EPR studies on fluorocarbon microspheres. Dynamic polarization of fluorine nuclei and adsorbed He3

M. Chapellier, L. Sniadower, G. Dreyfus, H. Alloul, J. Cowen

To cite this version:
EPR studies on fluorocarbon microspheres.
Dynamic polarization of fluorine nuclei and adsorbed He$^3$

M. Chapellier
Orme des Merisiers, CEN-Saclay et Laboratoire de Physique des Solides (*), Bât. 510, 91405 Orsay, France

L. Sniadower
Orme des Merisiers, CEN-Saclay, 91191 Gif sur Yvette, France

G. Dreyfus
Ecole Supérieure de Physique et Chimie Industrielle (ESPCI), Paris, France

H. Alloul and J. Cowen
Laboratoire de Physique des Solides (*), Bât. 510, 91405 Orsay, France

(Reçu le 25 novembre 1983, accepté le 8 février 1984)

Résumé. — Nous avons mis en évidence la présence d’un grand nombre (2,8 $\times$ 10$^{18}$/cm$^3$) de centres paramagnétiques électroniques dans les microbilles de fluorocarbone. Ces centres sont des radicaux peroxydes. Nous les avons utilisés pour produire pour la première fois une polarisation dynamique de l’He$^3$ adsorbé en surface. Néanmoins l’origine du couplage entre noyaux de fluor et He$^3$ observé dans ce système n’est pas encore établie.

Abstract. — We have found an unexpectedly large number (2.8 $\times$ 10$^{18}$/cc) of electronic paramagnetic centres in microspheres of fluorocarbon. These centres are peroxy-radicals. We have used them to produce for the first time a dynamic polarization of He$^3$ adsorbed on the surface of the particles. However the origin of the coupling between He$^3$ and fluorine nuclei observed in this system is not yet understood.

1. Introduction.

The coupling of He$^3$ spins with a solid surface or wall is a long-standing problem which is far from completely resolved. It dates from twenty years ago with the observation of the effect of the vessel on the longitudinal relaxation time of gaseous or liquid He$^3$ [1-3], at temperatures from room temperature for the gas to 0.5 K for the liquid. Since this early period, the range of low temperatures has been tremendously extended, down to the millikelvin region, and many experimental situations have been explored. In particular many experiments have involved more or less restricted geometries [4] for which walls are the only source of relaxation. A salient fact is the « special » behaviour of the adsorbed first monolayer, which generally has a much shorter relaxation time than the bulk, whatever the substrate. This is illustrated by the drastic change observed when a monolayer of He$^4$ is added to the wall. There is, to our knowledge, no clear-cut experiment where the coupling to a well defined substrate (with known paramagnetic impurity content, rugosity, etc...) could be compared with existing theories [5, 6].

Studies of $T_1$ of He$^3$ adsorbed on a supposedly clean wall, namely microspheres of fluorocarbon (*), were recently started at Cornell University by Richardson and co-workers, and the following unusual phenomenon was observed [7] : the spin orientation of the adsorbed He$^3$ nuclei follows very quickly the orientation of fluorine nuclei. For example, a satura-
...the electronic Non-Zeeman system is very often on speaking term with all nuclear Zeeman systems, the coupling being accomplished by the dipolar term $S_i^z I_i^z$ in the Hamiltonian describing the interaction between an electronic spin located at $r_i$ and a nucleus located at $r_I$. The energy balance is accomplished by one nuclear spin flip plus one or more electronic flip-flops.

Let us sum up: if there is no short nuclear relaxation to the lattice due to sources other than these electrons, and providing that electrons are not too strongly coupled to the lattice, then all nuclei and the Non-Zeeman form a simple bath, and one will observe then modification on one nuclear spin system if the second nuclear spin system is disturbed, as was observed between F$^{19}$ and He$^3$ nuclei in the Cornell experiment. It was then very tempting [11] to postulate the existence of electrons which would have been responsible for the phenomenon. In any case, if electronic centres do exist in this type of materials, they could be used to produce a dynamic nuclear polarization of F$^{19}$ (and He$^3$). A microwave irradiation slightly off resonance for these electronic centres can produce a low temperature $T_{NZ}$ of the Non-Zeeman system by pumping population from the lower to the upper electronic sublevels. This temperature being communicated to the nuclei, the enhancement of the nuclear magnetization is observed. For example, figure 1b, an irradiation at a frequency smaller than $\omega_0$, transporting population from area 1 to area 2, produces a low positive $T_{NZ}$ which corresponds to an enhancement $A^+ = T/T_{NZ}$ of the nuclear magnetization. Irradiation at $\omega$ slightly higher than $\omega_0$ produces a low negative $T_{NZ}$ and an enhancement $A^- = T/T_{NZ}$ of the nuclear magnetization.

An attempt with 10 GHz microwaves revealed an enhancement of the polarization of F and He$^3$, showing that some paramagnetic impurities were present [11]. This was done in an experiment where we did not try to observe EPR (which was supposed, at that time, to arise from electrostatic charges produced on the surface of the microspheres).

After an unsuccessful attempt to polarize in high field $^{(2)}$ (25 kG-70 GHz), it was decided to begin a study of the nature of the paramagnetic centres responsible for the dynamic polarization observed at 3 K, and to try to correlate this spectrum to the coupling between F and He$^3$. In the course of these experiments, the crucial behaviour of the $T_1$ of F nuclei with respect to the oxygen content of the sample was observed. This has also an effect on the polarization which may be achieved. The rôle of oxygen has also been extensively studied at Cornell [13].

2. EPR studies.

2.1 Apparatus. — We have used a Varian X band microwave spectrometer (Serie V 4500) and a He flow variable temperature Oxford Instrument ISR 9, which allowed a fast cooling from room temperature to 3.8 K. A rectangular cavity, of type TE 012, with an

---

$^{(2)}$ This was done in collaboration with H. Glättli and J. Coustham.
adjustable coupling was used. The sample was a pressed cylinder, of 3 mm in diameter and about 6 mm in length. It was introduced in a quartz tube of internal diameter 3 mm and outer diameter 4 mm, which just fits in the Oxford Dewar. A pumping system provided the cleaning and eventually the flushing with He\textsuperscript{4} which in principle was enough to remove the oxygen from the sample. It was necessary to leave some gaseous He (He\textsuperscript{3} or He\textsuperscript{4}) to ensure rapid cooling.

2.2 EXPERIMENTAL RESULTS. — An intense EPR signal was easily detected at room temperature. This spectrum is the same, whatever the atmospheric condition (dryness). It is the same even if one puts the sample into water and then dries it. These paramagnetic centres are « intrinsic » to this type of material and very stable. When compared to the Varian standard (strong pitch) it appears that the concentration of paramagnetic centres is about 2.6 \times 10^{18}/\text{cm}^{3}. The line is obviously complex with probably two components. Its shape changes very quickly with temperature, from 320 K to 3.8 K (see Fig. 2). It may change also below that temperature but we have not extended EPR experiments below 3.8 K.

2.3 HEAT TREATMENT. — When the sample is heated under vacuum at 200 °C for half an hour, the room temperature spectrum is strongly modified. One observes extra peaks probably arising from the hyperfine interaction with fluorine. Heating at 200 °C for a longer period does not induce any further change. If the sample is then left in a poor vacuum, it will return to its original state and all hyperfine peaks will vanish. If the sample is heated at 300 °C during 30 min, then the signal nearly vanishes.

Another teflon powder (Aldrich Chemical Company, size about 1 μ) does not show any visible EPR line, which suggests very strongly that the observed EPR in the DLX 6000 sample is not associated with electrostatic charges but rather with radicals specific to this powder.

Spectra similar to those of DLX have been observed in the past [14, 15] on bulk teflon irradiated with γ rays in vacuum. Hyperfine interactions appeared and disappeared when the sample was left in contact with oxygen. The two lines are attributed to mid-chain peroxy radicals and end-chain peroxy radicals. The mid-chain is able to lose its oxygen reversibly, even at room temperature, when the vacuum is of the order of 10^{-4} torr. Owing to the size of the spheres, the reoxygenation should be very fast in our case.

2.4 γ IRRADIATION. — Finally we have γ irradiated a sample of DLX 6000 previously heated at 300 °C. The ESR spectrum is found to be very similar in shape. This tends to confirm that these centres are the two peroxy radicals observed in teflon. Let us now recall briefly the properties of this type of centre [15, 16].

a) The peroxy radicals have different g values $g_{||} = 2.038$ and $g_\perp = 2.002$.

b) At room temperature, there is a motional narrowing by molecular movements of the radicals which explain the observed linewidth of 12 G.

c) At 77 K, the two g values can be distinguished and the line is broadened to about 60 G.

d) We have decreased the temperature down to 3.8 K and there are still large changes in the motions which further broaden the line, filling for example the valley between the two main g values as can be seen in figure 2. Part of the shape at the lowest temperature is probably due to a transfer of population between hyperfine levels as one sweeps from one side of the line to the other [16].

To emphasize what is relevant for our experiments of dynamic polarization we would say that at $T < 4.2$ K the line is very broad and inhomogeneous in nature owing to the distribution of g values between $g_{||}$ and $g_\perp$. 

Fig. 2. — Shapes of the EPR lines obtained with DLX 6000 samples at different temperatures. The vertical scale is the same for all temperature, but saturation at low temperature reduces the size of the signal. The point of maximum positive enhancement is indicated by an arrow.
3. Dynamic polarization and relaxation of $\text{He}^3$ and $\text{F}^{19}$

3.1 First evidence for a dynamic polarization. — The very first experiment was done with a standard low temperature pulse NMR probe with limited space inside the cryostat. A TE 001 cavity (Fig. 3) was designed to fit inside the cryostat and was therefore filled with teflon in order to reduce the cavity size by a factor $\sqrt{2}$. The cavity was excited through a coaxial cable but the coupling, fixed at room temperature, could not be modified at low $T$ and was not very good. A lot of reflections in the coaxial cable occurred as well. A DPPH sample allowed us to distinguish the cavity tuning from the reflections in the cable. We did not even attempt to detect any ESR signal from the DLX sample as we did not expect the sample at that time to be heavily doped by paramagnetic impurities. The radiofrequency coil was a $2 \times 3$ turns of $\varnothing = 0.2$ mm wire, wound on the cylinder containing the DLX 6000. The turns of the coil were carefully located in a vertical plane to avoid screening of the microwave oscillating field (which is vertical in the TE 001 mode). The magnetic field was horizontal and the radio-frequency coil had to be correctly oriented. The field was around 3.4 kG which corresponds to a frequency of 11.2 MHz for $\text{He}^3$ nuclear spins. The sample was pressed in a plastic box made of stycast 1266 which allowed us to heat it to 100 °C without damage. The NMR pulse apparatus used was of the conventional variable frequency type. The signal, which was often taken slightly out of resonance was simply measured on an oscilloscope. From 4.2 to 1.5 K we detected essentially the signal of $\text{He}^3$, the signal of $\text{F}$ nuclei being superimposed on that of the filling material in the cavity. By switching on and off the microwave power, it was possible either to increase the signal or to observe its decay. The sample of DLX 6000 was cleaned by pumping for several days at 100 °C, followed by $\text{He}^4$ flushing to remove the oxygen, a method used at Cornell University. $\text{He}^3$ was introduced either as a complete or a half monolayer, or as a saturated film at 4.2 K (the pressure was 70 torr at 4.2 K). The results are summarized in table I.

Table I. — Results of the DNP experiments on $\text{He}^3$ at 3.4 kG. The data for $T_1$ of $\text{He}^3$ (which is probably the $T_1$ of $\text{F}^{19}$), for the positive enhancement $A^+$, one negative enhancement $A^-$ for various temperatures and $\text{He}^3$ coverages. For half coverage $T_2$ was found to be about 0.6 ms.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$T_1$ (s)</th>
<th>$A^+$</th>
<th>$A^-$</th>
<th>Number of layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>7</td>
<td>-2</td>
<td></td>
<td>saturated film</td>
</tr>
<tr>
<td>4.2</td>
<td>15</td>
<td>25</td>
<td></td>
<td>1/2</td>
</tr>
<tr>
<td>4.2</td>
<td>78</td>
<td>18</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>1.4</td>
<td>170</td>
<td>10</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

Correlation with ESR spectra. — We again used the Varian cavity and the Oxford circulation cryostat which allows fast cooling to 3.8 K. We placed around the silica tube a plastic holder (Fig. 4) so that a NMR coil could be built within a vertical plane, at least in the central part of the cavity (which is a rectangular TE 012). This was necessary in order to avoid disturbing the cavity. We were then able to try to correlate the enhancement of $\text{F}^{19}$ or $\text{He}^3$ with the electronic spectrum but we realized that the $T_1$ of $\text{F}^{19}$ depends

Fig. 3. — TE 001 cylindrical cavity of reduced size used for dynamic polarization at 10 GHz.

Fig. 4. — Rectangular Varian cavity used with the Oxford rapid cooling dewar. The dashed lines represent the microwave $H_1$. The tube and the NMR coil are represented outside the cavity.
strongly on the sample preparation and that the enhancement was very sensitive to (and only to) the $T_1$ of $F^{19}$.

The dependence of the $F^{19}$ positive enhancement and $T_1$ on the sample preparation was the following. In an «off the shelf» sample, the $T_1$ was short (around 10 s) and the enhancement poor (around 3). If the sample is heated slightly (69 °C) and pumped for a short time (10 min), or pumped at room temperature and flushed with He$^4$ for a very long time, then $T_1$ is longer (50-60 s) and the enhancement is maximum (20). Heating at higher $T$ curiously reduced $T_1$ very strongly. As detailed in section 2 the EPR spectrum remains unchanged upon the moderate temperature heat treatments which yield a modification of $T_1$. Therefore it seems reasonable to infer that some additional oxygen is present in the sample (or at the surface) which did not contribute to the observed ESR.

The results are summarized in table II, giving for $F^{19}$ the positive enhancement $A_+$ and $T_1$ at 3.8 K and 3.3 kG, for different sample preparations. As usually found for DNP in inhomogeneous systems, the maximum polarization was obtained at the point of maximum slope of the ESR line which, in the standard derivatives spectra of figure 2, corresponds to the high field side of the line and to positive enhancement [12]. It corresponds to an irradiation at a frequency smaller than the average electronic Larmor frequency. The smaller negative enhancement was not studied in detail. It can thus be concluded that DNP is due to the centres observed by ESR, but the enhancement is limited by the $^{19}$F relaxation time. $T_1$ values shorter than 10 s suggest that, if the extra relaxation is due only to oxygen, this oxygen is located within the microspheres and not on the surface. A very short surface relaxation, by diffusion of magnetization inside the spheres would give a diffusion limited $T_1$ of 20 s [17].

This is the first time that an artificial (dynamic) enhancement is observed on He$^3$ in a dense form, although related observations have been made with the gaseous form by optical pumping. Considerable progress has been made recently in this field with the use of laser sources [18]. Let be noticed that, at the present time, large polarizations cannot be expected on such a system, the maximum enhancement observed here does not depend very much on the microwave power, which could be reduced by more than 30 dB without any change in $A_+$. The electronic centres are easily saturated and we believe that we essentially observe a differential solid effect [12]. One could expect to increase the polarization of fluorine by increasing the fluorine $T_1$, which could be achieved by lowering the temperature. Another possible way to increase the obtained polarization of $F^{19}$ would be to try to find other types of paramagnetic centres which may be more efficient in the dynamic polarization process of $F^{19}$ nuclei. However, in the presence of He$^3$, we do not expect a large increase of $T_1$, which is ultimately governed by the He$^3$ relaxation itself, especially for large coverage. Therefore we can hardly expect, unfortunately, to obtain large polarizations of adsorbed He$^3$ by this technique.

4. Conclusion.

We have observed, in fluorocarbon microspheres, an unexpectedly large number of paramagnetic centres. They are believed to be peroxy radicals previously observed in irradiated and oxygenated bulk teflon. A drastic decrease of the $F^{19}$ relaxation time $T_1$ with increasing oxygen content has been observed, although the EPR spectra are not significantly altered. The paramagnetic centres have allowed for the first time a microwave polarization of adsorbed He$^3$, which is less efficient when $T_1$ of $F^{19}$ is reduced by increasing the oxygen content. Although a coupling between He$^3$ and $F^{19}$ is mediated by the paramagnetic impurities responsible for the ESR spectra, the present experiments do not demonstrate that this is the dominant coupling. Indeed such an interaction should be reduced at low temperatures, for which the paramagnetic impurities are saturated by the application of moderate fields. Preliminary data [19, 20] indicate that this is not the case and therefore that the dominant coupling might have a distinct origin.

<table>
<thead>
<tr>
<th>$T_1$ (s)</th>
<th>$A_+$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>20</td>
<td>sample outgassed at room temperature during days and flushing of He$^4$.</td>
</tr>
<tr>
<td>&lt; 10</td>
<td>2</td>
<td>sample heated at 190 °C !</td>
</tr>
<tr>
<td>~ 15</td>
<td></td>
<td>new sample badly pumped.</td>
</tr>
<tr>
<td>30</td>
<td>7</td>
<td>pumped 3 days at 150 °C and flushed with He$^4$.</td>
</tr>
<tr>
<td>&lt; 10</td>
<td>2</td>
<td>left in bad vacuum during 2 days before experiments.</td>
</tr>
<tr>
<td>very short !</td>
<td>none</td>
<td>240 °C and flushing He$^4$.</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>pumped 1 min. at room temperature. No flushing.</td>
</tr>
<tr>
<td>60</td>
<td>20</td>
<td>pumped during 10 min. at 60 °C (330 K) with flushing of He$^4$.</td>
</tr>
</tbody>
</table>

Table II. — Results of the joint ESR and DNP experiments on $F^{19}$ at 3.8 K and 3.3 kG for different sample preparations.
Acknowledgments.

We would like to thank Pr. R. C. Richardson for supplying the DLX 6000, and both him and L. J. Friedman for interesting discussions. We would like also to thank Philippe Monod for an extensive loan of his EPR apparatus and very useful help and comments during the experiments. This work was partially carried out under contract DRET 81/431.

References


GODFRIN, H., Thèse Grenoble, 1981.