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Injected electron lifetime in ultra-purified liquid argon

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Abstract. A procedure for the purification of Ar is described by means of which a concentration of electron-trapping impurities of the order of 0.3 ppb is obtained and maintained for a period of 9 months. The lifetime of excess electrons was measured along the saturated liquid curve up to the critical point. A representative lifetime is 150 μ s near 150 K.

1. Introduction

As part of the programme to measure the Hall mobility of electrons injected in liquid Ar, it was decided to purify the gas so as to minimise the influence of impurities that may have an effect on the properties of injected electrons. In this paper we describe the gas purification procedure and the results of the measurement of electron lifetimes.

Understanding the electronic properties of condensed matter has traditionally depended on improved control of sample composition and, in crystals, lattice perfection. As an example, in semiconductors, the minority-carrier lifetime has been used for a long time as a measure of how well such a goal was attained. For electrons in insulating liquids [1, 2] significant purification was necessary before the motion of electrons, as opposed to that of ions, could be detected. It is in this spirit that the present results are presented.

2. Gas purification system

The gas purification system (figure 1) consisted of two parts. One is a modified Vacorb pump containing a 4A molecular sieve. This portion is pumped by a well trapped diffusion pump. The molecular sieve was baked at 350 °C for over 100 days so as to assure that the resulting pressure when the molecular sieve was hot was under 10^{-5} Torr. It will be used to pre-purify the gas and is inspired by the pioneering work in [3, 4].†

The second part of the purifier is an all-metal system made out of type 304 stainless steel. All vacuum gaskets are of OFHC copper. It is connected on the one side to the Vacorb pump by means of an UHV valve and on the other side through additional UHV valves to the sample cell. Part of the stainless steel tubes making up the purifier was enclosed in an oven that could be heated to 800 °C. Inside this portion of the purifier

† This was made by Varian Associates. The modification consisted in substituting the rubber overpressure stopper with an overpressure relief valve. The molecular sieve was manufactured by Linde, a division of United Carbide.

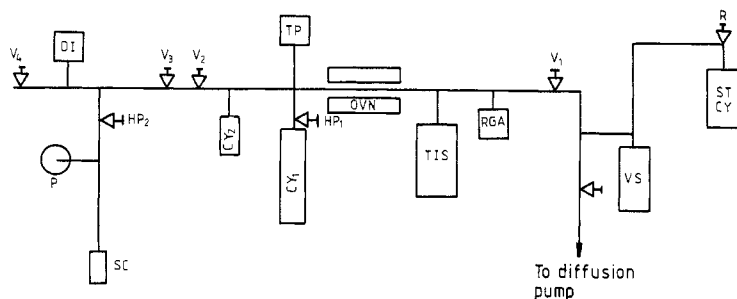


Figure 1, Schematic diagram of the gas purifier: STCY, storage cylinder; R, pressure reducer; VS, Vacsorb pump; v_2 , v_3 and v_4 , UHV valves; RGA, residual gas analyser; TIS, Ti sublimation pump; OVN, oven surrounding the stainless steel tubing containing the Ti shavings; CY_1 and CY_2 large (4 l) and small (0.25 l) sample cylinders; TP, triode ion pump; DI, differential ion pump; HP_1 and HP_2 , high-pressure valves; P, pressure gauge; SC, sample cell.

there were packed Ti shavings whose function was to react with any non-rare-gas impurities that might remain in the Ar after it evaporated from the Vacsorb pump.

The portion of the purifier beyond the UHV valve v_1 was baked while being pumped with a triode ion pump (20 l s^{-1}). Its pressure was approximately 10^{-9} Torr when the oven was at 750°C and the remaining part of the purifier was near 300°C .

The sample cell portion of the system had a 20 l s^{-1} DI pump and different portions of the system were baked to between 200 and 350°C . The sample cell portion of the system can be disconnected from the purifier at the Conflat flange connecting v_2 and v_3 (figure 1).

Conflat flanges were used for all joints. It is our experience that mini-conflat flanges will withstand without difficulty a pressure of 150 atm.

The sample cell was suspended at the end of a stainless steel tube $\frac{3}{4}$ in OD through which passed all the wires necessary for the measurement of the Hall mobility of the injected electrons, the four wires for measurement using a Pt resistance thermometer, as well as the coaxial cables used to measure the capacitance in order to determine the density of the liquid. These coaxial cables were constructed using thin-wall stainless steel tubes $\frac{1}{8}$ in in OD, stainless steel wire and mullite insulator tubes. The remaining wires were insulated by threading them into a four-bore quartz capillary so as to decrease the microphonics that would arise from their relative motion.

The top of the $\frac{3}{4}$ in tube supporting the sample cell was connected to a 16 in Bourdon tube manometer (Heise Corporation, Newtown, CT) and to a high-pressure valve that isolated the sample portion of the experiment from the ion pump and associated vacuum components. Inside the tee connecting the pressure gauge to the high-pressure valve and the sample cell there were five pills of Zr-V-Fe non-evaporable getter 10 mm in OD (SAES Getters, alloy ST 707) that were activated during the bake-out of the system.

During the bake-out of the system the pressure in the sample cell portion reached about 1×10^{-9} Torr; part of the tube supporting the sample cell and the sample cell itself remained at about 350°C for 3 days. After the bake-out the ion pump current indicated a pressure of 10^{-10} Torr.

3. Sample cell construction

A sketch of the electrodes used for the measurement of both the Hall mobility and the electron lifetime are given in figure 2. The function of the two alumina plates C and C'

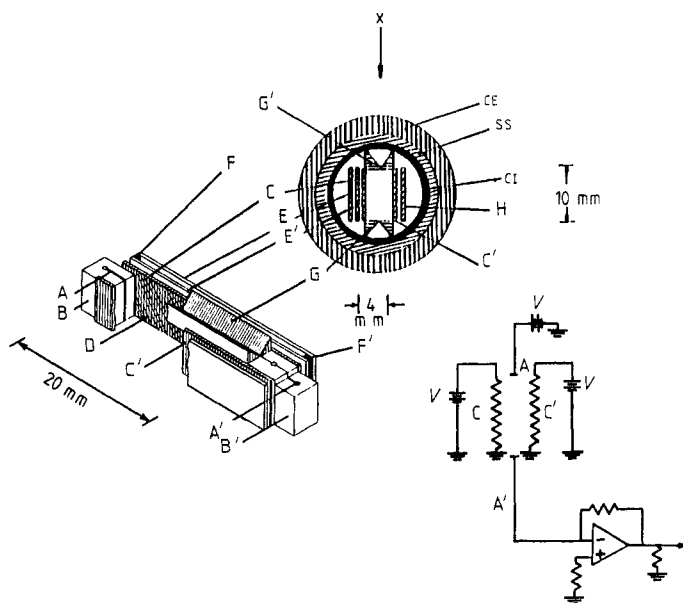


Figure 2. Sample cell and electrodes for Hall and TOF measurements: A and A', metallic strip on the Macor spacers B and B'; C and C', alumina plates on which the resistive films D and D' are printed; G and G', Macor part, a high-resistance film is printed in the V-shaped trough of each one of these parts; E and E', alumina plates on which a Pt is printed (these plates form the parallel-plate capacitor used in the measurement of density); F and F', glass spacers, about 0.1 mm; H, another alumina plate on which a Pt film has been printed (this film is grounded); CE, thick Cu tube into which the sample cell ss was pressed; CI, Cu liner inserted in the sample cell. On the right bottom is a schematic diagram of the connection of the different electrodes to outside power sources and measuring devices. The electrode A is connected to the top of the resistive films printed on G and G'; the electrode A' is connected to the bottom of the same films.

and the two Macor (Corning Glass Works, machinable glass ceramic) parts G and G', on each of which a high-resistance film 2 cm long is printed, is to produce a uniform field directed along the axis of the cell in the volume limited by these four electrodes. The two thin metallic strips A and A' (1 mm wide) deposited on the top and bottom Macor spacers connect the top and bottom of the V-shaped resistive films deposited on the pieces G and G'. Their function is to correct for the electric field inhomogeneities resulting from the termination of the resistive films; they will also be used as electrodes for the lifetime measurements. In this case the same potential will be applied by three different sets of batteries to the plates C and C' and to the parallel combination of G and G'. One of the metallic strips—either A or A'—will be connected to a current-measuring circuit (figure 2).

The electron-ion pairs were produced by a collimated x-ray beam (3.5 mm × 5.5 mm) obtained from the impact on a Pb target of a 4 MeV electron beam (6 mA peak, 1 μs wide) produced by a small linear accelerator. The x-ray beam traversed 2 mm of brass that made up the Dewar walls, 3 mm of Cu and 3 mm of stainless steel before emerging into the volume containing the liquid. The beam then traversed the V-shaped electrodes G and G' and passed between the two plane electrodes C and C'. The direction of incidence of the x-ray beam is labelled x in figure 2.

As a result of this geometry the TOF signal is a composite of the signal due to the motion of the electrons along the axis of the cell in the volume bound by C, C', G, G', A and A', and those moving between the resistive films deposited on G and G' and the metallic walls of the cell.

4. Sample preparation

The gas that was to be further purified had a nominal total impurity content of 5 ppm.

After extensive baking of the molecular sieve and the remaining intermediate-pressure region of the vacuum system that was to be in contact with the Arg, and repeated flushing of the pressure reducer R on the gas cylinder STCY the gas was liquefied into the molecular sieve and kept there for 12 h at a temperature between 84 and 87 K. This temperature was reached by immersing the Vacorb pump in an appropriate mixture of liquid N and liquid O. No effort was made to circulate the liquid in the molecular sieve.

Therefore the UHV valve V_1 was opened and the Ar was slowly transferred into cylinder CY_2 that had been cooled to about 77 K. In the process the gas had to pass over the packed Ti shavings held at approximately 700 °C. Residual impurities such as O_2 , CO, CO_2 , H_2O and hydrocarbons that might escape from the cold molecular sieve should react with the hot Ti. After this transfer into CY_2 , and if necessary into the larger cylinder CY_1 , valve v_1 was closed and the Ar that remained in the molecular sieve container was pumped out through the liquid-Ni trap over the diffusion pump. The gas in CY_2 is thereafter slowly transferred and frozen in the container TIS surrounding the Ti sublimation pump. Any unreacted Ti film that might exist will help in the gas purification. During this transfer the gas passes again over the hot Ti shavings. The gas is then transferred again into either CY_1 or CY_2 , passing for a third time over the hot Ti shavings.

The Ti shavings are then cooled to room temperature and the Ar gas is passed twice more over the cold Ti shavings in an attempt to remove any H_2 that could have been introduced by the hot Ti or remained mixed in the Ar as a result of the decomposition of either water or hydrocarbons.

After this last step the required amount of gas is condensed in the sample cell. The high pressure valve HP_2 is closed and eventually the purifier is disconnected from the experimental system at the flange joining v_2 and v_3 .

The activated getter pills in the tee joining HP_2 and P remain in contact with the gas for the whole duration of the experiment, i.e. 9 months. We can estimate the contribution of the getters to the maintenance of the sample purity from the fact that the limiting pressure measured by the current in a 20 l s^{-1} ion pump was about 10^{-10} Torr. From these data, we would expect the outgassing at the end of 9 months to correspond to about 3×10^{-6} mol so that the total impurity of the fluid should be about 1 ppm. This must be compared with a constant O content (the main impurity affecting electron lifetimes) of about 0.3 ppb estimated from the electron lifetimes.

5. Electron lifetime

Since the principal aim of this experiment was the measurement of the Hall mobility of electrons injected into liquid Arg, the sample cell was not optimised for measurement of the electron TOF over relatively large distances. The major difficulty for carrying out

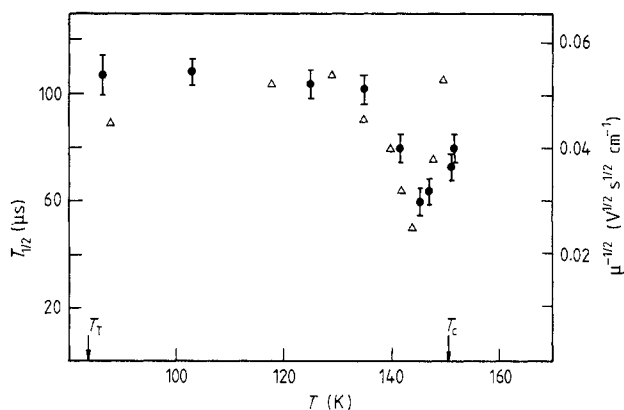


Figure 3. Temperature dependence of the time necessary for the electron current to reach half its initial value (●). The values of $\mu^{-1/2}$ (Δ), where μ is the electron mobility [7], are also shown. All the temperatures correspond to points on the saturated liquid–vapour coexistence line.

such a measurement are the space requirements for additional electrical feedthrough and the problems associated with noise that may arise from the additional wires.

As pointed out in § 4, the TOF signal is derived from electrodes A and A' (figure 2) that connect, respectively, the top and bottom of the resistive films deposited on the V-shaped Macor pieces G and G'. As a consequence the observed signal is a composite of the signal due to electrons moving along the axis of the sample cell and electrons moving between G and G' and the metallic walls of the sample container. With an axial field of 1.5 V cm^{-1} that was used for these measurements, the latter represent the major signal source at short times (about $30 \mu\text{s}$ or less) while the former dominate beyond times longer than about $40 \mu\text{s}$. On account of the geometry of the sample cell the field between the centre portion of G and G' and the cell walls is always much larger than the axial field.

The first electron lifetime measurements were made 3 months after filling the cell with liquid Ar. The measurements plotted in figure 3 were made using the aforementioned axial field of 1.5 V cm^{-1} , with the exception of the data at 86 K, where the measurement was also taken at 23.5 V cm^{-1} . At such low fields the lifetimes are field dependent since significant 'hot electron' effects appear at fields that are at least 10 times larger than those used here. With a 1.5 V cm^{-1} field and a mobility [1, 2] μ of $500 \text{ cm}^2 \text{ V s}^{-1}$ the electrons only drift about 1 mm during their lifetime (about $150 \mu\text{s}$). This must be compared with the 20 mm separating A and A'. Since the collimated x-ray beam has a cross section of $3.5 \text{ mm} \times 5.5 \text{ mm}$ and the current decayed in times of the order of a few hundred microseconds, this time is a direct measurement of the electron lifetime.

No effort was made to separate the different mechanisms that may contribute to the electron disappearance: geminate recombination, and trapping by either impurities or intrinsic localised states. It is believed that both geminate recombination and recombination with additional positive ions remaining from previous x-ray pulses are not important in so far as the results were unchanged when one or more successive pulses were used, when the repetition rate of the x-ray pulses was varied, or when the x-ray intensity was changed. The number of electrons contributing to the current was always about 2×10^{10} or less. It is also easy to show that diffusion of the electrons to the resistive

films D and D' cannot account for the current decay since they diffuse only about 0.3 mm in 150 μs .

If an ion has the same diffusion coefficient as a neutral argon atom [5], $D_a \approx 4 \times 10^{-5} \text{ s}^{-1}$, during the shortest time between x-ray pulses that was used (0.25 s) a positive and a negative ion will neutralise each other if they are less than 0.03 mm apart. Positive ions, in the form of self-trapped holes, may have a much larger diffusion constant. In solid argon near the triple point [6], $D_h \approx 1.4 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and an activation energy near 35 meV. If this could be extrapolated to the liquid, it would indicate a diffusion constant nearly twice as large at 100 K. The efficient neutralisation of positive and negative ions explains why no space-charge effects were seen in these measurements.

Beyond the initial 30 μs the decay of the current was nearly exponential. Deviations from an exponential decay are comparable with the uncertainties associated with the residual contribution of the initial current to the walls of the cell and to noise. In figure 3 the times for the current to reach half its initial value are given as a function of temperature. All points are along the vapour-liquid equilibrium line that extends from the triple point to the critical point.

These data were taken over a period of 6 months and no changes in the electron lifetime were detected. During this time the temperature of the cell was cycled several times up to room temperature and the cell was irradiated on an almost daily basis. We are thus able to conclude that this purification method is able to provide a sample of clean fluid that remained uncontaminated for 9 months despite the unfavourable ratio of surface to volume of the sample cell, and the mixing of gases desorbed from the metal and dielectric surfaces with the fluid under study.

As is seen in figure 3, the temperature dependence of the square root $\mu^{-1/2}$ of the inverse of the mobility [2, 7] resembles the temperature dependence of the electron lifetime. If we assume that the electron lifetime is diffusion controlled, we may give a lower-bound estimate of the impurity concentration.

According to this line of thought, during its lifetime an electron samples a spherical volume whose radius r is $(D\tau)^{1/2}$. Here D is the electron diffusion coefficient ($D/\mu = kT/e$), μ the electron mobility and τ the electron lifetime. If one assumes that, when an electron approaches a trapping centre at a distance $y \ll r$, the electron is certain to be trapped, then the lowest possible concentration of trapping centre is r^{-3} . With a lifetime of 150 μs , a mobility μ of 500 $\text{cm}^2 \text{ V s}^{-1}$ and $T = 100 \text{ K}$, the minimum concentration of traps is about 10^4 cm^{-3} . Such a concentration is unrealistic and indicates that an electron collides many times with a trapping centre before being captured.

A completely different estimate of the concentration of traps is obtained from a comparison with the data in [3] and the use of trapping parameters for O_2 obtained in [8]. Our lifetimes are about twice as long as those reported in [33], where it was estimated that the concentration of O traps was about 0.6 ppb. Other impurities whose trapping cross sections are smaller than that of O [8] can be present in higher concentrations; however, in the absence of an analysis for trace impurities, we cannot identify them. Chemical analysis in the parts per billion range is to say the least at the limit of present-day technology. O has been traditionally identified [1-3, 8] as the most likely source of traps. With a concentration of traps of 0.3 ppb, i.e. about $6 \times 10^{12} \text{ cm}^{-3}$, and a lifetime of 150 μs , we can calculate the trapping cross section: $\tau^{-1} = \nu\sigma N = (3kTm^{-1})^{1/2} \sigma N$, from which $\sigma \approx 1.6 \times 10^{-16} \text{ cm}^2$. This cross section is comparable with the cross section of neutral electron traps in either Si or Ge [9]. A major difference between our result and those in [3] is that we could not detect any sample deterioration up to 9 months after the initial condensation of the fluid. We believe that this is the result of the use of the above-mentioned getters.

It is appropriate to compare our temperature dependence of the electron lifetime with the results in [7]. Using electron densities comparable with those used in this work, a trapping rate was determined in [7]. Then the electron density was significantly increased and the change in the trapping rate assigned to electron-ion recombination. This recombination is assumed to contribute to the exponential decay of the density; this additional rate is the recombination rate reported in [7]. As in the case of the trapping rate reported at present, it has a maximum which correspond to the mobility maximum.

6. Conclusions

We have described a process of Ar purification that lowered and kept the O concentration in liquid Ar in the range of 0.3 ppb for a period of 9 months without any sign of deterioration. The electron lifetime has been measured along the saturated liquid line. The electron lifetime is about 150 μ s near the triple point and reaches a minimum which corresponds to the mobility maximum.

Acknowledgments

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