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NAME:
Haiyan Gao

PHONE:
660-2622

CLIENT_EMAIL:
gao@phy.duke.edu

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Attempts to Increase the Nuclear Relaxation Time of a ^3He Gas at Low Temperatures

Valérie Lefevre-Seguin and Jean Brossel

Laboratoire de Spectroscopie Hertzienne de l'ENS,* Paris, France

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In an attempt to increase, at temperatures of a few kelvins, the relaxation time of a dilute ^3He gas enclosed in spherical Pyrex or pure silica bulbs 3 cm in diameter, we have studied the relaxing properties of various coatings, such as solid O_2 and solid N_2 and multiple coatings of H_2 on N_2 , H_2 on O_2 , and H_2 on H_2O . Contrary to naive expectations, thin films of solid oxygen proved to be very efficient coatings, although single molecules are paramagnetic. When multiple coatings are compared, they even provide the best undercoating to hydrogen films. The longest relaxation time we measured at 4.2 K was 8000 min, i.e., more than 5 days. We also found that Pyrex and pure silica, either bare or coated, give comparable results below 50 K. These experiments enabled us to measure the adsorption energy of ^3He on O_2 , $\Delta W(^3\text{He}/\text{O}_2) = 130 \pm 15$ K, and of ^3He on N_2 , $\Delta W(^3\text{He}/\text{N}_2) = 200 \pm 50$ K. In the absence of any theoretical calculation, these energies still need to be confirmed by other experimental techniques.

1. INTRODUCTION

In surface physics, coatings have long been recognized for their ability to produce controlled modifications of the optical, electrical, chemical, and mechanical properties of a substrate. They find numerous applications in various fields, from lubrication, adhesion, and catalysis to microelectronics and optics. In atomic physics, when frequency standards based on maser oscillation were developed in the 1960s, fluorocarbons and Teflon films were widely used to stabilize the frequency and linewidth of the hyperfine transition leading to maser oscillation in a rubidium or atomic hydrogen vapor.¹⁻³ Optical pumping has provided a means to study in detail the mechanisms of hyperfine relaxation of rubidium, for instance, on such coatings.⁴ The work presented here belongs to the same class of experiments. It consists in measuring the relaxation time of a low-density ^3He gas

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(typically 6×10^{16} at/cm³) oriented by optical pumping. For a dilute gas the dipole-dipole coupling is negligible,^{5,6} and the nuclear relaxation occurs during the dwelling time of ³He atoms on the walls of the sample cell. When such experiments are conducted at low temperatures, below 20 K, it is necessary to coat the glass walls with cryogenic coatings in order to reduce the sticking time of ³He atoms on the walls and thereby the probability of a nuclear spin flip in the local fluctuating magnetic field. Solid neon^{6,7} and hydrogen coatings^{8,9} have been shown to lengthen the nuclear relaxation time T_1 observed on bare glass by several orders of magnitude. Solid hydrogen also proved its efficiency in giving long relaxation times of ³He in ³He-⁴He mixtures¹⁰ and in helping the stabilization of a spin-polarized hydrogen gas.¹¹⁻¹³

Previous experiments¹⁴ on the nuclear relaxation of a dilute oriented ³He vapor around 4 K allowed us to measure the adsorption energy of ³He on solid H₂, D₂, and Ne, with results in good agreement with theoretical predictions.¹⁵ These experiments also strongly suggested that the relaxation originated from magnetic impurities, located inside the Pyrex walls, acting on ³He atoms while adsorbed on these coatings. The screening provided by these solid films was found to be limited by their finite thickness of a few atomic layers. Although T_1 was already very long in these experiments (as long as 60 h at 4.2 K), it nevertheless seemed possible to increase it further if the Pyrex magnetism could be sufficiently reduced.

Any improvement of the relaxation time of an oriented ³He vapor is worth consideration in experiments on nuclear spin-polarized ³He. First, it clearly means a longer time to study the specific properties of this fluid. For instance, the measurement of its spin-wave coefficients and thermal conductivity would have been easier with longer T_1 's.¹⁶⁻¹⁸ Second, the high polarization required in those experiments is obtained by a double-cell technique.¹⁹ Such a scheme is efficient only if the building time of the polarization, which is governed by the diffusion time of the oriented ³He atoms from one end of the cell to the other, is shorter than T_1 . In experiments where long diffusion times cannot be avoided, it may be desirable to rely on the longest possible T_1 in the low-temperature cell to get a high polarization.

At first it might seem that a superfluid ⁴He film covering solid H₂ is the most straightforward and efficient way to get a very thick coating preventing a spin-polarized atom from coming close to the Pyrex wall. While this is verified for spin-polarized hydrogen, it is not quite true for ³He, because these atoms are able to penetrate the ⁴He film. The very detailed experiments of Himbert and Dupont-Roc²⁰ show that the weak relaxation they observe occurs during the dwelling time of ³He atoms in the ⁴He layers located close to the solid hydrogen film; once a few layers

of ^4He are deposited, no further increase of the relaxation time is observed despite the presence of a very thick ^4He film. The first step to achieve longer T_1 's at low temperatures is therefore to weaken the relaxation of ^3He on solid H_2 .

We investigated several techniques designed either to suppress the magnetic centers present in the Pyrex or to screen them more efficiently with very thick, solid coatings of different kinds. We first tried to replace Pyrex by very pure fused silica and to change the cleaning process of the sample cells. In a second series of experiments, we worked on Pyrex cells coated with thick deposits of organic material such as polyethylene, Teflon, or silanes. Finally, we studied the effect of adding other gases, such as Ne, O_2 , N_2 , and H_2O vapor, to make an intermediate coating between the Pyrex wall and the solid hydrogen film. In the course of these experiments we were able to measure the adsorption energy of ^3He on glass (Pyrex and pure fused silica) and on solid O_2 and N_2 .

The general outline of nuclear relaxation of gaseous ^3He on solid surfaces is introduced in Section 2. The apparatus and sample preparation are described in Section 3. Our results are set out and commented on in Section 4.

2. NUCLEAR RELAXATION OF GASEOUS HELIUM-3 ON SOLID SURFACES AT LOW TEMPERATURES

We recall here the basic principles of our experiment. We refer the reader to ref. 14 for a more detailed description. Because we study the relaxation of a dilute ^3He gas, the only relevant mechanism is the relaxation occurring during the sticking time τ_s of a ^3He atom on the wall of the sample cell. The vicinity of the wall, if care is taken to suppress any external magnetic field gradient, is the only place where local magnetic field inhomogeneities are very difficult to avoid. While moving through this local field, a ^3He atom experiences a fluctuating perturbation $\delta B(t)$, which may induce transitions between the two sublevels of its nuclear spin $1/2$. The random nature of this process leads to the relaxation of the initial polarization toward its thermodynamic equilibrium value, which in our case is practically zero. This well-known phenomenon is described, in the case of weak transition probabilities, by the so-called "motional narrowing" theory.²¹ Since at thermal equilibrium there is a constant exchange of atoms between the two phases consisting of adsorbed atoms on one hand and free atoms in the gas on the other, this mechanism leads, on the whole, to the depolarization of the ^3He vapor. The efficiency of this mechanism is governed by two parameters. The first is the residence time τ_r of a ^3He atom on the wall. It depends on the van der Waals forces, which bind a ^3He atom

near the surface of the sample walls. The use of cryogenic coatings such as solid hydrogen is precisely intended to reduce these van der Waals forces and thereby τ_s in comparison with bare glass. This is why these coatings produce a considerably weaker relaxation. The advantage of such inner surfaces is also that they produce a quasiuniform potential varying mainly with the distance of a ^3He atom away from the surface. Moreover, the attractive part of this potential is so weak that there is in general only one relevant bound state of energy $-\Delta W$.¹⁵ In our experiments, by adjusting the ratio $\Delta W/kT$, we deliberately work in a regime where the number of adsorbed atoms N_a is very small, either by reference to the monolayer coverage N_s or in comparison with the number of atoms N_v in the gaseous phase. More precisely, we always have $N_a \ll N_s \ll N_v$. The interaction between adsorbed atoms can then be ignored and the N_a adsorbed atoms can be considered as a perfect two-dimensional gas in equilibrium with a perfect three-dimensional gas of N_v atoms. From the equality of the chemical potentials one has

$$\frac{N_a}{N_v} = \frac{\lambda S}{V} \exp\left(\frac{\Delta W}{kT}\right) \quad (1)$$

where λ is the de Broglie thermal wavelength, $\lambda = h/(2\pi mkT)^{1/2}$, of a ^3He atom, k is the Boltzmann constant, and S and V are, respectively, the inner surface and volume offered to the gas. Equation (1) also provides a definition of the mean sticking time τ_s of a ^3He atom in the adsorbed phase. The equality of the fluxes of atoms impinging on the wall or desorbing from it, if the sticking coefficient is taken equal to 1, leads to

$$\frac{N_a}{S\tau_s} = \frac{N_v \bar{v}}{4V} \quad (2)$$

or

$$\frac{N_a}{\tau_s} = \frac{N_v \bar{v} S}{4V} = \frac{N_v}{T_v}$$

so that

$$\tau_s = (4\lambda/\bar{v}) \exp(\Delta W/kT) \quad (3)$$

where $\bar{v} = (8kT/\pi m)^{1/2}$ is the mean thermal velocity of a ^3He atom. Formula (3) shows how the sticking time τ_s follows an exponential variation versus T^{-1} , as predicted by Frenkel's law for adsorption. It also expresses the sensitivity of τ_s to changes of the van der Waals attraction produced by the substrate.

The second parameter that controls the relaxation efficiency is the average of the correlation function of the fluctuating local field $\delta B(t)$,

labeled here $\langle \delta B^2 \rangle$. This parameter is directly related to the relaxation time in the adsorbed phase T_a . In the "extreme motional narrowing regime" corresponding to our experimental situation, one has

$$1/T_a = \gamma^2 \langle \delta B^2 \rangle \tau_s \quad (4)$$

where, following the results of ref. 14, the sticking time τ_s is taken as the correlation time of the perturbing magnetic field.

Because we study a very weak relaxation mechanism (i.e., $T_a \gg \tau_s$) concerning a small number of atoms (i.e., $N_a \ll N_v$), the relation of T_1 , the relaxation time of the vapor, to T_a is very simple. It reads

$$\frac{1}{T_1} = \frac{N_a}{N_v} \frac{1}{T_a} \quad (5)$$

$$\frac{1}{T_1} = \frac{4\lambda^2 S}{\bar{v}V} \gamma^2 \langle \delta B^2 \rangle \exp\left(\frac{2\Delta W}{kT}\right)$$

The experiments of refs. 14 and 22 have shown that this simple model gives a satisfying account of the observed variation of T_1 versus temperature for surfaces of solid H_2 , D_2 , and Ne . The results presented here will also be interpreted within the same framework, so that in the following we shall constantly refer to formula (5). It predicts that the variation of T_1 versus T^{-1} is dominated by the exponential factor as soon as $kT \ll 2\Delta W$. It also gives the dependence of T_1 with respect to the magnetic inhomogeneities.

The last parameter that can seriously affect T_1 is the surface of the sample. In (5), S is, as a matter of fact, the effective surface area, which measures the number of sites of adsorption. From our experiments on solid hydrogen, we estimate the effective surface area to be two or three times the geometrical area. In other experiments, where much thicker H_2 coatings were involved, a ratio close to nine has been evaluated.²³ One difficulty that arises when making thick coatings to increase T_1 is the need to maintain a low effective surface area.

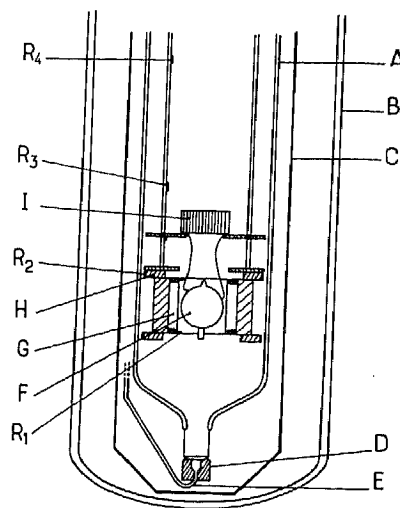
3. EXPERIMENTAL APPARATUS

A sketch of the experiment is displayed in Fig. 1. We refer the reader to refs. 14, 22, and 24 for a detailed description.

3.1. Optical Pumping

Contrary to the usual technique by which a medium is polarized in a high magnetic field combined with temperatures as low as possible, the nuclear orientation is provided in our case by optical pumping. This method, invented by A. Kastler (see, for instance, ref. 25), has been successfully

Fig. 1. Sketch of the experimental setup viewed along the optical axis. The central Dewar (A) and inside vacuum chambers (B) (gilded glass) and (C) (copper shield thermalized on the liquid nitrogen reservoir) can be filled with gaseous or liquid helium through the copper heat exchanger (D) and capillary tube (E) connected to the liquid helium reservoir. The sample cell (F) is mounted inside the fused silica framework of the NMR crossed-coils device (G, H). The optical pumping 10-MHz discharge is produced through transformer (I). The temperature of the central Dewar is monitored by carbon resistors R_1 to R_4 , stripped of their magnetic contact leads.



applied to ^3He with conventional light sources²⁶ until the recent advent of specially designed lasers, which currently yield a 60% nuclear polarization at room temperature.²⁷ However, a laser source is not as profitable when used directly on a sample at low temperatures.²⁸ We therefore used discharge lamps, which operate more easily. This compensates for the few percent of polarization they allow for.

3.2. Sample Cells Cleaning and Filling Procedures

In previous experiments, we had ascertained a good reproducibility of our measurements from one sample to another by always following the same careful cleaning and filling procedure of the spherical 3-cm-diameter Pyrex bulbs.¹⁴ The most important cleaning step was to outgas the vessels under vacuum at 440°C for 15 h (step labeled "H" below), and then to maintain as long as necessary a strong rf discharge in helium (step "D"). One might wonder if the bombardment of the surface by the metastable atoms and ions does not damage it, making it more inhomogeneous and rough than before.

We therefore decided to make measurements on cells submitted to different cleaning treatments but otherwise similarly filled. We prepared three series of samples: cells labeled "HD" were cleaned as usual (outgassing at 440°C + rf discharge cleaning) to provide a reference. Cells "P" were only pumped at room temperature before the admittance of ^3He and H_2 (no heating, no discharge). Cells "H" were only heated under vacuum at 440°C (no discharge).

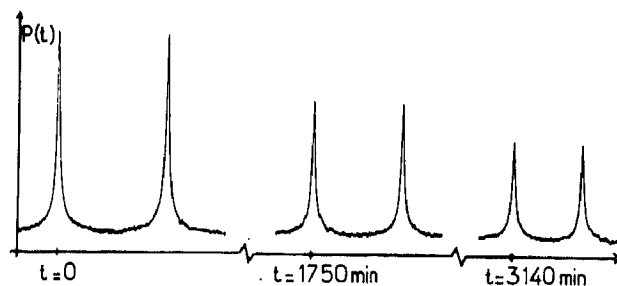


Fig. 2. Experimental recording of three adiabatic fast passages (including return passages) at times $t=0$, 1750, and 3140 min on a cell with 1.9 Torr ^3He and 1.5 Torr H_2 , 2% polarized at $t=0$. In that case, the value of T_1 derived from these and subsequent measurements, not shown here, was 4000 ± 100 min.

The possible effects of different cell cleaning treatments were tested with Pyrex vessels as well as with pure fused silica. The results of these experiments are described in Sections 4.1 and 4.2.

While the study of N_2 , O_2 , H_2 , or Ne coatings only meant adding the desired amount of these gases when filling the cells, the organic coatings involved different techniques: polyethylene and Teflon coatings were evaporated by rf heating a small amount of powdered material deposited on a piece of iron coupled to an induction coil.⁴ Silanized cells were obtained by a chemical grafting reaction described in Section 4.6.

3.3. Cryostat, Magnetic Field Homogeneities, and NMR Detection

The optical cryostat used to cool the samples and maintain a fixed temperature has been described elsewhere.¹⁴ Its main quality is the great autonomy provided by large reservoirs of liquid nitrogen and helium, combined with a very good amagnetism, since no magnetic materials (stainless steel, tin-lead solder, ...) were introduced closer than 30 cm from the cell. This ensured a magnetic field inhomogeneity less than 1 mG over the 3 cm of the cell diameter, which was regularly checked by measuring the transverse relaxation time T_2 .¹⁴

To measure the exponential decay of the ^3He polarization $P(t)$ prepared by optical pumping, we kept the same crossed-coils apparatus operated at 120 kHz to obtain a fast-adiabatic passage signal proportional to $P(t)$ as shown on Fig. 2.

4. RESULTS

We first describe in Section 4.1 the effect of replacing the Pyrex substrate by pure silica. We then report on how we obtained increased T_1 's when we

changed the cell cleaning procedure (Section 4.2). This motivated further experiments on the adsorption of He on bare glass and on solid oxygen and nitrogen coatings (Section 4.3). We then describe our results on multiple coatings (Section 4.4).

For the sake of comparison, we collect in Fig. 3 our previous results on standard cells filled with ^3He and H_2 submitted to the complete cleaning

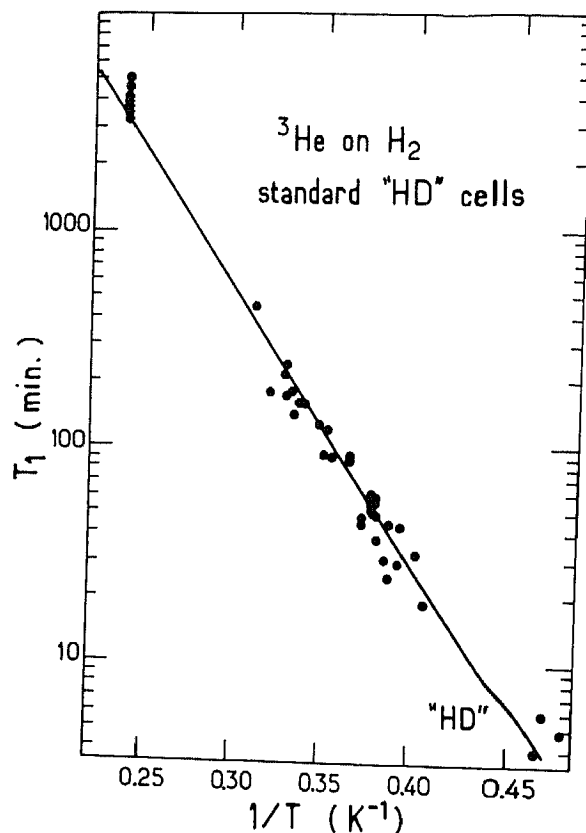


Fig. 3. Relaxation time T_1 of ^3He on solid H_2 , plotted on a logarithmic scale versus $1/T$. To allow for the comparison with later results, this figure gathers measurements on Pyrex cells cleaned along the standard procedure ("HD"), filled with ^3He between 1 and 2 Torr plus H_2 between 0.6 and 3 Torr. The best fit line of this figure is shown in Figs. 4, 9, and 10 as a reference. We also recall here that, given the 3 cm diameter of our spherical sample cells, a filling pressure at room temperature of 0.06 Torr corresponds to one solid layer of H_2 if the effective surface area is taken equal to the geometrical one.

procedure described above, which ensured a good reproducibility of our measurements.

4.1. Comparison of Different Types of Glass Covered with H_2

We investigated the effect of replacing the Pyrex substrate by two types of pure fused silica, both manufactured by the firm Heraeus, named Tetrasil and Suprasil. They are both synthetically produced from high-purity silicon chloride compounds. They are very homogeneous and of very high chemical purity. Their iron content, in particular, is less than 0.1 ppm, compared to about 100–300 ppm for Pyrex. In addition, compared to Pyrex, whose working temperature is in the range of 1200°C, pure synthetic silica requires temperatures higher than 1700°C to shape it; at these temperatures, the vapor pressure of SiO_2 is quite substantial. This often produces smoky zones on the glass of high surface area, resulting from the uncontrolled deposition of SiO_2 vapor. We mention these characteristics because they probably explain why we sometimes obtained bad results with these glasses.

The experimental results are shown in Fig. 4. We attribute the dispersion of T_1 observed on Tetrasil to the rather poor aspect of the cells delivered by the glass manufacturer. On the other hand, Suprasil cells appear to be quite comparable to Pyrex cells, although they give slightly shorter T_1 's.

At first, it seems surprising that pure silica substrates do not give longer relaxation times than Pyrex, since we thought that its iron content, associated with its higher magnetic susceptibility, was responsible for the wall relaxation observed with Pyrex. As a matter of fact, the results of Fig. 2 make this interpretation questionable. One can wonder if the relaxing centers should not rather be associated with the silica network itself, which can allow for the presence of many kinds of magnetic centers, such as O^- non-bridging oxygen atoms, trapped electrons, or hydrogen atoms.

4.2. Changing the Cell Cleaning Procedure

In this section, we report on the effect of changing the glass cleaning procedure on hydrogen-coated cells. Our first result along this line came several years ago from one cell that had only been evacuated at room temperature instead of the rather heavy cleaning process labeled "HD" ("H" standing for "heating under vacuum at 440°C" and "D" for "discharge cleaning"). This cell gave the best results we had ever obtained at that time with hydrogen coatings, at 4.2 K and below. Because we questioned the reproducibility that could be obtained, we delayed further experiments in this direction. Nevertheless, this result motivated a more systematic study on similar cells, labeled "P", whose results appear in Fig. 5. The relaxation times are clearly longer, roughly by a factor 2 at 4.2 K and by a factor 1.7

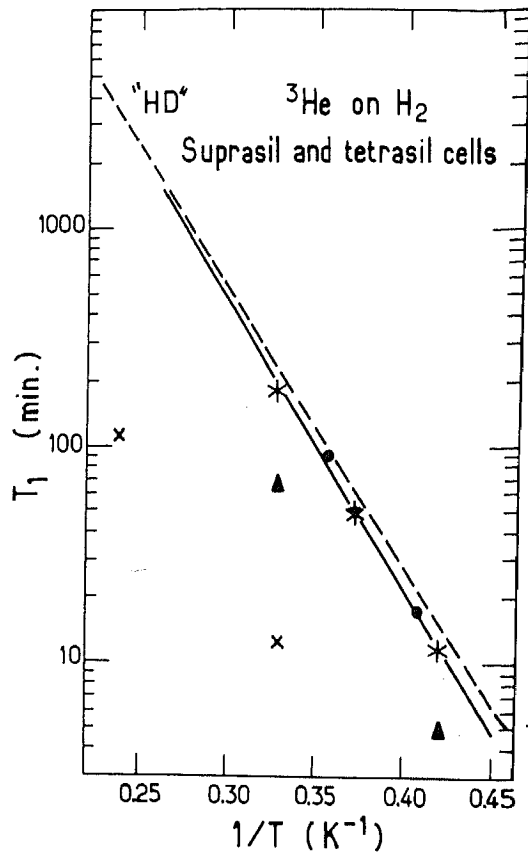


Fig. 4. Relaxation time T_1 of ^3He on H_2 versus $1/T$ for pure fused silica cells, all filled with 1.9 Torr ^3He + 1.5 Torr H_2 (+, and ●) Cells made of Suprasil; (*, x, ▲) Tetrasil. The cleaning treatment is of type "HD" (heating + discharge cleaning), except for (x, which is of type "P" (only vacuum pumped at room temperature).

at 2.5 K. These cells provide the longest relaxation time of ^3He that have ever been observed, even at room temperature or above, $T_1 = 7200\text{--}8000$ min, that is, $5\text{--}5\frac{1}{2}$ days. A least-square fit of our results gives a slope of $\log T_1^{-1}$ versus $1/T$ slightly higher than on "HD" cells, but this deviation is not really significant in view of the relatively low number of measurements performed on these cells. Figure 5 also shows the very satisfying reproducibility obtained with "P" cells. The increase of T_1 is therefore reliable. As with "HD" cells, we checked that the relaxation times T_1 were not affected, for instance, by a 30-min discharge ten times stronger than necessary for

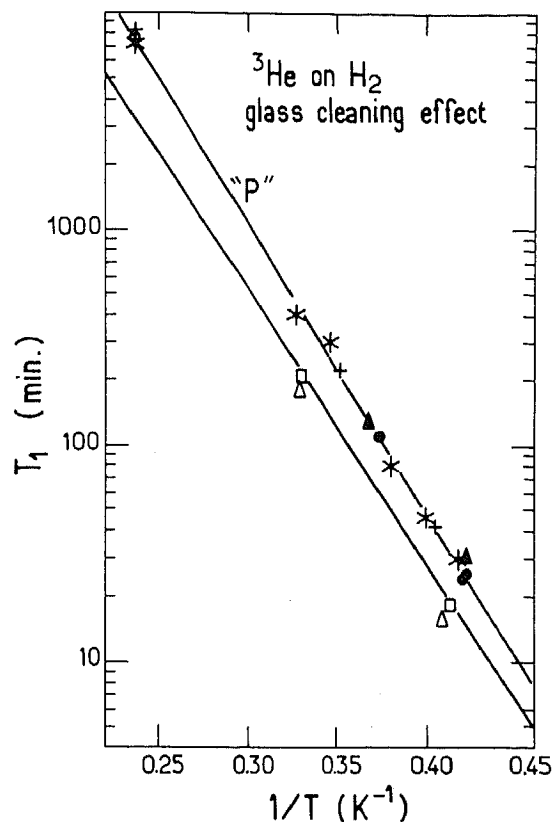


Fig. 5. Effect on T_1 of different cleaning treatments. All these cells contain 1.9 Torr ^3He +1.5 Torr H_2 . (+, ●, ▲, *) "P" cells, showing very reproducible results (even 4 years after they were made). The best fit line deduced from these measurements serves as a reference to appreciate the performances of multiple coatings (see Figs. 9 and 10). (□) Results on a cell of type "H" and (△) on a cell of type "HDH", which are comparable to "HD" cells (see Section 3.2 or Fig. 4 for cell type designations).

optical pumping, performed at 4.2 K, just before a measurement began. Similarly, we also verified, as we always did in new situations, that, once the polarization of the sample had been obtained, the solid hydrogen coating of these "P" cells could be evaporated by heating the cell up to 35 K and then recondensed without any effect on the subsequent value of T_1 . Such a test is intended to discard the possibility that some products of the discharge trapped in the hydrogen coating are responsible for the nuclear relaxation we observe.

Figure 5 also includes our results on a cell of type "H" (heated at 440°C under vacuum before being filled) and on a cell "HDH" (heated again under vacuum after the discharge cleaning and before being filled). At this stage, it seems that the heating under vacuum process rather than the discharge cleaning accounts for the difference in T_1 , but this needs to be confirmed by measurements on "D" cells (evacuated and then directly submitted to a helium discharge).

It is difficult to interpret the improvement of T_1 obtained on cells "P". These cells might retain adsorbed species, such as O_2 , N_2 , and H_2O , which are more or less eliminated when the vessel is heated under vacuum or submitted to the bombardment of He metastables and ions in a strong rf discharge. Whether these adsorbates act on the surface to smooth it and diminish its effective surface area or to modify its magnetism (or both at the same time), cannot be settled by our experimental technique.

Anyhow, in order to get more information about the effect of the glass cleaning treatment and the behavior of different glasses, we investigated the relaxation times of ^3He on bare glass and on coatings of solid nitrogen and oxygen.

4.3. Relaxation of ^3He on Bare Glass at Low Temperature

The nuclear relaxation of ^3He on bare (i.e., uncoated) glasses of different types has already been studied by Walters and co-workers²⁹ between 55 and 350 K. These experiments revealed the interplay of adsorption at low temperatures and permeation at higher temperatures to govern the residence time of He atoms at the walls of the sample. They also showed that quartz surfaces, because of their higher permeability, gave poor results compared to Pyrex over all this range of temperature. Our purpose was to carry out these experiments at lower temperatures.

We concentrated our measurements from 26 up to 55 K. Above this temperature, we observed that the relaxation of the nuclear polarization seldom followed a single exponential and often was not reproducible. Besides, when it was possible to measure T_1 , it was shorter than expected from an extrapolation of the low-temperatures results. This probably indicates that permeation effects begin to influence T_1 above 55 K. It is not surprising that these effects are difficult to control, since the permeation efficiency is very sensitive to the precise configuration of the sites where a He atom enters inside the glass network. Slight variations of the lattice spacing, for instance, can produce large variations of the permeation barrier and tunneling times in and out the glass substrate. Below 26 K, T_1 becomes rapidly shorter than 1 min so that optical pumping cannot operate.

Figure 6 displays our results on Pyrex and Suprasil for cleaning treatments "HD" and "P". We shall interpret them according to formula (5).

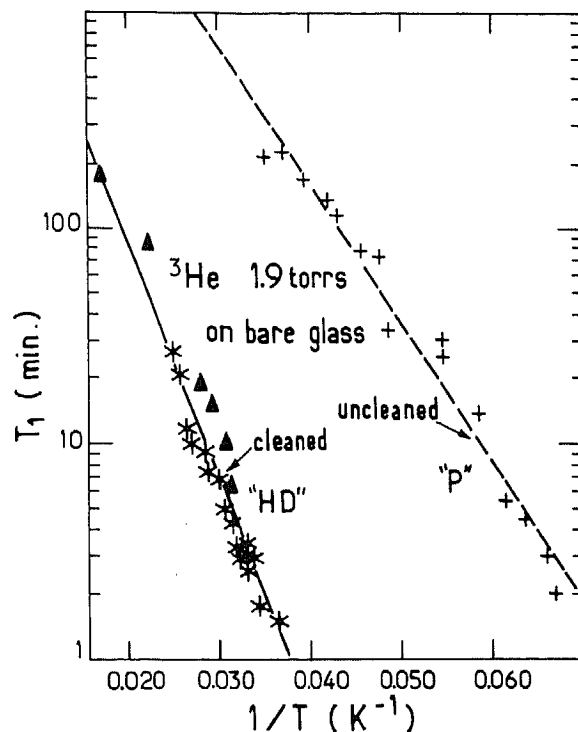


Fig. 6. Relaxation time of ^3He (1.9 Torr) on bare glass. (*) "HD" Pyrex, (\blacktriangle) "HD" Suprasil, (+) "P" Pyrex. Cleaned (i.e., "HD") Suprasil and Pyrex cells give consistent T_1 values, which correspond to an adsorption energy of 130 ± 20 K. The uncleaned "P" Pyrex cell gives much longer T_1 values, associated with an adsorption energy of about 75 K.

Although glass certainly offers several band states for adsorption to He, the coverage of the surface by adsorbed atoms is very low in our experiments, so that it is reasonable to consider that only the lowest lying state contributes to the relaxation.

It can be noticed that, as observed with H_2 coatings (see Section 4.1), Pyrex and pure silica surface give the same relaxation times. This is an even more sensitive situation than with a solid hydrogen coating. This result supports the hypothesis mentioned above that the iron content of Pyrex is not responsible for the relaxation we measure.

The value obtained here for the adsorption energy of ^3He on bare cleaned glass ("HD" cells), $\Delta W \approx 130 \pm 20$ K, agrees with the result given in ref. 29.

We now concentrate on the comparison between cleaned and uncleaned glass. The difference between cells "HD" and "P" is more striking in the

absence of the solid hydrogen coating, as shown in Fig. 6. First, the adsorption energy derived for "P" cells, $\Delta W \approx 75$ K, is lower than for "H" cells. This could be due to the presence of hydrogen atoms originating from adsorbed water molecules or silanol SiOH groups present at the glass surface. "P" cells might retain water molecules adsorbed on surface silanol SiOH groups, since the corresponding binding energies are in the range 10 kcal/mole, i.e., about 5000 K.^{30,31} Even if adsorbed water is completely eliminated under vacuum, surface silanol groups certainly remain at room temperature. The reaction by which two adjacent silanol SiOH are removed giving off a water molecule and leaving behind a siloxane bridge Si-O-Si releases 150 kcal/mole, i.e., 6.5 eV.³⁰ These surface SiOH groups are removed by outgassing at high temperatures, but it is believed that at room temperature the coverage by SiOH is practically complete, while outgassing at 400°C gives a ratio of SiOH to Si-O-Si groups of about 1/2.^{32,33} The tendency of the hydrogen atoms to point outward from the surface could provide for the low adsorption energy observed with "P" cells. The measurement of the adsorption energy of helium on a condensed water coating could give some support to this interpretation. Second, it can be seen in Fig. 6 that the ratio

$$T_1(\text{"P"}) \exp(2 \times 75 \text{ K}/T) / T_1(\text{"HD"}) \exp(2 \times 130 \text{ K}/T)$$

at 28.5 K is roughly equal to 4. This is consistent with a smaller local field inhomogeneity and/or a smaller effective surface area for "P" cells.

4.4. Relaxation of ³He on Solid Oxygen

At the beginning, experiments with oxygen were intended to find out how much oxygen was necessary to lower T_1 , since molecular oxygen carries an electronic spin magnetic moment. We first made measurements on a cell filled with O₂ in addition to the usual content of ³He and H₂. To our surprise, these O₂ subcoatings turned out to provide the longest relaxation times we ever measured, as described below. We therefore decided to investigate the relaxing properties of solid oxygen coatings alone and to compare their properties to bare glass surfaces. The triple point of O₂ (1.14 Torr at 54.36 K) corresponds to a filling pressure at 300 K of 6.29 Torr. With a moderate filling pressure, the oxygen film will condense in the vicinity of the triple point, where the coexistence of solid and liquid is favorable to complete wetting, that is, to the formation, layer by layer, of a very thick film.³⁴

We first determined that optical pumping was efficient between 20 and 30 K. Below 20 K, T_1 becomes rapidly shorter than the polarization building time. This low-temperature limitation corresponds to intrinsically short relaxation times (measured with the discharge switched off), whereas on

H_2 , D_2 , and Ne coatings, the low-temperature limit of optical pumping corresponds to very short relaxation times in the presence of the discharge, while the "intrinsic" wall relaxation time (i.e., measured with the discharge switched off, as usual) is much longer, by several orders of magnitude, at the temperature where optical pumping ceases to be efficient^{9,24} Incidentally, nitrogen films are seen to behave as oxygen coatings. This difference with coatings of light elements might have its origin in the much higher latent heat of sublimation of O_2 and N_2 (1100 and 940 K, respectively) compared to H_2 , D_2 , and Ne (108, 158, and 291 K, respectively). This may confer on coatings of heavier elements a greater resistance against evaporation when metastable He atoms are deexcited by wall collisions. On the other hand, the high-temperature limit for optical pumping efficiency around 30 K corresponds to the same density of O_2 in the vapor phase that was observed to inhibit optical pumping in experiments with H_2 , D_2 , or Ne.

The relaxation time variation with temperature is plotted in Fig. 7. The observed values of T_1 fall between the lines corresponding to "HD" and "P" bare Pyrex cells. This means that solid O_2 coatings do not lead to disastrous relaxation times, as expected naively. On the contrary, they give longer relaxation times than bare, cleaned glass. Bulk, solid oxygen as well as thin films deposited on glass are known to exhibit antiferromagnetic order at low temperatures.³⁵⁻³⁷ This property can be preserved in our experiments, so that the local magnetic field is not appreciably disturbed at the surface of our oxygen films (except on a scale of the order of the intermolecular spacing, on which the magnetic inhomogeneity may be averaged out by the movement of the ^3He adatoms).

One of the cells we measured (^3He : 1.9 Torr; O_2 : 10 Torr) corresponds to a filling pressure greater than the triple-point pressure. We tried repeatedly to anneal the film in the vicinity of the liquid-solid coexistence region, with no observable effect.

We also included in Fig. 7 a few measurements of T_1 (with the discharge switched off, of course), which correspond to a very sharp decrease of T_1 above 34 K. The very small vapor density of O_2 at this temperature ($1.5 \times 10^{12}/\text{cm}^3$) cannot lead to appreciable relaxation in the gaseous phase; we wonder whether this observation might indicate a modification of the oxygen film magnetism related to a phase transition of the film, as described in ref. 37. The characterization of this effect would require more sophisticated experiments that were out of our immediate interest.

Discarding T_1 values above 34 K and following formula (5), our experiment leads to an adsorption energy $\Delta W(^3\text{He on O}_2) = 130 \pm 15$ K, which has never been measured before to our knowledge. It coincides with the adsorption energy on bare glass surfaces. Because the adsorption energy of a He atom is governed by several parameters characterizing the substrate

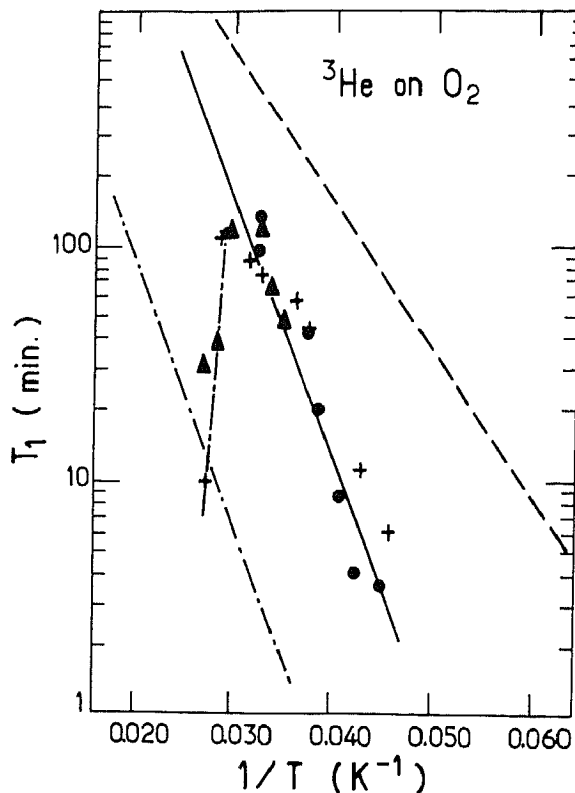


Fig. 7. Relaxation time of ^3He on solid O_2 . The cells are in Pyrex and of type "HD". For the sake of comparison, we include the lines fitting our results on (---) bare, cleaned ("HD") glass and (-·-) bare uncleaned ("P") glass. (▲) 1.9 Torr ^3He + 0.40 Torr O_2 ; (●) 1.9 Torr ^3He + 10 Torr O_2 . These two cells correspond to an adsorption energy of 130 ± 15 K. (+) The results on one cell filled with 1.9 Torr ^3He + 1.48 Torr H_2 + 9.99 Torr O_2 , for which we did not find any trace of a solid H_2 film. Its behavior rather suggests the presence of a bare, solid O_2 film. A sharp decrease of T_1 can be noticed above 34 K, which is not interpreted.

(van der Waals attraction toward He, density of the solid, zero-point vibrational displacement of the atoms in the last layers of the solid surface), such a coincidence does not seem unreasonable.¹⁵

4.5. Experiments on N_2 Coatings

These experiments were conducted in a way similar to our work on oxygen coatings. As on O_2 and for the same reasons, the proper temperatures

for optical pumping range between 20 and 30 K. Our results are shown in Fig. 8.

The fit of our measurements according to formula (5) yields an adsorption energy of about 200 K, higher than on O_2 or glass. This seems surprising because the empirical Lennard-Jones interaction potentials between O_2 and He or between N_2 and He that one can derive from combining laws as given in ref. 38 are very similar. Because the densities of solid oxygen and

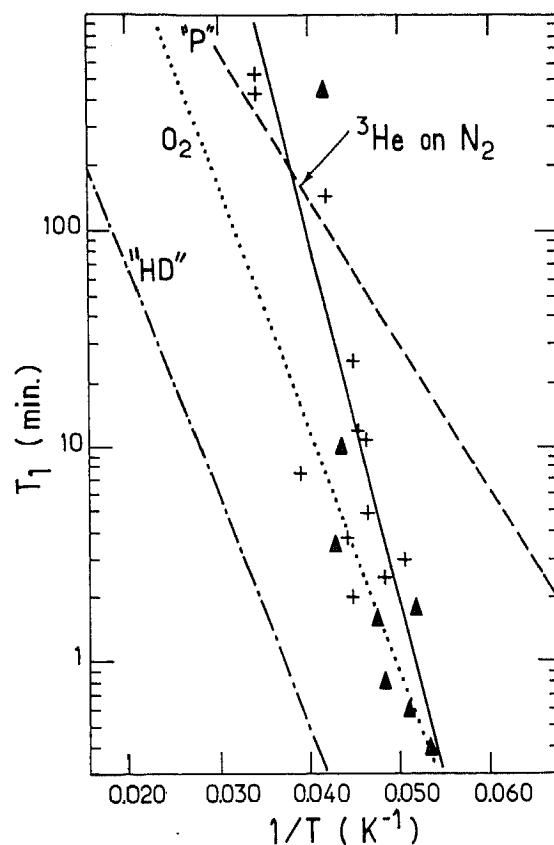


Fig. 8. Relaxation of ^3He on solid N_2 . (\blacktriangle) 1.9 Torr ^3He + 1.1 Torr N_2 ; (+) 1.9 Torr ^3He + 0.5 Torr N_2 . These cells are in Pyrex and of type "HD". The adsorption energy is 200 ± 50 K. The dispersion of T_1 is greater than with O_2 coatings for unexplained reasons, which results in a poor precision on this adsorption energy. (---) Results on bare, cleaned and (- -) uncleaned glass and on O_2 , shown for the sake of comparison.

nitrogen are also very close, the approximate potentials that can be estimated for He on these solids would give roughly the same adsorption energies in both cases. However, this type of approximation does not take into account the discrete nature of the solid substrate and is quite inefficient, for instance, in the case of He adsorbed on Ne (for which the zero-point delocalization of the Ne atoms is not too important). Anyhow, in the absence of any theoretical calculation or experimental determination by other techniques, this value of the adsorption energy of He on solid nitrogen seems rather large and still needs to be confirmed.

4.6. Nuclear Relaxation of ^3He on Multiple Coatings

The common purpose of experiments with multiple coatings is to find a combination that at the same time increases the distance of a ^3He adatom to the glass substrate and diminishes the magnetic field inhomogeneities, without producing a high effective surface area.

We first explored the possibilities of solid coatings such as Teflon or polyethylene deposited on the glass substrate by evaporation under vacuum, the sample cell being then filled with the usual amount of ^3He and H_2 . On some of these cells we were able to measure the correct adsorption energy of ^3He on H_2 , but we could never obtain reproducible results from cell to cell. With one of them we even observed, once it had been cooled to liquid helium temperature, that parts of the thin polyethylene film had detached from the wall. It is certainly difficult to control the thickness, porosity, and surface area of such films. We therefore turned to another technique, silanization, which consists in the grafting to a glass substrate of a long-hydrocarbon-chain silane compound forming a high-coverage monolayer of definite thickness (given by the length of the hydrocarbon chain). The silanization of our Pyrex cells was performed with D. Ausserre by the so-called retraction method,³⁹⁻⁴¹ using octadecyltrichlorosilane ($\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$) as the reactant. The principle of the silanization process is that the Cl atoms of this molecule react with silanol (SiOH) surface groups to produce HCl, leaving the rest of the molecule grafted to the surface through a Si-O-Si bond. This technique proved to be very efficient on oxidized silicon wafers, but this treatment applied to our Pyrex cells was disappointing.

Whether the silanization on Pyrex bulbs was not as homogeneous as on pure quartz or oxidized silicon plates, or whether the final sealing of our cells ruined the efficiency of this treatment, we never obtained any improvement of T_1 (although we did not encounter the same difficulties as with polyethylene or Teflon films).

We then turned to multiple coatings formed by the successive condensation of several gases. Following the improvement of T_1 observed on "P"

cells (cells not submitted to heating under vacuum and discharge cleaning), we decided to investigate the relaxation properties of multiple coatings, such as H_2 on H_2O , on N_2 , or on O_2 . This line of experimentation was complementary to our projects with multiple coatings of solid rare gases.

The principle of these experiments is the following. Let us consider, for instance, a cell filled with ^3He (1 Torr), H_2 (1 Torr), and Ne (1 Torr), all pressures measured at room temperature. One can expect that during the cooling of such a cell Ne will condense first, around 14 K, while the H_2 content will solidify on top of it between 7.6 and 6.7 K. Since the van der Waals attraction of H_2 to Ne is smaller than toward glass, one can wonder whether the number of uniform layers will not be smaller on Ne than on glass. Predictions on this question are rather difficult in the absence of a detailed knowledge of the adsorption properties of Ne on glass and of H_2 on Ne. Nonetheless, because the gain in potential energy for a given total thickness is greater with Ne plus H_2 than with H_2 alone, one can hope that the number of uniform layers of a multiple coating of Ne + H_2 will be greater than with H_2 alone. The same reasoning can be applied to other combinations of solid coatings. Some of them, such as O_2 and N_2 , also offer the advantage that a moderate filling pressure allows for the coexistence of liquid and solid, which is considered to favor complete wetting.

Multiple coatings made from molecular gases must, of course, be treated with care. One should never strike the discharge at room temperature or above the temperature of condensation of H_2 , otherwise reactions such as $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ or $\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O}$ take place. But once the coatings are formed, we never observed any effect of the discharge on T_1 . Furthermore, the filling pressure in H_2 has to be considered carefully. We once experienced that, whereas a cell containing 0.4 Torr of H_2 and 0.4 Torr of O_2 behaved as expected, one cell filled with 1.9 Torr of ^3He , 1.5 Torr of H_2 , and 10 Torr of O_2 gave no sign of the presence of H_2 : the H_2 content seemed to have dissolved completely inside the O_2 coating, so that the measurements on this cell were quite consistent with those of cells filled with ^3He and O_2 only (see Fig. 7). It is therefore advisable to provide for a moderate ratio of the filling pressures of the different gases.

Our results on multiple coatings of H_2 on Ne and H_2 on N_2 are collected in Fig. 9. They should be considered only as indicative. Because these first results did not show any improvement over pure H_2 coatings, in contrast with the results reported below on $\text{H}_2 + \text{O}_2$ coatings, we did not experiment further on these multiple coatings. However, it would be interesting to test if it is possible to condense a very thick coating of N_2 . Although it seems unlikely that N_2 gives much better results than O_2 (we refer here to the cell with 1.9 Torr of ^3He , 20 Torr of H_2 , and 8 Torr of O_2 see below), this possibility cannot be discarded from the few results presented here.

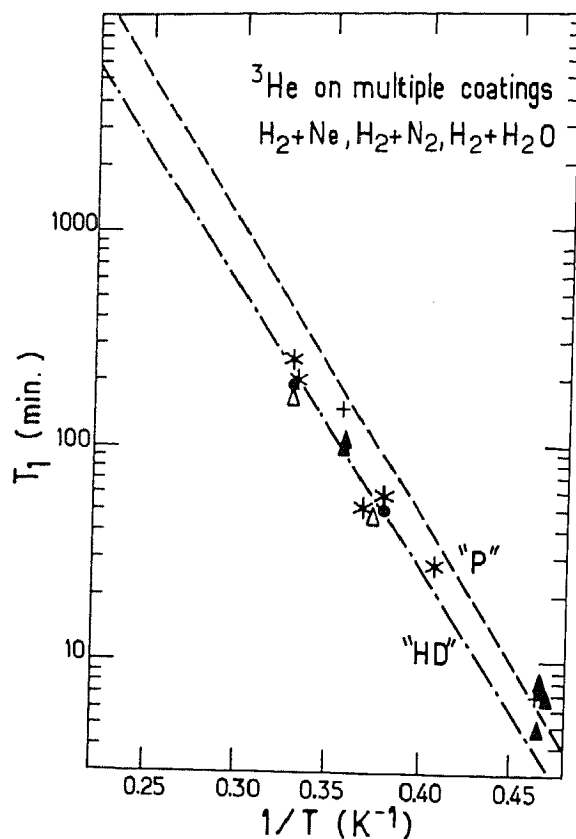


Fig. 9. Relaxation time of ${}^3\text{He}$ on multiple coatings of hydrogen deposited on Ne, N_2 , or H_2O . (Δ) 1.9 Torr ${}^3\text{He}$ +0.78 Torr H_2 +0.63 Torr Ne ("HD") Pyrex. (\bullet) 1.9 Torr+1 Torr H_2 +0.41 Torr N_2 ("P") Pyrex. ($*$) 1.9 Torr ${}^3\text{He}$ +1 Torr H_2 +0.41 Torr N_2 ("HD") Pyrex. (\blacktriangle) 1.9 Torr ${}^3\text{He}$ +1 Torr H_2 +3.96 Torr H_2O ("HD") Pyrex. ($+$) 1.9 Torr ${}^3\text{He}$ +1 Torr H_2 +1 Torr H_2O ("HD") Pyrex. Results obtained on simple H_2 coatings for (---) "HD" cells and (---) for "P" cells (see Section 2.2 or Fig. 4 for the meaning of "P" and "HD").

Figure 9 also shows our results on $\text{H}_2+\text{H}_2\text{O}$ coatings. It can be noticed that the two cells we have measured give results similar to those of "P" cells. This is reminiscent of our interpretation that "P" cell surfaces retain SiOH groups. The improvement of T_1 we observe is unfortunately limited, even on the cell that contains 33.7 Torr of H_2O , enough to make about 500 layers.

It is on coatings of H_2 deposited on O_2 that we obtained our longest relaxation times. As already mentioned in Section 4.4, the antiferromagnetic properties of solid oxygen at low temperatures are probably responsible for the low relaxation produced by oxygen coatings in our experiment. However, at small enough concentration or coverage, O_2 molecules certainly recover their paramagnetic character, thereby becoming able to severely shorten T_1 , as reported in ref. 42.

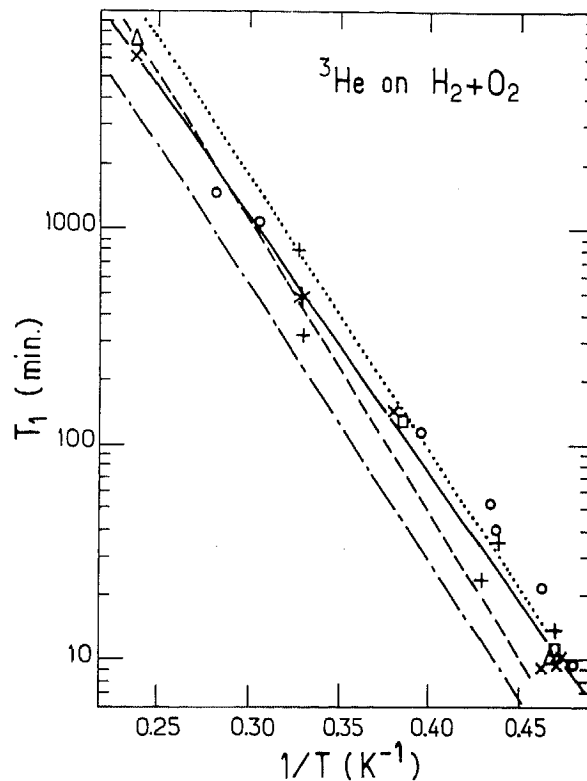


Fig. 10. Relaxation time of ^3He on composite coatings of H_2 covering O_2 . (O) 1.9 Torr ^3He +1.48 Torr H_2 +0.4 Torr ("HD") Pyrex. (Δ) 1.9 Torr ^3He +1.48 Torr H_2 +0.4 Torr O_2 ("P") Pyrex. (\times) 1.9 Torr ^3He +0.80 Torr H_2 +0.4 Torr O_2 ("HD") Pyrex. ($*$) 1.9 Torr ^3He +0.43 Torr H_2 +0.4 Torr O_2 ("HD") Pyrex. (\square) 1.9 Torr ^3He +4.41 Torr H_2 +1.96 Torr O_2 ("HD") Pyrex. ($+$) 1.9 Torr ^3He +20 Torr H_2 +8 Torr O_2 ("HD") Pyrex. Same comment as in Fig. 9 concerning ($-\cdot-$) and ($- - -$). ($- -$) A fit of all the measurements shown here. ($\cdot \cdot \cdot$) A fit of the measurements with $T \approx 2.63$ K, which discards eventual effects of permeation occurring above this temperature. It is seen to give an adsorption energy in better agreement with our results on plain H_2 coatings.

If the improvement of T_1 is clearly seen in Fig. 10, below 2.6 K, the relaxation times between 4.2 and 2.6 K tend to meet those of "P" cells with no oxygen. A tentative explanation could be that the few layers of O_2 deposited on O_2 are more permeable to He than when condensed directly onto Pyrex. This can happen if the compression of these layers by the substrate is smaller. Permeation is likely to shorten T_1 in the "high temperature regions, as has been observed in our earlier attempts to make thick coatings of hydrogen on Pyrex."¹⁴

Figure 10 shows that the relaxation times measured below 2.6 K are longer than on solid hydrogen alone, by a factor two when compared to "P" cells and by a factor three when compared to "HD" cells. We did not observe any dependence of T_1 on the filling pressure of O_2 (at least in the range of pressures studied here).

It can be noticed in Fig. 10 that a different cleaning treatment of the cell does not bring any change when an O_2 subcoating is present.

These results on multiple coatings are difficult to interpret, even with some knowledge of each constituent separately, because several physical quantities are liable to change and affect T_1 in those experiments: they are, on one hand, the effective surface area of the H_2 coating, which can, in turn, depend on the geometrical structure of the subcoating, and, on the other hand, the mean thickness of the combined coatings, which determines to what extent the local magnetic field is reduced.

5. CONCLUSION

We have presented here several attempts to increase the nuclear relaxation time T_1 of a ^3He vapor at liquid helium temperatures on a solid hydrogen coating. The best results around 2.5 K were obtained when a subcoating of oxygen was condensed under the hydrogen film. But the longest recorded T_1 at 4.2 K, 8000 min, i.e., $5\frac{1}{2}$ days, was measured on uncleaned "P" cell.

In trying to increase T_1 , we have, on several occasions, encountered a limitation due to permeation effects. Permeation of helium by tunneling inside the first layers of a substrate is a well-known phenomenon for classical substrates such as glass or polymers.⁴³ Graphite has recently been shown to provide an especially low barrier to helium permeation of about 100 K. Little is known on the permeation of helium into solid rare gases or solids O_2 , N_2 , and H_2 , but it certainly puts a constraint on the longest T_1 that can be obtained with such coatings.

In the course of this work, we have shown that at low temperatures, when permeation effects are negligible, Pyrex and pure silica exhibit the same relaxing properties for ^3He . This result suggests that the iron content of Pyrex is not responsible for the relaxation we observe, at least in the

rather low magnetic field of our experiment. It also brings up again the question discussed in ref. 14, as to whether the relaxing centers could be paramagnetic species produced in the discharge and then adsorbed or dissolved in the cryogenic coating. Evidence against this hypothesis now comes from an even greater number of experiments than before: with all the coatings we have studied, we have always observed the same relaxation times after evaporation and recondensation of the coating under study. It seems unlikely that in such a process, the density of relaxing species created by the discharge can remain unchanged with so many different coatings. Anyhow, stronger support against the role of the discharge still comes from experiments on double cells,¹⁴ which allowed for the measurement of T_1 in a bulb free from any discharge effects, with results identical to those of single cells. Altogether, our experimental results suggest that the relaxing centers are located inside or at the surface of the glass substrate, but their exact nature and distribution are still unknown.

To complete this work, it would be interesting to investigate bare, solid H_2O coatings and to go further into the role of H_2O molecules and different types of OH groups on the glass surface, by comparing the effects of different cleaning treatments on bare silica and Pyrex substrates. Besides, while thin films of solid O_2 have been found capable of increasing T_1 , this does not presume on the effect of very thin films or isolated oxygen molecules. Experiments where the amount of O_2 would be progressively diminished could probably show at which stage antiferromagnetic order is destroyed.

Finally, our measurements on O_2 and N_2 coatings have provided a preliminary determination of the adsorption energy of ^3He on these solids, $\Delta W(^3\text{He}/\text{O}_2) = 130 \pm 15 \text{ K}$ and $\Delta W(^3\text{He}/\text{N}_2) = 200 \pm 50 \text{ K}$.

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