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PROGRESS REPORT FOR DEPARTMENT OF ENERGY CONTRACT NO: DE-AC02-79ER10375,

ENTITLED: "Study of the Motion of Electrons in Non Polar Classical Liquids. Measurement of Hall Effect and f.i.r. Search for Low Energy Traps."

Date: March 10, 1981 Project Director: G. Ascarelli

ABSTRACT

This progress report covers the last 12 months. It reports progress on experiments aimed at the measurement of the Hall mobility of injected electrons in classical non polar insulating liquids and the optical absorption associated with electrons captured by shallow traps in the liquified rare gases. Theoretical work aimed at a better understanding of the trapping kinetics of electrons by SF_6 and O_2 dissolved in rare gas liquids was also carried out. Its conclusion is that the electric field dependence of the trapping probability can be explained, basically without adjustable parameters, by considering the Poole-Frenkel-Schotky ionization of the excited state of the traps.

From the analysis of published data on the motion of electrons in liquid ethane it is tentatively concluded that at low temperatures the trapping of electrons in the liquid involves a Jahn-Teller like distortion of a single ethane molecule while at higher temperatures it is necessary to consider a small molecular cluster, possibly made up of 2 molecules.

PROGRESS REPORT

At the time of the previous progress report we indicated that we had completed most of the electronics for the Hall experiment. We had designed and ordered parts for the construction of equipment for the f.i.r. photoconductivity experiment.

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DISCLAIMER

The Fourier spectrometer for the experiment had been constructed but had neither been tested nor interfaced to a minicomputer.

a) Hall Mobility

During the last year we tested our technique for the measurement of the Hall mobility in insulators by measuring the Hall mobility of photoelectrons produced by X-rays (obtained from a linear accelerator pulse) in both CdS and air. The agreement with other researchers in the case of high purity insulating CdS was excellent (293 cm^2/Vs), well within the range of the scatter of the values reported in the literature.[1-4] In the case of air (atmospheric pressure) $\mu = 500\ cm^2/Vs$, the deviations from the data of "pure" dry air[5] were ~ 25%. This is natural since the laboratory air is various gases; e.g., the H_2O vapor content is not controlled, there are NO_x and other oxides, etc.

These measurements were carried out to test our use of the Redfield technique with known samples, and with the x-rays produced by the linac rather than light. The possibility of spurious signals is increased with the linac. The signal from CdS is ~ 100 times larger than that expected from $Si(CH_3)_4$ while that from Air is about 10 times smaller than what is expected from the liquid.

In order to carry out these measurements we had to develop a set of thick metal film plates with resistances between $10^6\ \Omega$ and $10^7\ \Omega$ (to be able to use everything with batteries). This was accomplished with the help of Prof. Vest in the Materials Engineering Department and Centralab - Electronics (Division of Globe Union, Inc.) using the techniques developed for Cermet resistors. This technique by which a metal oxide is bonded to saphire should not introduce any contamination into the liquid.

Based on our experience with CdS and Air we designed a glass sample holder in which the plates would be supported by Pt wire, around which glass was fused. To our surprise, we found sufficient leakage resistance between the plates (≈ 10^{12} Ω) to nearly saturate our sensitive amplifier. Modifications of the details of the construction were unsuccessful, leading us to conclude that some contaminant is introduced inside the space between the plates and in the glass container during the construction and/or annealing of the sample chamber. We have thus decided to construct a sample chamber similar to what was used for the CdS in which the Cermet plates are outside a glass tube containing the liquid. This is basically what was used for CdS where mylar substituted glass. This has now been accomplished and tried with CdS.

We were worried that in the case of $Si(CH_3)_4$ sample preparation would be a significant difficulty. A first trial in December '80 was successful in the sense that we were able to observe the drift of injected electrons. However, breakage of the glass system did not allow us to complete the Hall measurements.

A new trial was done in February, '81 following the rebuilding of the glass system. Possibly due to changes in some of the steps of the sample preparation no fast carriers were observed. A new sample is being prepared and we hope to have measurements by mid April '81.

The successful measurements in CdS and Air, discussed with researchers at the Gordon Conference on Insulation Phenomena, led to arrangements by which we shall attempt to measure the Hall mobility of electrons in polyethylene (PE). According to Y. Inuishi the drift motion of electrons in this insulator is limited by the time spent in deep traps. While in the conduction band the electron mobility should be ~ 10 cm^2/Vs, i.e., near the lower limit of our estimated sensitivity. Dr. Forster from Exxon sent us samples for these trials. Preliminary results indicate that a measurement may be possible, close to the limit of the s/n ratio of our apparatus. Such measurements are of particular interest to the electrical utility companies.

b) Optical Absorption and Photoconductivity of Electrons in Liquid Ar

We completed the construction, the testing and the interfacing of the Fourier spectrometer. A detailed drawing for the sample chamber was made and put in the shop (Fig. 1, for a simplified sketch).

In order to increase either the maximum accelerator current or the maximum applied field we decided to use a sapphire tube as the side walls of the sample cell. Unfortunately this has led to a delay of over 6 months because its delivery was shifted from April to September.

We abandoned the idea of a contemporary photoacoustic measurement because after simplified simulated trials it became obvious that the frequency response would be insufficient to justify the additional effort.

A major difficulty I had was hiring a research associate. The associate from Italy, B. Zambon, turned out not to be a success. I have not succeeded in finding a replacement despite a series of letters to colleagues and advertisements in Physics Today in January, March and September 1980. As a result an offer was made last June to the only candidate who appeared remotely qualified (R. J. Kennedy). This offer was declined. The search was reopened with advertising in Physics Today (December '80, January '81, March '81) and approximately 100 personal letters to investigators in related fields. The only apparently qualified applicant was not interested in taking a position, presumably for financial reasons.

The mechanical construction aspects of this experiment have been essentially completed. The different parts are being tested to assure they will work as planned. Both the vacuum system and most of the sample cell are completed. The fabrication of some glass parts is still incomplete.

c) Theoretical Work

1. Electron Trapping During this last summer, prodded by the invitation for a seminar at the Gordon Research Conference on Insulating Phenomena, and by a comment by U. Sowada at the last Colloque Weyl, I calculated the expected electric field dependence of the capture probability of electrons by SF_6 and O_2 in the liquid rare gases. The measurements were carried out by Bakale *et al.*[6]

The calculation is based on the realization that the capture process proceeds through a diffusion among excited states of the impurity.[7-9] At each step there is a probability that the electron can either gain or lose energy. Like in the case of semiconductors, a state whose binding energy $\mathcal{E}$ is a few kT below the conduction band can be considered as a boundary: if the electron reaches a more tightly bound state it is eventually permanently trapped, if not, it is re-emitted in the conduction band.[9,10] The state whose energy is $\mathcal{E}$ determines the whole kinetics. The effect of the electric field is primarily that of decreasing the binding energy of this state, therefore increasing the probability of re-emitting the electron into the conduction band. This is the Poole-Frenkel-Schotky effect.[11-13] From a very simple calculation one concludes that the capture rate constant per unit concentration of impurities (k) has a dependence on the electric field F such that

$$k^{-1} = A + B \exp c\sqrt{F} \quad .$$

This describes very well the experimental data. The value of c obtained experimentally agrees within a factor ~ 2 with what is calculated for a singly charged hydrogenic impurity. The value of c is proportional to the effective charge necessary to trap the electron divided by the square root of the local dielectric constant. In the hydrogenic approximation, I took for K the dielectric constant of the liquid. This is certainly an over-estimate because shielding of the "charges" of the impurity by the atoms of the liquid is clearly over-estimated. The value of the "charge" is not one either since it depends on the detailed wavefunction of the electron that is trapped to make an O_2^- or an SF_6^- ion.

It is interesting to notice that the problem must be treated quantum mechanically.[8,9] The classical treatment along the lines of Ref. 7 was recently applied to liquids by Tachiya.[14] It predicts a field dependence proportional to $(C^2 + B^2F^2)^{\frac{1}{2}}$ that is not observed. C is a constant inversely proportional to the electron mobility while B is another constant inversely proportional to temperature. Tachiya's model is valid for diffusion limited trapping.

The fact that it is unnecessary to invoke hot electrons to understand the field dependence of the trapping of O_2 and SF_6 is further confirmed if one accepts the results of Bakale _et al_.[6] that the trapping involves first order kinetics. If the population of electrons whose energy is ~ 0.5 eV above the bottom of the conduction band would be important, impact ionization and impact (or Auger) recombination should take place as well (the electron affinity of O_2 gas is ~ .45 eV) and contrary to observation the trapping kinetics should not be first order. For reasons of space limitations the figures corresponding to O_2 in Xe and Ar and SF_6 in Xe were not included in the paper submitted to the Journal of Chemical Physics.

2. _Trapping of Electrons in Ethane_ Data recently published[15] indicate that in the case of ethane electronic transport is thermally activated. Since C_2H_6 has several weakly bound excited states with A and E

symmetry[16] and the ground state of C_2H_6 has A_g symmetry,[16] I speculated that the wave function of the unrelaxed $C_2H_6^-$ has E symmetry that is expected to undergo a Jahn-Teller distortion by coupling with an E_g like lattice vibration.[17] A vibration of the appropriate symmetry exists[18] between ~ 1150 cm^{-1} and ~ 1190 cm^{-1}. At low temperature (< 250 K) the activation energy for the mobility is (1110 ± 20)cm^{-1}. Since the polarizability of C_2H_6 is small this indicates that the electron must be weakly bound in the unrelaxed molecule and a large fraction of the energy will be used for the Jahn-Teller distortion.

From the observation that a good Arrhenius plot is obtained for the electron mobility despite the fact that there are large changes of the density of C_2H_6 ($\gtrsim 2$) over the range of temperatures studied (~ 111 K to ~ 340 K) it is concluded that the traps cannot be due to large clusters of molecules. Since in general, the first peak of the radial distribution function of a dense fluid remains at a constant position with changes in density (the number of nearest neighbors changes) I am led to speculate that the traps observed in ethane are associated with very few molecules; at the lowest temperatures (110 K - 250 K) with the single molecule, at higher temperatures with a very small cluster.[19]

3. Controversy over the Importance of Hot Electrons for the Interpretation of the Field Dependence of the Electron Mobility in Ar, Kr, Xe .

G. Freeman and W. Schmidt *et al*. objected to my interpretation of the field dependence of the time of flight of electrons in rare gas liquids as limited by shallow traps.[20] They also objected to my arguments that the influence of added impurities (e.g., H_2, N_2, CH_4) on the time of flight of electrons in Ar, Kr, Xe had nothing to do with hot electrons. Their comments, were submitted to the Journal of Chemical Physics, and so was my reply.

One of Schmidt's points is taken up in the paper on trapping mentioned above. Detailed arguments pointing out the difficulties of Lekner's theory have been given by Jahnke _et al._,[21] and Basak _et al._[22] Hot electron effects are extensively explored in the vast literature on hot electrons in semiconductors.[23-27] For reasons of space limitations (1200 words) they were not repeated in the publication, for similar reasons it does not seem appropriate to repeat them here. Lately Gryko and Popielanski[28] provided further numerical results demonstrating the inapplicability of the independent scatterer model for the description of the motion of electrons in liquified rare gases.

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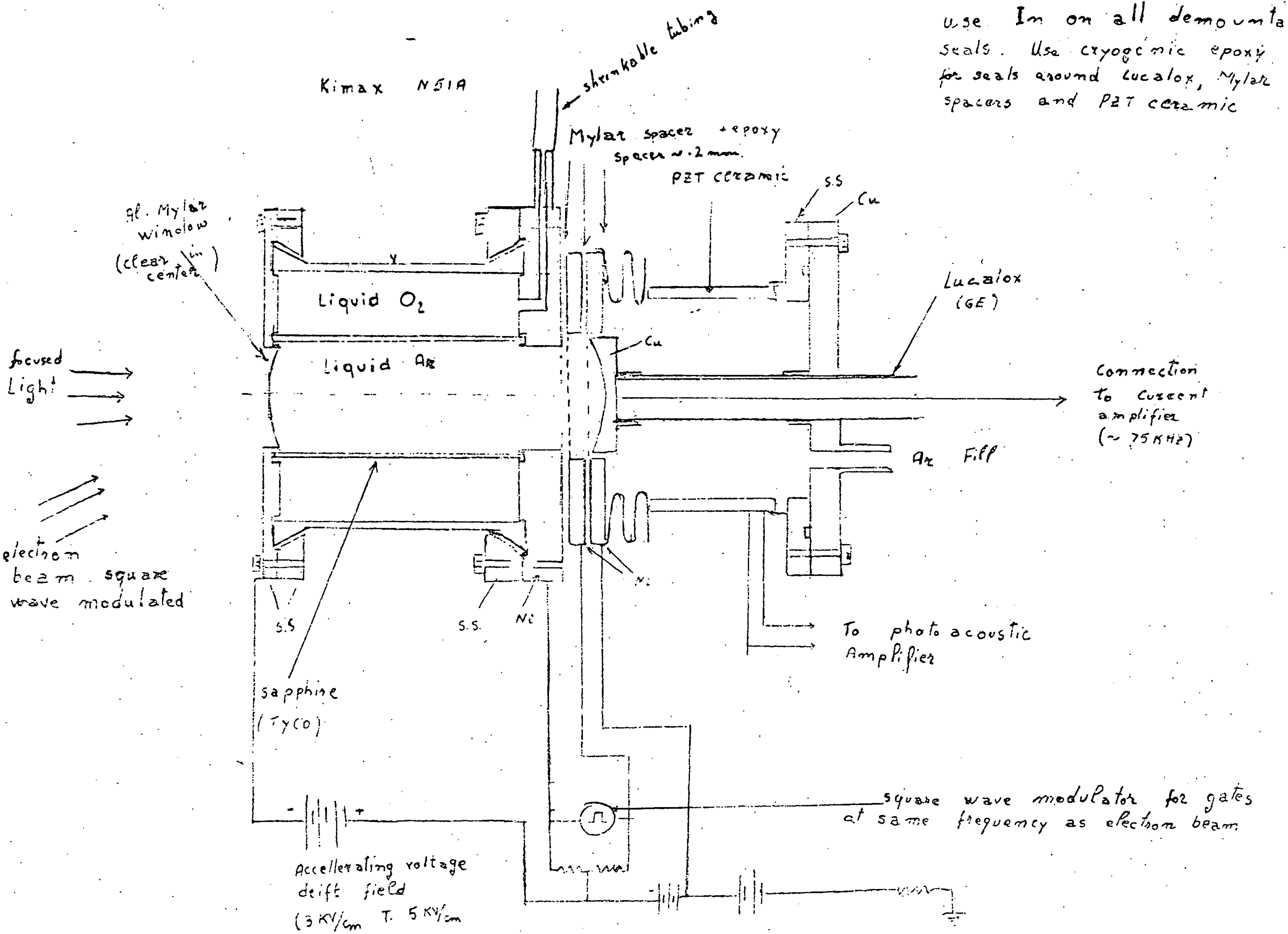

use In on all demountable seals. Use cryogenic epoxy for seals around Lucalox, Mylar spacers and PZT ceramic

Figure 1