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Physical explanation of the coupling between ^{19}F nuclei and ^3He nuclei on the surface of fluorocarbon spheres

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Résumé. — Nous proposons d'expliquer le fort couplage entre ^3He et ^{19}F observé par L. J. Friedman, P. J. Millet et R. C. Richardson quand ^3He est adsorbé à la surface de billes du fluorocarbène. Le mécanisme physique nous semble dû à la présence en surface d'électrons piégés. On suggère des possibilités intéressantes de polarisation dynamique.

Abstract. — It is suggested that the coupling between ^3He and ^{19}F nuclei recently observed by L. J. Friedman, P. J. Millet and R. C. Richardson at the surface of small fluorocarbon particles is mediated by electrons trapped on the surface. Possible consequences are analysed.

In a recent nuclear magnetic resonance experiment Friedman, Millet and Richardson (FMR) [1] have observed a surprisingly strong coupling between ^{19}F nuclei in small fluorocarbon particles and ^3He nuclei adsorbed on the surface. The experiment was done in a magnetic field of 0.39 tesla, and at temperatures between 4.2 and 0.5 K. The essential observation is that the ^3He nuclear polarization follows the ^{19}F nuclear polarization with a time constant of 200 ms. The time constant is nearly independent of temperature over the range studied.

FMR attribute the effect to a nuclear magnetic dipolar coupling at the interface. A direct nucleus-nucleus interaction is insufficient, however, to produce the polarization phenomena observed. Two different nuclei couple together directly and quickly only if their resonant frequencies are very close, within their linewidths. Under these conditions spin-flip processes conserving the total energy become possible.

In the experiment of FMR, the Larmor frequencies are $\nu_{^3\text{He}} = 12.6$ MHz and $\nu_{^{19}\text{F}} = 15.6$ MHz, with linewidths not more than 20 kHz and 300 Hz, respectively. So, the energy condition is not fulfilled (we have checked experimentally that the ^3He linewidth does not increase, when it is adsorbed on fluorocarbon particles).

We now would like to point out that a mixing between different nuclear spins similar to that reported at Cornell was observed a long time ago in LiF [2], a completely different system (^{19}F and ^7Li nuclei in LiF doped with F centres). Later the phenomenon has been seen in three different systems [3, 4, 5], and a theoretical framework has been established [6, 7, 8, 9]. The experiment discussed here is the first observation of a coupling between nuclei located in two separate phases.

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The phenomenon is seen only in the presence of electronic paramagnetic centres. A simplified explanation works as follows :

The electronic system is described by two Zeeman levels plus what is called the « non Zeeman » terms including all terms broadening the initial levels. This broadening is caused by : spread of g values, hyperfine interactions with the surrounding nuclei, or by the secular interactions between electronic spins including exchange and dipole-dipole interactions (which depend on the concentration and the spatial distribution of paramagnetic centres). If only the last term is present, the non Zeeman term is the usual spin-spin interaction.

In such a system, the non Zeeman term commutes with the Zeeman term which means that no exchange of energy occurs between the two systems, and that one could find two different temperatures T_Z and T_{NZ} to describe the Boltzmann distribution among the two Zeeman levels and among the sub-levels. In figure 1a $T_Z = T_{NZ}$ but in figure 1b $T_{NZ} \ll T_Z$.

A situation as described in figure 1b could be established by microwave irradiation at a frequency slightly smaller than the electronic Larmor frequency. It produces a temperature T_{NZ} lower than T_Z (but positive). If the applied frequency is bigger than the Larmor frequency, a negative low temperature T_{NZ} is produced. The electronic non Zeeman system is on speaking terms with all nuclear Zeeman systems, sometimes with nuclear frequencies much bigger than the width of the electronic line [6, 8]. This is accomplished by the dipolar terms $S_z^\pm I_\pm$ in the hamiltonian describing the interaction between an electronic spin S^e and a nuclear spin I . Energy balance is possible by a one nuclear spin-flip plus two or more electronic flip-flops. The non Zeeman system could then act as a transmitter between nuclei of different gyromagnetic ratios (Fig. 2).

In the experiment of FMR, we would suggest that electronic charges on the surface of the spheres play the role of paramagnetic centres. It is known that electrostatic charges develop on

Fig. 1. — Simplified picture of Zeeman and non Zeeman systems : a) with the same temperature ; b) with $T_{NZ} \ll T_Z$. This could be obtained by microwave irradiation at a frequency ω slightly smaller than the electronic Larmor frequency ω_e .

Fig. 2. — Connection between ^{19}F nuclei in the bulk and ^3He on surface.

fluorocarbon surfaces very easily with charge densities around 5×10^{-4} Coulomb/m² if only electrons are present. This number varies considerably from sample to sample, the upper limit is given by a charge which produces a Corona effect. If both positive and negative charges are present, an even higher density could develop (during the process involved to obtain these spheres, and also by mechanical friction).

Paramagnetic resonance of electrons was recently observed on similar materials with linewidths of the order of 30 MHz [10] and obviously one should try to observe the charges on the small fluorocarbon spheres by this method.

In an attempt to estimate the mixing time we first note that the heat capacity of the ^{19}F nuclei mixing with ^3He nuclei within a time of 0.2 s is 50-100 times larger [1] than the heat capacity of the ^3He monolayer on the surface. From the rate equations [8] it is then apparent that the mixing time is determined by the rate W_3 for equilibrium between electrons and ^3He . For W_3 we adopt the expression :

$$W_3 = \frac{1}{2} c A^2 (1 - P_e^2) \delta / (\pi \omega_3^2) \quad (1)$$

derived by Goldman, Bouffard and Cox [8] for application to LiF. For the purpose of a qualitative discussion, and regarding the uncertainties involved, (1) is equally well applicable in the present case.

In (1) c is the concentration of electronic centres in proportion to « coupled » nuclei. δ is derived from the electronic lineshape and depends on the concentration and distribution of electronic centres over the sites available to them. Comparing with the experiment of Cox *et al.* [5], we find approximately the same value for c with the electron concentration suggested above. There is no basis for assuming a different δ . The constant A^2 measures the strength of the $S_z^e I_{\pm}$ coupling. Because there is only one atomic layer of ^3He , A^2 is reduced with the factor $\pi/24$. The important characteristic feature of (1) is the factor $(1 - P_e^2)/B_0^2$, expressing the dependence on temperature and external field B_0 via the electronic polarization P_e and the Larmor frequency ω_3 of the ^3He nuclei ($P_e = \tanh(\hbar\omega_e/2 k_B T)$).

The experimental data of Cox *et al.* could be expressed by $W_3 = 2.8 (1 - P_e^2)/B_0^2 (\text{tesla})^2 \cdot \text{s}^{-1}$. FMR had $B_0 = 0.4$ tesla and as temperature decreased from 4.2 K to 0.5 K, electronic polarization P_e (if present, as we assume) would increase from 0.06 to 0.49. The resulting rather weak change in $1 - P_e^2$ is consistent with the FMR data [11]. For the order of magnitude we get

$$W_3^{-1} \sim (\pi/24) \times 2.8 \times 1.2/0.4^2 \text{ s} = 0.4 \text{ s}.$$

Obviously it will be very important to observe with better accuracy the dependence on $1 - P_e^2$ since this factor links the phenomenon directly with electronic magnetic moments.

If the coupling comes from the electrons, microwave irradiation on the edge of electronic resonance will produce dynamic polarization of F nuclei as well as ^3He nuclei. Then one could expect production of a highly polarized (either positive or negative) ^3He monolayer even at lattice temperatures around one Kelvin.

Preliminary experiments of that type have produced for the first time microwave enhancement of ^3He polarization [12]. At 4.2 K, with a coverage corresponding to a half filled monolayer we observed polarization to be enhanced by a factor 25. The negative polarization produced by pumping on the opposite edge of the resonance was smaller which indicates the composite nature of the electronic centres.

One can even go further : If the efficiency is good, it could be possible to build a « microwave pump » able to produce polarized liquid in a continuous experiment provided that some spin exchange takes place between liquid and adsorbed ^3He [13].

Dynamic transmission of polarization to solid ^3He [14, 15] might also be possible. A high pressure will be needed to avoid short relaxation times of bulk ^3He [16].

If the number of natural electronic centres is not sufficient it will certainly be possible [17] to put internal centres in these spheres by α , x or γ irradiation.

To conclude, we think that the presence of electronic paramagnetic centres offers the most probable explanation of the observed coupling since microwave enhancement cannot exist without such centres. It suggests promising experiments, but more knowledge is needed on the nature of these centres.

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