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POLARIZED NUCLEI : BEYOND THE HYDROGENS

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ABSTRACT

The nuclei other than the hydrogen isotopes which have been polarized dynamically, are compiled in a table, together with some of the relevant information for potential users of polarized nuclei.

1. Introduction

Since the advent of polarized nuclei, the overwhelming majority of experiments were in the field of particle physics. The interest was therefore concentrated on polarized protons and neutrons (deuterons). For some applications, however, polarized nuclei other than those of hydrogen have been of use, and may be useful in the future :

- In the study of nuclear magnetic ordering, highly polarized nuclei provide the initial state of low entropy needed to achieve an ordered phase after adiabatic demagnetization [1]. In these experiments, the ^{19}F nucleus has often be used, its NMR properties being very close to that of ^1H .

- The polarization of the nuclei results in an increase in detection sensitivity and is therefore helpful in a variety of NMR studies in solid state physics and in chemistry. As an example, the dynamic enhancement of the ^{13}C polarization is performed routinely for organic chemistry studies.

- Thermal neutron scattering is a powerful tool to study both static and dynamic properties of condensed matter. The basic interaction neutron-nucleus is spin dependent. Its knowledge gives additional information in thermal neutron scattering experiments. The use of polarized nuclei is the most direct, if not the only, way to measure the spin dependent scattering length (which is equivalent to the so-called pseudomagnetic moment μ^*) [2].

- Spin effects play a role in nuclear physics and polarized nuclei have often been helpful in solving problems, e.g. in spin assignments of neutron resonances.

The present report consists essentially in a table. It lists the nuclei which have been dynamically polarized.

The large class of nuclei, which can be and have been polarized statically are not included in the table. By static polarization, one designates the fact that the nuclei are in thermal equilibrium at a given temperature T and magnetic field H such that their polarization is given by the Brillouin function.

High static polarizations are most easily obtained with transition metals where moderate external fields (<1 Tesla) are sufficient to align the internal or hyperfine fields (typically 10-100 Teslas) yielding high nuclear polarization at moderately low temperatures. For example, the equilibrium nuclear polarisation of ^{165}Ho in holmium ethylsulfate (with the magnetic field parallel to the crystal axis) is 34% at 1K, and that of ^{59}Co in the metal is 1.5% at the same temperature.

2. Explanation of the table

The table lists the nuclei which have been polarized dynamically.

The second column gives the maximum polarization achieved, at the conditions of field and temperature listed in the third and fourth column. No distinction has been made between positive and negative polarizations, their absolute values being most often close.

The substance in which the nuclei were polarized is given in column five, together with the paramagnetic centers used for the dynamic polarization. For irradiated samples, the kind of radiation is indicated rather than the actual defects responsible for polarization, which are quite often not precisely known.

Column six indicates the particular method of dynamic polarization. By solid effect (s.e) we mean all schemes where microwave irradiation close to the EPR line of fixed paramagnetic impurities is used to polarize the nuclei via the dipolar interaction between the electron spin and the magnetic moments of the surrounding nuclei. No attempt is thus made to distinguish between the different mechanisms included in this definition, like resolved solid effect, thermal mixing or differential solid effect. A review of these mechanisms can be found in ref. [3].

Polarization methods other than the solid effect have only been anecdotal up to day. As an example, the population transfer between the two hyperfine lines of Tm^{2+} , present as the polarizing impurity for ^{19}F in CaF_2 , leads easily to complete polarization of the ^{169}Tm nuclei [5]. The only method besides the solid effect which is promising for the future is optical

pumping. In ^3He gas, this method has already achieved 70% and this figure is only limited by the available laser power [6].

Column seven lists the aim of the study, i.e. the reason for which the nuclei have been polarized. An empty space means the polarization has been a useless or even undesirable side effect. HE stands for experiments in nuclear or particle physics. NMR indicates general magnetic resonance studies. NMO means nuclear magnetic ordering experiments and μ^* is written where the polarization was used to measure the spin-dependent scattering lengths neutron-nucleus. ^3He as a special case, is interesting for its low temperature properties as a solid, liquid or quantum gas.

3. Additional remarks

In all the studies, where the author was involved (μ^*), the maximum polarizations listed are not the result of long optimization of sample and/or paramagnetic impurity, since they were, with very few exceptions, high enough for our aim, i.e. the measurement of the pseudomagnetic moment. In fact, most of the time, they were obtained on the first sample studied. The typical sample size was 0.3cm^3 .

In opposition to the general habit, but in accordance to an often expressed and rarely fulfilled wish, we will give a small list of substances, in which we tried to polarize nuclei without success.

These indications may save some time in future attempts to polarize. No measurable enhancement was found at 2.5 Tesla and dilution temperatures in

- $\text{Pb}_3(\text{PO}_4)_2$, after γ -irradiation ($\sim 20\text{Mrad}$ ^{60}Co), although the same irradiation produces a few % of polarization of ^{31}P in $\text{Ca}_3(\text{PO}_4)_2$.

- KCl , with F centers produced by additive colouring. γ -irradiation works, however, probably due to other defects which help relax the F-centers.

- KI , after γ -irradiation of $\sim 20\text{Mrad}$

- CH_4 after γ -irradiation and full conversion to ground A state to yield long proton relaxation times.

As a final remark, we would like to mention one of the main problems involved in studies with polarized nuclei: the

measurement of the nuclear polarization. The standard method consists in comparing the NMR absorption signal of the polarized nuclei with a signal of the same nuclei at known polarization (thermal equilibrium or TE signal). The TE signal can, however, be too weak if one or more of the following conditions are fulfilled :

low abundance

small magnetic moment

$I > 1/2$ in non cubic substances, particularly if the sample is not a single crystal

very long T_1

A modified version of the standard method is often possible, if the sample contains any kind of magnetic moments (nuclear or even electronic) with a gyromagnetic ratio γ_2 , a known concentration and a visible TE signal. This TE signal serves then simply to calibrate the NMR apparatus and a signal of the polarized nuclei of interest (γ_1), taken with the same apparatus at the same frequency is sufficient to calculate their polarization. If $\gamma_2 < \gamma_1$, the measuring frequency does not correspond to the polarizing field (generally chosen as the maximum field of the magnet). Some sort of frozen target technique must then be used for the time of the calibration measurement [7].

At high polarizations, the NMR line shape can be a sensitive measure of the nuclear polarization. This method can be absolute if it is possible to calculate the line shape for a given sample as a function of polarization, a problem which is by no means evident [7,8]. Inhomogeneities of the polarization or the magnetic field, crystal strains and nonequilibrium populations amongst the different quadrupole levels and misalignment of single crystals or imperfect powder samples are a few of the possible pitfalls in comparing the experimental shape to the theoretical calculation.

If NMR methods are inapplicable, one has to look for a known property of the polarized nuclei, eg. $p\uparrow$ scattering, thermal neutron scattering and absorption, or resort to macroscopic magnetization measurements. SQUID magnetometers may be an answer to the problem in cases where a sizeable magnetization exists but where the NMR lines are too broad to be detectable.

TABLE

	P_{\max} %	H Tesla	T K	substance	method	aim	ref.
^3He	70			gas	optic. pump.	quant. gas	[6]
^6Li	70	6.5	dil	$^6\text{LiD: irr. e}^-$	se	HE	[9]
^7Li	83	6.5	dil	$^7\text{LiH: irr. e}^-$	se	NMO	[10]
^{11}B	57	2.5	^3He	EA, BA	se		[11]
^{13}C	53	2.5	dil	propanediol Cr^{V}	se		[7]
^{14}N	12	2.5	dil	$\text{NH}_3: \text{irr. e}^-$	se		[12]
^{15}N	12	2.5	dil	$\text{NH}_3: \text{irr. e}^-$	se		[12]
^{17}O	10	2.5	dil	$\text{Ca}^{17}\text{O: irr. n}$	se	μ^*	[13]
^{19}F	>90	2.7	dil	$\text{CaF}_2: \text{Tm}^{2+}$	se	NMO	[14]
		5.5	0.5	LiF: irr. n	se	NMO	[15]
^{25}Mg	3.5	1.2	1.6	$\text{Mg}_2\text{SiO}_4: \text{Cr}^{3+}$	se	NMR	[16]
^{27}Al	17	1.1	1.5	$\text{Al}_2\text{O}_3: \text{Cr}^{3+}$	se	NMR	[17]
^{29}Si	15	2.5	dil	a-Si	se	μ^*	[18]
^{31}P	20	3.3	dil	$\text{TmPO}_4: \text{Yb}^{3+}$	se	NMO	[19]
^{35}Cl	15	2.5	dil	$\text{KCl: irr. } \gamma$	se	μ^*	[20]
^{37}Cl	15	2.5	"	" "	se	μ^*	[20]
^{39}K	7	2.5	"	" "	se	μ^*	[20]
^{43}Ca	80	2.7	dil	$\text{CaF}_2: \text{Tm}^{2+}$	therm. mix.	NMO	[21]
^{79}Br	2	2.5	dil	$\text{KBr: irr. } \gamma$	se	μ^*	[20]
^{81}Br	2	2.5	"	" "	se	μ^*	[20]
^{139}La	50	1.8	1.2	LMN: Nd^{3+}	se	NMR	[22]
^{169}Tm	100	2.7	dil	$\text{CaF}_2: \text{Tm}^{2+}$	pop. transf.	NMR	[5]
	60	3.3	dil	$\text{TmPO}_4: \text{Yb}^{3+}$	se	NMO	[19]

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