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

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

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Résumé. — Nous avons mis en évidence la présence d'un grand nombre ($2,8 \times 10^{18}/\text{cm}^3$) 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'He³ adsorbé en surface. Néanmoins l'origine du couplage entre noyaux de fluor et He³ observé dans ce système n'est pas encore établie.

Abstract. — We have found an unexpectedly large number ($2.8 \times 10^{18}/\text{cc}$) 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 He³ adsorbed on the surface of the particles. However the origin of the coupling between He³ and fluorine nuclei observed in this system is not yet understood.

1. Introduction.

The coupling of He³ 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 He³ [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 He⁴ 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 He³ adsorbed on a supposedly clean wall, namely microspheres of fluorocarbon ⁽¹⁾, 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 He³ nuclei follows very quickly the orientation of fluorine nuclei. For example, a satura-

(*) Laboratoire associé au CNRS (LA n° 2).

⁽¹⁾ Dupont de Nemours, trade mark DLX 6000.

tion of the F nuclei results in a zero magnetization of He^3 within a time $\tau \simeq 0.2$ s. If one applies a π pulse to invert the F magnetization, the He^3 magnetization will also be rapidly inverted. This was done at temperatures between 4.2 K and 0.5 K and in a field of 4 kG where the resonance frequencies of He^3 and F^{19} are very different.

We now recall a phenomenon at low temperatures in solids doped with paramagnetic impurities. In 1968 [8], it was proved that the electronic spin-spin reservoir is strongly coupled to the nuclei and could serve as a coupling mechanism between nuclei having different gyromagnetic ratios, even in very high fields in which resonance frequencies differ considerably. We shall give here only a simplified explanation, but more details can be found in the specialized literature [9, 10].

The electronic system is described by [10] $\mathcal{H} = \omega_E S_z + \mathcal{H}'_{\text{dip}} + \sum_i \Delta_i S_z^i$; the first term is the total Zeeman energy, the second the usual truncated interaction between electronic spins, the last describes the possible spread of g values. If we remark that the term $\mathcal{H}'_{\text{dip}} + \sum_i \Delta_i S_z^i$ called the Non-Zeeman energy commutes with S_z , then we know that the system may have two different temperatures. One is called the Zeeman temperature and describes the distribution between spin up and spin down states. The second, called the Non-Zeeman temperature, describes the distribution among sublevels. An equilibrium situation, where the two temperatures are equal to the lattice temperature is represented figure 1a. We shall explain later how one can produce temperatures which differ both in sign and magnitude.

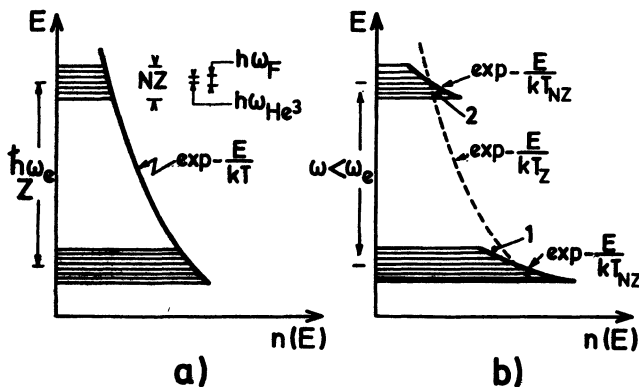


Fig. 1. — Sublevel distribution of paramagnetic centres in a solid, in a magnetic field. a) With the same T_Z and T_{NZ} temperature; b) After irradiation at frequency $\omega < \omega_e$, which produces $T_{NZ} < T_Z$ and polarizes the nuclei on speaking term with the Non-Zeeman bath. The transport of population occurs between area 1 and 2.

The electronic Non-Zeeman system is very often on speaking term with all nuclear Zeeman systems, the coupling being accomplished by the dipolar term $S_z^i I_+^j$ in the Hamiltonian describing the interaction between an electronic spin located at r_i and a nucleus located at r_j . 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 ω_e , 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 ω slightly higher than ω_e 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 kG, 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^4 which in principle was enough to remove the oxygen from the sample. It was necessary to leave some gaseous He (He^3 or He^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

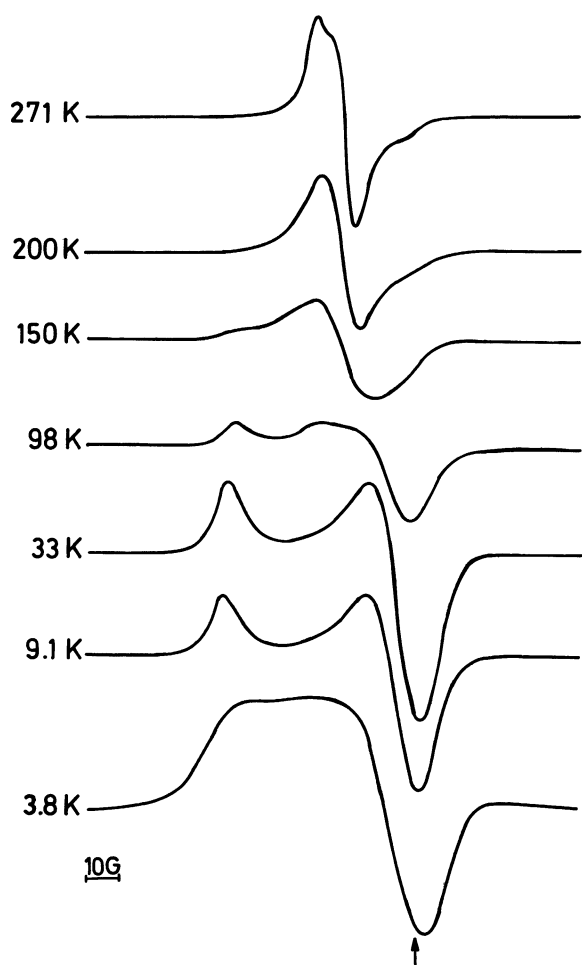


Fig. 2. — Shapes of the EPR lines obtained with DLX 6000 samples at different temperatures. The vertical scale is the same for all temperature, but saturation at low temperature reduces the size of the signal. The point of maximum positive enhancement is indicated by an arrow.

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 $g_{\parallel} = 2.038$ 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_{\parallel} and g_{\perp} .

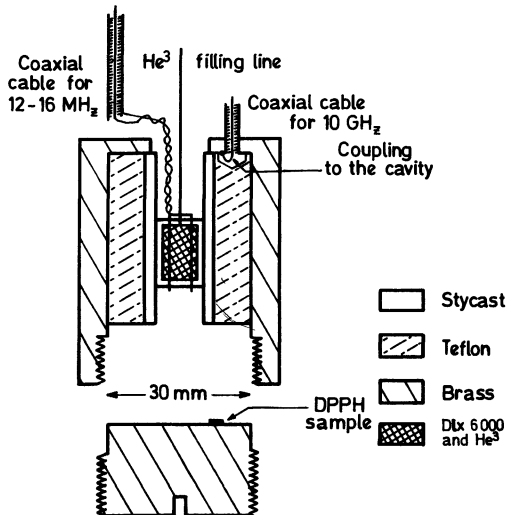


Fig. 3. — TE 001 cylindrical cavity of reduced size used for dynamic polarization at 10 GHz.

3. Dynamic polarization and relaxation of He^3 and 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 $\sqrt{\epsilon}$. 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 2×3 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 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 He^3 , the signal of 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 He^4 flushing to remove the oxygen, a method used at Cornell University. 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 He^3 at 3.4 kG. The data for T_1 of He^3 (which is probably the T_1 of F^{19}), for the positive enhancement A^+ , one negative enhancement A^- for various temperatures and He^3 coverages. For half coverage T_2 was found to be about 0.6 ms.

T (K)	T_1 (s)	A_+	A_-	Number of layers
4.2		7	-2	saturated film (100 g of vapour)
4.2	15	25		1/2
4.2	78	18		1
1.4	170	10		1

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 F^{19} or He^3 with the electronic spectrum but we realized that the T_1 of F^{19} depends

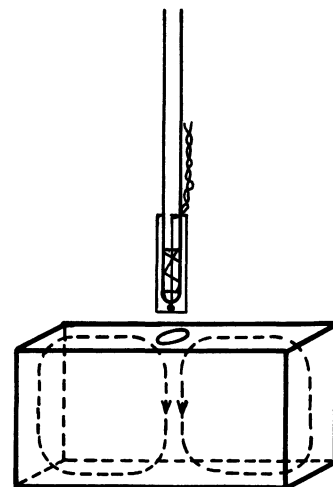


Fig. 4. — Rectangular Varian cavity used with the Oxford rapid cooling dewar. The dashed lines represent the microwave H_1 . The tube and the NMR coil are represented outside the cavity.

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

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.*

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

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.

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