

Preliminary spectroscopy measurements of Al-Al₂O_x-Pb tunnel junctions doped with single molecule magnets

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Tunnel junctions have been fabricated in which the insulating barrier of Al-Al₂O_x-Pb have been doped with single molecule magnets. Low frequency resistance measurements show that the molecules are present in the insulating barrier. The samples were cooled below the T_c of Pb, and spectroscopy shows that the doped samples are tunnel junctions.

Single molecule magnets (SMMs) have been of much interest since their first discovery in 1993 [1]. These molecules are interesting due to their superparamagnetic-like properties and small (nanoscale) size, which make them ideal candidates for information storage in quantum computers. The ability to create large quantities of identical molecules allows for easy measurement of their properties, due to ensemble behavior. The bulk of SMM research to this date has focused on magnetization properties of crystals of SMMs [2]. In this project, the design of an apparatus to measure tunnel junctions and preliminary measurements of the characteristics of tunnel junctions doped with SMMs is reported. Inelastic electron tunneling spectroscopy (IETS) will be used to probe for inelastic excitations of the molecules in the barrier. IETS involves the measurement of the first and second derivatives of the conductance of the tunnel junction as a function of the voltage applied across the sample [3]. It is our hope that we will be able to measure the vibrational frequencies of these molecules at energy scales of hundreds of millivolts using IETS. Due to the large spin of these molecules (S=10 ground state), we also hope to measure magnetic-field dependant tunneling spectroscopy. These molecules can have 21 different spin orientations with distinct energies, and the

application of a magnetic field will break the degeneracy, possibly creating a resonant tunneling effect that would be measurable [4].

This report is on measurements of metal-insulator-superconductor (MIS) tunnel junctions in which the insulating barrier is doped with SMMs using a novel technique employing a photoresist spinner, with a dilute solution of SMMs in a surfactant. Low frequency resistance measurements show that the SMMs are in the insulating barrier, giving rise to a larger normal state resistance. In addition, tunneling resistance data show that the doped samples are indeed tunnel junctions.

The apparatus for this experiment consisted of a liquid helium dewar, vacuum pump, and sample probe. The helium dewar is a Cryofab CSM-35 with a liquid nitrogen outer jacket. This dewar, which was placed inside a screen room, is connected to a Welch 1397 vacuum pump located outside the screen room. A base pressure of 30 mTorr can be reached in the helium space of the dewar with this pump. The pumping line can also be backfilled with gaseous helium for liquid helium transfers, and the exhaust of the pump can be hooked up to a helium recovery system to avoid wasting helium. The sample probe is a sealed probe, with a tapered seal around the sample space, and a port on the top of the probe for evacuation. The sample area has 12 different leads for measuring multiple samples, a silicon diode thermometer with a range from room temperature to 1.5K, and a thin-film platinum thermometer with a temperature range from room temperature to 30K. In addition, the probe is equipped with a heater for regulating the temperature inside the probe.

The tunnel junctions used in this experiment were made by first evaporating Al through a shadow mask onto a clean glass substrate. The samples were grown in a

vacuum system at a pressure of 10^{-7} torr. Following the Al deposition, the sample was exposed to air in order to oxidize the surface. This created a thin layer ($\sim 20\text{\AA}$) of aluminum oxide, the insulator for the MIS tunnel junction. After exposure to air, the sample was doped with the SMM compound Mn_{12}Pr (molecular formula $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{CH}_3)_{16}(\text{H}_2\text{O})_3$), which was diluted in methylene chloride. The SMMs were placed at the surface of the Al_2O_x using a photoresist spinner. A solution of SMMs were dropped onto the sample, and the excess liquid was spun off the sample as it rotated on the spinner. Any remaining methylene chloride evaporated during the deposition of the counter electrode, due to its high vapor pressure. The counter electrode for the MIS tunnel junctions used in this experiment was Pb. Pb was used because the observation of an energy gap is the only way to distinguish tunneling from an Ohmic short. Since Pb becomes superconducting at 7.2 K, cooling the sample to liquid helium temperatures allowed for measurement of the gap. Approximately 5000\AA of Pb was deposited through a shadow mask, creating 5 junctions per sample. The areas of the junctions are

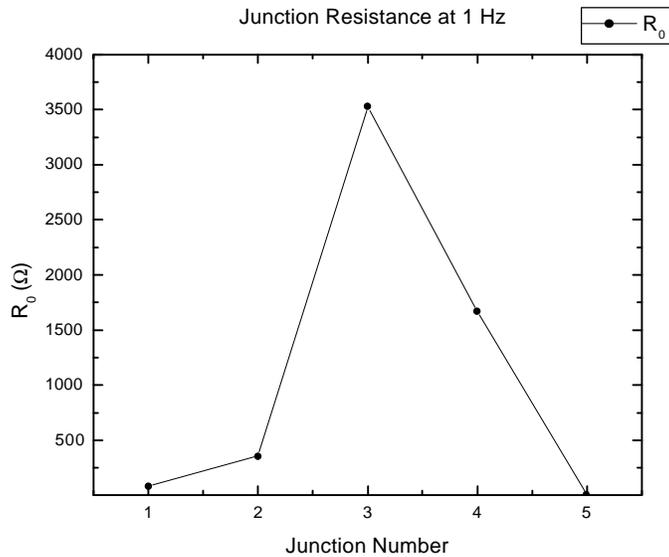


FIG. 1. Resistance values at 1 Hz for five junctions on a common glass substrate. A drop of SMMs in solution was placed on the middle of the sample, where the resistance is much higher. Due to the sample being spun to remove excess solution, the barriers of the adjacent junctions were also doped.

approximately $1 \times 10^{-2} \text{ cm}^2$. Frequency-dependent impedance measurements were performed on the samples to investigate the presence of SMMs in the insulating barrier of the MIS junction. A plot of the resistance vs. junction number for a typical sample is shown in Fig. 1. In this particular sample the solution of SMMs was placed on the center of the sample. Here, the resistance is much higher, and the junctions on the edges of the sample have much lower resistances, suggesting that SMMs are present in the insulating barrier.

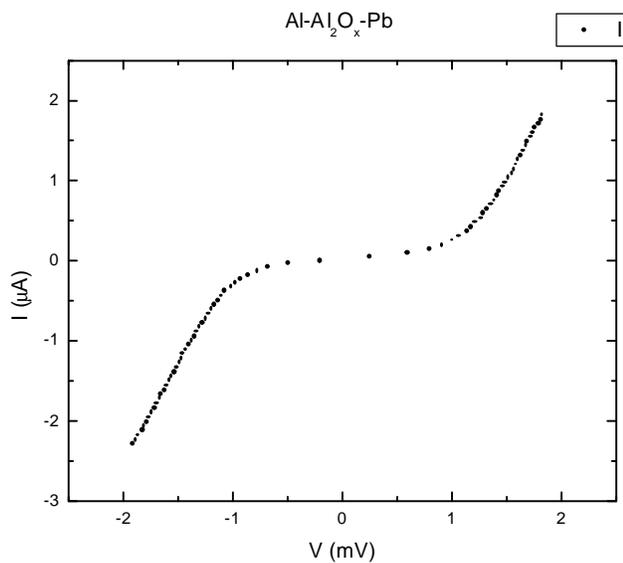


FIG. 2. Current-Voltage characteristic for an Al-Al₂O_x-Pb tunnel junction. Notice that the gap is not perfectly flat, possibly due to a partial short in the junction. Also, there is a small offset in the voltage amplifier, causing the gap to be asymmetric about V=0.

The junction studied for this report had a normal-state resistance of 958 ohms. After the sample was fabricated, it was then cooled to a temperature of 2.1 K, and an I-V characteristic of the junction was measured. A plot of this is shown in Fig. 2. In the normal state, the I-V characteristic should be a straight line (due to Ohm's law). However, since Pb becomes superconducting at 7.2 K, there is an energy gap in the Pb electrode, and as a result, there is a voltage region where transport is forbidden. After the voltage has been increased above the energy of the Pb gap (1.8mV), transport is

I-V Measurement Circuit

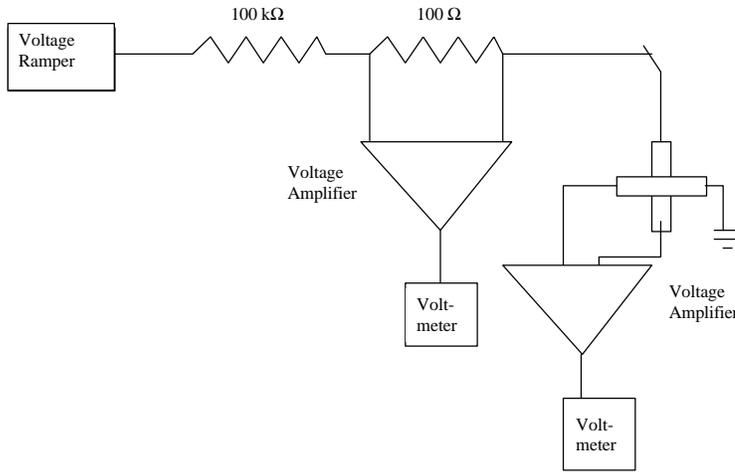


FIG. 3. Diagram of circuit used for measuring I-V of tunnel junctions. Princeton Applied Research model 116 voltage amplifiers were used to amplify the signals, in order to increase the signal to noise ratio. The voltage ramper is battery operated, and has a range of $-1.4V$ to $.4V$.

allowed, and the I-V curve is roughly linear, with a slope equal to that of the normal state.

The circuit used for measuring the I-V characteristic is shown in Fig. 3. Due to the small signals that are being measured in tunneling experiments, it is essential that sources of

dV/dI Measurement Circuit

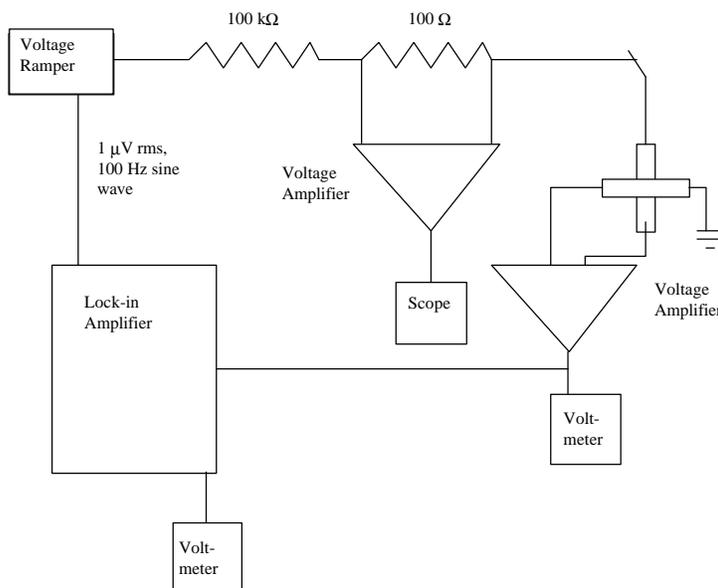


FIG. 4. The circuit shown here is similar to the circuit in Fig. 3, with the lock-in amplifier being the major addition. The purpose of the lock-in is twofold: to provide a small ac signal in addition to the dc current across the junction, and to measure voltages across the junction at the same frequency. The oscilloscope is used to monitor the current.

noise be eliminated in order to increase the quality of the measurement. The voltage ramp and voltage amplifiers used in this circuit are powered by lead-acid batteries in order to eliminate signal noise from electrical outlets. The ballast resistor is used to limit the amount of current going through the sample, and the 100 ohm resistor acts as a current sensing resistor. The data were taken in a screen room to eliminate background noise from the laboratory.

To observe excitations in the barrier of the MIS tunnel junction due to the presence of SMMs, a measurement of the differential conductance (or differential resistance) of the junction must be performed. It is our hope that excitations of the SMMs will lead to small changes in the I-V characteristic, which will show up as inflection points in the differential conductance data (much like phonon structure). The presence of these molecules will provide an additional conductance path through the barrier, changing the spectroscopy of the junction. A diagram of the circuit used to measure differential resistance is shown in Fig. 4. Summed into the dc voltage ramp is a small ($\sim 1\mu\text{V}$) ac signal at a frequency of 100 Hz. A Princeton Applied Research model 124 lock-in amplifier is used to detect small excitations across the tunnel junction at the signal frequency. A plot of data taken using this circuit is shown in Fig. 5. The voltage was swept from -14mV to 4mV , due to limitations in the voltage source and the high impedance of the junction. The excitations at -9mV and -5mV are the well known phonon excitations of Pb [3]. It is hoped that similar excitations will be produced due to the presence of SMMs, but they were not observed in this voltage range. However, due to instrument limitations, we were not able to go to a voltage level where excitations

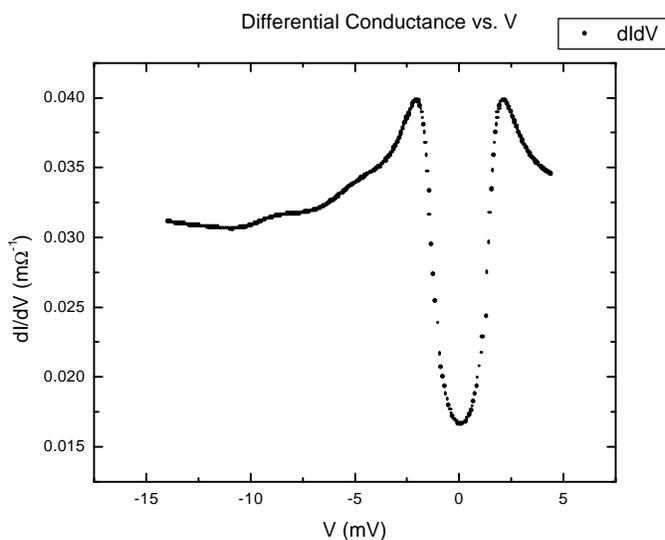


FIG 5. A plot of the differential conductance is shown from $V = -15$ to 5 mV. The data shows the phonon structure of Pb, and the energy gap around $V = 0$.

would be expected. A voltage ramp that sweeps from -200 to 200 mV is desirable to look for the effect.

In conclusion, an apparatus to characterize MIS tunnel junctions was constructed, and preliminary data show that MIS tunnel junctions were doped with SMMs. However, the preliminary IETS measurements do not show any evidence of additional conduction paths through the junction due to the presence of these molecules. Modifications of the apparatus are needed in order to perform spectroscopy at higher voltages, and magnetic-field dependent measurements are needed.

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