the position of the principal vibrational modes of the oxide as measured with infrared for oxide films grown at 450 °C on the Cr film. The arrows shown in these optical data correspond with those shown in the tunneling spectra. Although the sharpness of the tunneling spectra is not as good as the infrared data, the agreement in position is seen to be good. It was not possible to obtain optical data to check the peak at about 27 mV.

Yttrium

Figure 3 shows the spectrum d^2I/dV^2 versus V for a Y-(Y oxide)-Pb diode. The structure between 25 and 100 mV is similar in character to the Cr

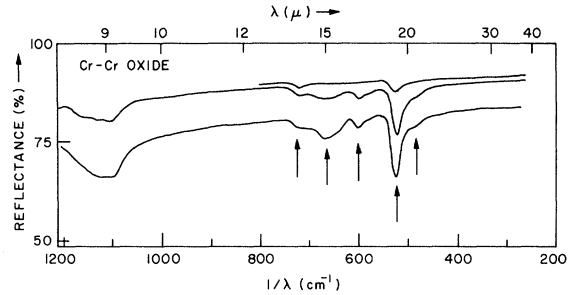

FIG. 2. Reflectivity of Cr-(Cr oxide) films versus wavelength (μ) or wave number (cm^{-1}). The oxide was grown at 450 °C and the thickness was approximately 200 Å for the lowest curve. The arrows indicate frequencies of reflectance dips associated with absorptions by vibrational modes.

case and is of comparable intensity. Although it is not resolved in this figure, the Pb phonon peaks in the 0–10-mV range were easily seen. The vibrational structure for the Y-oxide-metal case is sharp enough that the presence of the Pb superconducting energy gap improved the resolution slightly. Otherwise the peaks were unaffected by magnetic fields up to 17 kG. It was noted also that a peak which is believed to be an OH peak was consistently seen at 450 mV. The OH stretching mode has been observed in Y_2O_3 crystal absorption spectra.[13] Note that above a few hundred mV, the background was varying quite rapidly.

The reflection of a Y film oxidized at 200 °C to a thickness of 5000 Å is shown in Fig. 4. The base metal film was about 4000-Å thickness before oxidation. Note that the various peaks indicated by arrows correspond to the arrows in Fig. 3 and are in reasonable agreement with the tunneling peaks. The origin of the peaks at 105 and 133 mV is not understood, although it is likely that one is due to an OH bending mode. Although the Debye temperature of yttrium (300 °K) would suggest the normal phonon peak to be present near 28 mV, no definite evidence for its presence was observed.

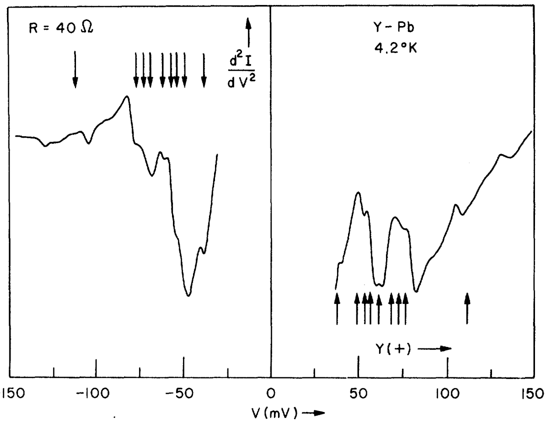

FIG. 3. Plot of (d^2I/dV^2) in arbitrary units versus applied voltage for a Y-(Y oxide)-Pb tunneling diode at 4.2 °K. The arrows indicate the structure associated with yttrium oxide vibrational modes. Modulation amplitude was 2.5 mV.

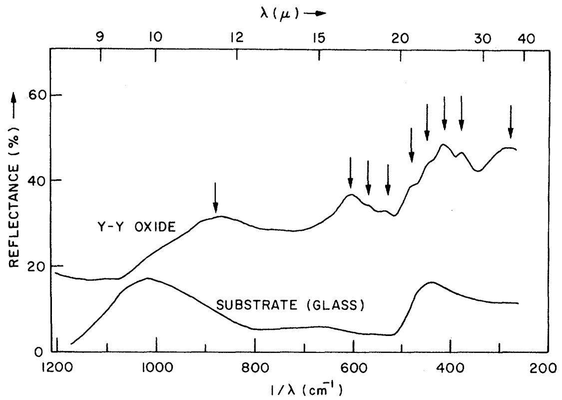

FIG. 4. Reflectivity of Y-(Y oxide) film versus wavelength (μ) or wave number (cm^{-1}). The oxide thickness was approximately 0.5 μ. The arrows indicate frequencies of peaks associated with absorption by vibrational modes. Note the over-all decrease in reflectivity from 100%.

CONCLUSION

The new structure described here for the two cases Y-(Y oxide)-metal and Cr-(Cr oxide)-metal is believed to be caused by inelastic excitations of the oxide vibrations. The energy range and intensities are both in agreement with that expected from infrared data obtained from grown oxides. It is not believed that such structure is caused by the metal electrodes since the results are independent of the type of top metal electrode. It has also been found that the large resistance anomaly about zero bias for the case of Cr-(Cr oxide)-metal can be avoided by clean evaporation and high-temperature oxidation. However, there is always a "remnant" of this zero-bias resistance maximum, which is strongly temperature dependent. In addition, Y_2O_3 was found to oxidize at a reasonable rate in an atmosphere of pure O_2. This has not been possible with Cr or Al, even at temperatures as high as 200 °C. Unfortunately, samples prepared with the Y-(Y oxide)-metal combination do not have good aging properties. The weakness of molecular spectra in the Cr-(Cr oxide)-metal diodes is not understood at this time. It is possible that, even for those instances where molecular spectra are observed, a special circumstance must exist to permit the molecules to be situated in such a way that they are not screened by being "buried" in the top metal film. Other explanations, of course, are also possible. The occurrence of molecular spectra in Y-(Y oxide)-metal diodes could not be tested.

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Measurement of the Anisotropic Resistivity Tensor of Silver Using Heliconlike Waves[*]

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Standing-wave resonances of heliconlike waves have been used to measure resistivity tensor elements R_{ij} in silver single crystals. Flat-plate samples were used. Data were taken for ±12° regions near the major directions [100], [111], [110], and [211]. Curves are presented of the variation of the R_{ij} elements with field direction. Data are also presented as functions of field strength with the field direction fixed along major directions. Reversing the field allowed the separation of terms even and odd in field. These data represent a more complete study of resistivity tensor elements in silver for field directions near major axes than has previously been available.

I. INTRODUCTION

Electromagnetic heliconlike waves have been used to measure the elements of the anisotropic resistivity tensor of silver as functions of crystallographic direction near the principal axes. The results are a more complete study of resistivity tensor elements for directions near principal axes than has previously been available. dc measurements of galvanomagnetic properties of metals have been used for some years to help determine Fermi-surface topology.[1] dc measurements of the transverse magnetoresistance[2] indicate that the silver Fermi surface makes contact with the Brillouin-zone boundary.

In the present ac experiments, flat-plate samples were used whose normals lay along the major crystallographic directions. The propagation direction for the waves was along the plate normal. The theory for helicons in this geometry is well