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TUNNELING SPECTRA OF IMPURITY MOLECULES IN Sn-Sn *AND* Pb-Pb *JUNCTIONS*

I. K. YANSON and N. I. BOGATINA

Physico-technical Institute of Low Temperatures, Ukrainian Academy of Sciences

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Tunneling spectra of impurity molecules adsorbed onto the oxide layer during the preparation of tunnel junctions are investigated. It is found that the structure of the second derivative of the current-voltage characteristic reflects the interaction between tunneling electrons and molecular excitations in the barrier layer. A vibrational spectrum of organic compounds characterized by the presence of CH (and OH) group absorption bands is observed for Sn-Sn junctions obtain by oxidation of the primary Sn film in ordinary air. The resolving power increases sharply at the superconducting transition of Sn. No vibrational bands were observed in spectra of Pb-Pb junctions.

TUNNELING spectroscopy, based on the inelastic passage of electrons through a potential barrier, has in recent years been developed as a new method of investigating the energy spectra of various molecules adsorbed on the surface of an oxide layer.[1,2] Almost all the experiments have thus far been performed with junctions of Al and its oxide.[1-3] These junctions present serious disadvantages despite the relative ease with which they can be prepared. First, the spectra of these junctions always include absorption bands of OH groups (interfering with the observation of the desired spectra), which result from the fact that aluminum oxide hydrate is a constituent of the barrier layer that cannot easily be eliminated. Secondly, the superconducting transition of Al occurs at a low temperature ($T_c \approx 1.2°K$), so that the experiments must be performed at very low temperatures.

It is extremely desirable to use superconductors as tunnel junction electrodes, for the following reasons: 1) The resolving power is much higher when superconductive films are used; 2) we do not have the problem of current and potential losses at a junction because of the partial voltage drop in normal-state films; 3) the initial segment of the current-voltage characteristic ($V < 2\Delta/e$, where 2Δ is the energy gap) can serve as a good indicator of tunneling in the sample, i.e., we can determine the fraction of the total current that results from the tunneling mechanism.

We are here reporting an investigation of tunneling spectra for Sn-Sn and Pb-Pb junctions in both the normal and superconductive states. It was our aim to determine the utilizability of these junctions for the tunneling spectroscopy of molecules. As is customary,[4] we plotted the second derivative $d^2I/dV^2(V)$ of the current-voltage characteristic, which is proportional to the density of states in the barrier.[4] The modulating voltage was a few mV, while the measured signal of the second harmonic in the sample did not exceed 1 μV. Impurity molecules entered the barrier during the oxidation of the lower tin film in "ordinary" air. The resistance of the junctions was 5–30 Ohms; their area was ~ 0.4 mm^2. At the superconducting transition of the films there were observed a sharp current rise at $V = 2\Delta/e$[5] and phonon characteristics of the state density of superconductors,[6] thus indicating the high quality of the samples. At the present stage of the experiments no attempt was made to artificially introduce impurities into the barrier.

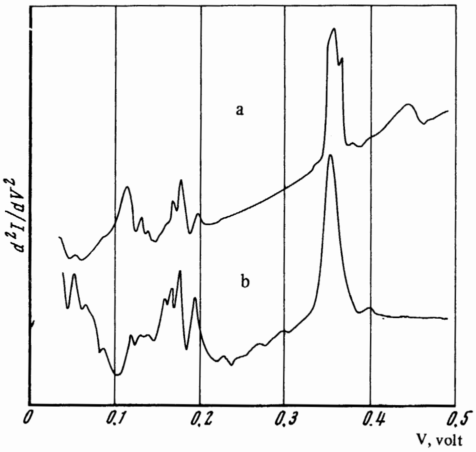

FIG. 1. Tunneling spectra of impurity molecules: a—for an Al-Pb junction, according to [1,2]; b—for a Sn-SnO$_2$-Sn junction. T = 4.2°K, V_1 = 4 mV (the modulating voltage), R_N = 12.5 Ohms. The scale of the ordinate axis is arbitrary.

In Fig. 1b the spectrum of impurities in the oxide layer of a Sn-Sn junction is compared with a similar spectrum for Al-Pb junctions given in[1] (Fig. 1a). We immediately observe structure common to both spectra in the 0.15–0.2-V region and an intense bands at 0.35 V. To the extent that vibrational and rotational molecular excitations are optically active, the tunneling spectrum repeats the IR absorption spectrum of the given materials. According to the IR spectroscopy of hydrocarbons[7,8] we have valence vibrations of the CH$_3$ group at 0.367 and 0.355 eV and valence vibrations of the CH$_2$ group at 0.362 and 0.353 eV. The addition of their intensities yields the observed band at V = 0.345–0.355 V in Figs. 1 and 2. The bending vibrations of the CH$_3$ group at 0.17 and 0.18 eV according to IR spectroscopy data can be compared with the observed bands at 0.166 and 0.176 eV, and the bending vibrations of the CH$_2$ group at 0.182 eV can be compared with the band in the tunneling spectrum at 0.19 V. The observed energies are seen to differ from the corresponding vibrational energies of molecules in their free state. The energy difference appears to re-

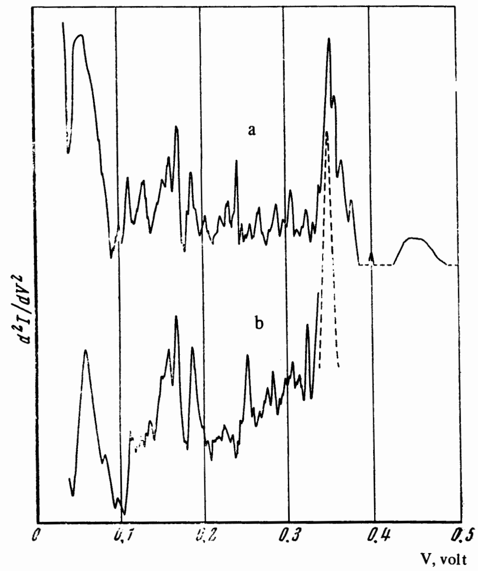

FIG. 2. Tunneling spectrum fine structure at the superconducting transition of Sn. Voltage is measured from the energy gap of tin ($2\Delta/e$ = 1.22 mV); T = 1.5°K; V_1 = 5 mV. a—positive polarity of the applied voltage; b—negative polarity of the applied voltage. The CH_3 vibrational band has been shifted downward on the ordinate axis.

sult from bonds between atoms of the impurity molecules and atoms of the surrounding crystal matrix.

A difference between the two spectra shown in Fig. 1 consists in the absence of valence (0.44 V) and bending vibration (0.12 V) bands of the O-H bond in the spectrum of Sn-Sn junctions. Only one of the six junctions investigated by us revealed OH vibrational bands (Fig. 2); when we repeated the registration of the spectrum these bands either disappeared or were drastically weakened. We must also point out the following characteristics of the spectra for all the junctions. The spectral intensity is greater when the lower film is negative. The superconducting transition of the films is accompanied by a notable shift of the CH bending vibration lines toward lower voltages. At the superconducting transition of Sn the spectrum reveals fine structure (Fig. 2) corresponding to transitions between low-lying energy levels (such as hindered rotations, torsional vibrations etc.) and indicating enhanced resolving power. We did not proceed to interpret the spectrum, but simply note here that Fig. 2 shows what detailed information regarding internal motion in molecules is obtained from tunneling spectra. It is interesting that the broad band at $V < 0.1$ Volt resulted from the absorption of tunneling-electron energy by optical phonons of the tin oxide.[9]

Proceeding now to describe the properties of Pb-Pb junctions, we note that in several experiments the oxidized film was specially cooled (300° > T > 200°K) to reduce desorption in the vacuum. However, in all cases we were unable to register impurity spectra. This means either that impurity molecules are weakly adsorbed on lead oxide, or that the spectra are very weak when lead is used to coat an electrode (the upper film). The latter explanation would conflict with data obtained for junctions of Al and its oxide.[1] Clarification would be obtained from further study of impurity molecule tunneling spectra in Sn-SnO-Pb and Pb-PbO-Sn junctions. We note that for Pb, as for Sn, a band was observed, representing the excitation of optical phonons in the oxide, in the 30—60-meV region.[9]

Our experiments indicate that the tunneling spectrum of impurity molecules in Sn-Sn junctions prepared by oxidation in "ordinary" air resembles the analogous spectrum for Al-Pb junctions,[1] although the absorption bands of OH groups in Sn-Sn junctions are suppressed, as a rule. On the other hand, the tunneling spectrum of Pb-Pb junctions contains no molecular excitation bands; this appears to indicate the absence of impurities in the barrier.

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