The new substances for dynamic polarization of 3He : the EPR, NMR and magnetic susceptibility measurements

氏　　名	MAMIN GEORGY
学位の種類	博士（学術）
学位記番号	博甲第679号
学位授与の日付	平成16年9月30日
学位授与の要件	課程博士（学位規則第4条第1項）
学位授与の題目	The new substances for dynamic polarization of ^{3}He.-The EPR, NMR and magnetic susceptibility measurements.- (^{3}He のダイナミク分極のための新しい物質。EPR, NMR および磁気帯磁率の測定。)
論文審査委員(主査)	鈴木　治彦（自然科学研究科・教授）
論文審査委員(副査)	樋渡　保秋（自然科学研究科・教授），藤下　豪志（自然科学研究科・教授），松本　宏一（自然科学研究科・助教授），阿部　　聡（自然科学研究科・講師）

学位論文要旨

The usage of liquid oxygen-nitrogen solution and carbonizate powders for nuclear dynamic polarization of noble gas has been studied.

The electron paramagnetic resonance (EPR) spectra and magnetic susceptibility have been measured at temperatures 45-90 K temperature and at all possible O_2 concentration in liquid oxygen-nitrogen solution. The suggestion about O_2-O_2-O_2 clusters appearing allows to explain the observed broad EPR line and high magnetic susceptibility. The very broad EPR lines make impossible the usage of dynamic polarization.

The EPR spectra, nuclear spin lattice relaxation (NSLR) and magnetic susceptibility have been measured in carbonizate powders at temperatures 1.6-280 K. The ^{3}He nuclear magnetic moments are found to interact with surface paramagnetic centers. The pyrolysis doesn't remove the protons possessing fastest NSLR which represent the channel for polarization leakage. Frequency dependences of ^{3}He and ^{1}H NSLR time show the magnetic field suppression of exchange process in paramagnetic center (PC) clusters.

The carbonizate powder with 150-250 μm particle size is appeared to be the best for dynamics polarization. The applied magnetic field must be below 0.5 Tesla to avoid the suppression of exchange interaction between paramagnetic centers.

The dynamic polarization of nuclear spin represents an efficient method for production of hyperpolarized gases. The method is based on polarization transfer from an electron subsystem to the magnetic moment of ^{3}He gas nuclei.

The first studied electron subsystem is liquid O_2-N_2 solution. The fine noble gas bubbles passes throw liquid and the oxygen magnetic moment interacts with ^{3}He spins on bubble boundaries. The special type of carbonizate powder is suggested as the second system. All paramagnetic centers (PC) are located on surface [1] near absorbed ^{3}He atoms, and the dynamic polarization of water protons had been observed [2].

The main object of present work is systematical study of magnetic properties of these two systems.

The electron paramagnetic resonance (EPR) spectra and magnetic susceptibility have been measured at temperatures 45-90K and all possible O_2 concentration in liquid oxygen-nitrogen solution [3]. At low concentration the EPR linewidth is anomalous broadened up to 6000 Oe, and effecitve magnetic moment of one oxygen molecule (M) growths up to 2 μ_B.

The quantum chemical calculations (Aminova R.M.) show the possibility of O_2-O_2-O_2 clusters appearance [4]. The effective spin of clusters increases up to 3/2 and consequently M is 1.66-2 μ_B. The intraclusters interaction split energy levels by $D\approx$27 GHz, and EPR line is highly broadened.

The phase diagram can be subdivided on two parts. The first part is 0-20 mol. % concentration area where clusters don't interact with each other (probability <1%). Then the intercluster averaging is negligible and EPR linewidth and magnetic susceptibility have their maximal values without temperature dependence. In 20-80% area there is short distance between clusters. The relative motion of cluster probably averages EPR spectrum. The transformation of adjacent clusters average magnetic moment. In contrast to motion averaging this process doesn't depend on temperature.

It was established that liquid oxygen-nitrogen solution cannot be used for dynamic polarization because of very wide EPR spectra.

Our measurements show that the paramagnetic centers (PC) in carbonizate are highly concentrated, possess an narrow spectrum and strong interaction with absorbed nuclear spin . The EPR spectrum can be saturated, so the dynamics polarization on ^{3}He nuclear magnetic moment can occur. It was appeared that the 150-250 μm powder are the most suitable for dynamic polarization method. However there are some restrictions for succesfull polarization. The main trouble is polarisation leakage throw protons just near PC with short nuclear spin lattice relaxation (NSLR) time (~0.02 sec. at 4.2 K). However these protons can be almost

removed after cleaning off by 900°C water steam. The ^{13}C nuclei show the slowest relaxation and cannot be considered as the sources for polarisation leakage.

At low temperature the ^{3}He atoms are absorbed by carbonizate. The NSSR time ^{3}He and EPR linewidth of paramagnetic centers show Curie temperature dependence, that corespond to adsorbed solid helium. The Hanh measurement [5] show that among adsorbed atoms there are located and high mobile helium atoms with self-diffusion coefficient ~10 cm^2sec^{-1} (1.8K).

The frequency dependence of NSLR time for ^{3}He and ^{1}H nuclei gives the evidence for two processes of relaxation. The first process coresponds to relaxation via isolated paramagnetic centers. At 50-70 K the corresponding NSLR time has minimum [6] like the minimum in EPR line width oxygen atmoshere [7]. The helium at this temperature is quickly disabsorbed, that leads to the NSLR time increasing in 10 times. Possibly the some transformation on surface occurred.

The second SLR process is temperature independent exponential decay. The temperature independence indicate tunneling character of exchange into PC clusters. Since exchange can partially be broken by rare gase [7], the magnetic field also can suppress it. At assumption about weak overlapping of outer electronic shells the corresponding NSLR rate should be exponential dependent on the apllied magnetic field or resonance frequency.

Such the dynamics polarization in ^{3}He-carbonizate systems can occur after cleaning off the fast relaxing protons. The applied magnetic field must be below 0.5 Tesla to avoid the suppression of exchange interaction between paramagnetic centers.

1 R.B. Clarkson, W. Wang, R.D. Brown, et. al. *Fuel*, **69**, 1405 (1990)

2 B.M. Odincov, R.F. Belford, P.J. Ceroke *Surface Science* **393**, 162 (1997).

3 A.N. Yudin, R.M. Aminova, V.N. Efimov, G.V. Mamin, D.A. Tayurskii, M.S. Tagirov *"Structure and dynamics of molecular system"*, Yalchik, **3**, 162 (30.06.2003-05.06.2003)

4 M.S. Tagirov, R.M. Aminova, G. Frossati, V.N. Efimov, G.V. Mamin, et. all. *Physica B.*, **329**, 433 (2001).

5 A.N. Yudin, G.V. Mamin, V.V. Naletov, M.S. Tagirov *"Structure and dynamics of molecular system"*, Yalchik, **3**, 17 (30.06.2003-05.06.2003)

6 G.V. Mamin, H. Suzuki, M.S. Tagirov, D.A. Tayurskii, A.N. Yudin *JETF letters*, **79**, 778 (2004).

7 G. V. Mamin, H. Suzuki, V.N. Efimov, M. S. Tagirov, and A. N. Yudin. *Physica B.* **329-333P2**, 1237 (2003).

学位論文審査結果の要旨

8月3日に学位論文審査会を開催した。

Mamin Georgy 氏の論文は医療診断の断層写真用のスピン分極 ^3He を如何に生成するかの研究である。その方法として液体 O_2-N_2 混合液を用いる方法である。即ち O_2 の磁性を用いて ^3He をダイナミック分極させようと言うものである。しかしその EPR の共鳴線巾が広いので実用には難しい。彼の仕事は、EPR、NMR、SQUID を用いた磁化測定から液体 O_2 がクラスターを生成するためにどんなに N_2 で希釈しても本質的に共鳴線巾が狭くならないと言うことを明らかにした。

もう一つのスピン分極 ^3He を生成する方法としてチャコールに ^3He ガスを吸収させ、チャコール表面のボンドが切れた C が磁性不純物として働きこの磁性不純物を用いてダイナミック分極を行うというものである。しかしこの時、予想より非常に少ない分極しか得られていない。その原因を探るために、同じく EPR, NMR, 磁化測定によって研究した。その結果吸着している水素が ^3He のスピン分極を緩和させて減衰させてしまうと言うことが分かった。それで吸着水素を取り除くために高温の水蒸気で洗うことにより効果が有ることが分かった。

以上のように新しい知見を含む興味有る研究成果であり審査員全員一致してこの論文が博士論文に値するものと判定し合格と認定した。