# 1997~2006

Russian Ministry of Education and Science Russian Academy of Science Russian Foundation for Basic Research Tatarstan Republic Academy of Science Kazan State University Zavoiskii Physical-Technical Institute Research Educational Center of Kazan State University Bruker Ltd (Moscow)

ACTUAL PROBLEMS OF MAGNETIC RESONANCE AND ITS APPLICATION

X International Youth Scientific School



"NEW ASPECTS OF MAGNETIC RESONANCE APPLICATION"



Kazan 31 October - 3 November 2006

### NEW ASPECTS OF MAGNETIC RESONANCE APPLICATION.

Proceedings of the X International Youth Scientific School "Actual problems of magnetic resonance and its application", 31 October – 3 November 2006, Kazan. Edited by professor M.S. Tagirov (Kazan State University) and professor V.A. Zhikharev (Kazan State Technological University).

The reports of young scientists submitted on X International Youth Scientific School "Actual problems of magnetic resonance and its application" carry out by Kazan State University and Zavoiskii Physical-Technical Institute in frameworks of Research Educational Center KSU (REC-007) are included in the present collection.

Compiler: I.G. Motygullin

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#### НОВЫЕ АСПЕКТЫ ПРИМЕНЕНИЯ МАГНИТНОГО РЕЗОНАНСА.

Труды X Международной молодежной научной школы «Актуальные проблемы магнитного резонанса и его приложений» 31 октября – 3 ноября 2006 г., Казань. Под ред. проф. Тагирова М.С. (Казанский государственный университет) и проф. Жихарева В.А. (Казанский государственный технологический университет)

В настоящий сборник включены доклады молодых ученых, представленные на X Международную молодежную научную школу «Актуальные проблемы магнитного резонанса и его приложений», проводимую Казанским государственным университетом и Казанским физико-техническим институтом им. Е.К. Завойского в рамках Научно-образовательного Центра КГУ REC-007

Составитель: Мотыгуллин И.Г.

ISBN 5-94605-015-X

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#### Vadim Aleksandrovich Atsarkin

(to  $70^{\text{th}}$  anniversary)



June, 13. 2006 is the 70<sup>th</sup> anniversary of Vadim Aleksandrovich Azarkin, Doctor of Science (in physics and mathematics), Professor, talented scientist whose name is world-wide known in Radiospectroscopy. His contribution to the development of the spin thermodynamics in solid electron and nuclear paramagnets turned to be fundamental.

Vadim A. Atsarkin graduated with excellent diploma from the Semiconductor Physics Department of the Moscow State University; however, his scientific research activities started in Quantum Electronics Laboratory headed by Doctor of Science, Prof. M.E. Zhabotinskii in the Radio Engineering and Electronics Institute of the Academy of Sciences of USSR. Initially, he searched and investigated materials for masers with improved parameters, i.e., recently discovered and put into foundation of Quantum Radio Engineering and Electronics supersensitive quantum amplifiers. The investigation method was Electronic Paramagnetic Resonance (EPR) discovered by Ye.K. Zavoiskii in 1944 in Kazan. This method made it possible to investigate efficiently various phenomena related to resonance absorption of radio waves by electron and nuclear paramagnets, which became a basis of masers' construction. In a domain yet unknown for him, V.A. Atsarkin quickly achieved a significant progress, successfully defended his candidate of science thesis, and started research in the spin thermodynamics in solid electron and nuclear paramagnets, that came into being during 60s and 70s of 20<sup>th</sup> Century. By that time, B.N. Provotorov already created a two-temperature theory of magnetic resonance which introduced into Physics the concept of a dipole order characterizing mutual orientations of spins in each other local fields, its experimental confirmation was obtained in NMR. However, some specialists were skeptical with respect to applicability in EPR of this two-temperature theory due to a chaotic distribution of paramagnetic impurities in magnetically diluted paramagnetic crystals and an inhomogeneous broadening of EPR lines. M.I. Rodak, a colleague of V.A. Atsarkin by the laboratory, proved that the two-temperature theory leads to a new effect, i.e., an induced irradiation under saturation on the wing of resonance line of spin system. A series of original experiments carried out by V.A. Atsarkin confirmed this prediction and turned in a "touchstone" for verifying the applicability of the two-temperature theory to EPR.

In further investigations V.A. Atsarkin along with colleagues discovered a direct heat contact between the electron dipole-dipole subsystem and the nuclear Zeeman subsystem, which generated the relaxation of nuclei via an electron dipole reservoir and now is serving as one of the basic mechanisms of Dynamic Nuclear Polarization (DNP). The cross-relaxation method of DNP, which is realized under cross-relaxation between EPR lines and does not require a saturation of forbidden electron-nuclear transitions, was also discovered at the same time. These outstanding results were put into foundation of his doctor of science thesis defended in 1971; later, in 1988, these results were recognized as a discovery. V.A. Atsarkin generalized an extensive cycle of works dedicated to DNP problems actual in those years in

his monograph "Dynamic Nuclear Polarization in Solid Dielectrics" (Moscow, "Nauka" Publishers, 1980) which up to now serves as one of fundamental handbooks in this field.

In 1973, V.A. Atsarkin predicted and proved together with O.A. Ryabushkin the effect of enhanced longitudinal susceptibility. The longitudinal susceptibility was measured first by Gorter as far back as in 30s; however, this important technique had a limited application in view of its low sensitivity. V.A. Atsarkin suggested that investigations should be carried out in the conditions of ERP line's saturation providing strong cooling of the electron dipole reservoir; this enhances the sensitivity by several orders ("Atsarkin effect"). The posterior development of this method by V.A. Atsarkin and his colleagues led to the direct observation of Nuclear Magnetic Resonance (NMR) in rotating coordinate systems. Under these conditions, a strong narrowing of NMR line is possible with which ordinary two-particle dipole-dipole interactions of nuclei disappear and the main role passes to significantly more weak multispin interactions, while the relaxation measurements can be carried out in small effective fields. This led to the development of a new method for detecting slow (at velocities  $10^2 - 10^4 \text{ c}^{-1}$ ) molecular movements (V.A. Atsarkin, T.N. Khazanovich, A.Ye. Mefed).

The new methods developed for ERP spectroscopy were successfully applied by V.A. Atsarkin and his colleagues to solving important problems of Solid State Physics, e.g., the question of the shape of hole burned out in dipole EPR spectrum, the investigation of regularities of spectral transition in non-ordered paramagnets, direct measurement of the time of spin-lattice relaxation of paramagnetic centers in High-Temperature Superconductors, the analysis of metal-dielectric translation in fullerids, the dipole broadening and exchange narrowing of EPR lines of paramagnetic centers on the solid body surface and concentration dependences of EPR spectra in manganites.

The outstanding scientific results, encyclopedic knowledge, professionalism, wide scope of interests, benevolence and readiness to discuss scientific problems with any person asking for help – all these virtues conciliated a universal respect to V.A. Atsarkin. He is member of Program Committees of many conferences and scientific schools on Magnetic Resonance and he is always in the focus of discussions on new scientific problems. On conferences, this is a rule to observe "live queues" of theorists and experimentalists desiring to discuss with V.A. Atsarkin a wide set of questions from various fields of Magnetic Resonance's physics' problems. Being a professional experimentalist, V.A. Atsarkin at the same time deeply knows the theory of phenomena under investigation. An evidence to this virtue was provided by a theoretical article concerning quasi-equilibrium stabilization in spin system of solid paramagnet (1985), where he constructed a clear physical picture of the process and gave an adequate mathematical apparatus, and thus solved long disputes among some theorists. A monthly All-Russia seminar on Magnetic Resonance under his supervision, known also as "Atsarkin' Seminar", works already more than 25 years in the Radio Engineering and Electronics Institute of the RAS. The characteristic style of this seminar is a detailed discussion with a reporter of the theme of his/her report before its placement into agenda and always bright, benevolent concluding words with the deep analysis of the reported work. This seminar became a real scientific school for many future candidates and doctors of science.

The colleagues, disciples, and friends of Vadim A. Atsarkin use this way to congratulate him with this significant date and wish strong health and new creative successes in all fields.

V.V. Demidov, F.S. Dzheparov, E.B. Feldman, N.P. Fokina, B.I. Kochelayev, T.N. Khazanovich, Ye.K. Khenner, A.A. Lundin, A.Ye. Mefed, N.Ye. Noginova, M.I. Rodak, O.A. Ryabushkin, K.M. Salikhov, M.S. Tagirov, V.A. Zhikharev, V.Ye. Zobov.

## **PROGRAM**

## **31 October**

9:00-9:15	OPENING CEREMONY				
	YOUNG SCIENTISTS SCHOOL'2006 PLENARY SESSION				
9:15-9:30	R.B. Zaripov "ESEEM study of dipole-dipole interaction in nitroxide biradicals"				
9:30-9:45	L.V. Mingalieva "EPR investigation of spin architectures built on a basis of chromium dimmers"				
9:45-10:00	A.R. Mursalimov "Monte Carlo simulations of the EPR spectra of charge separated states in photosynthetic reaction centres"				
10:00-10:15	A.A. Sukhanov "The analysis of the polycrystalline EPR spectra of Cu-Gd dimmers"				
10:15-10:30	I.V. Yatzyk "Observation of a Griffiths Phase in Paramagnetic La <sub>1-x</sub> Ba <sub>x</sub> MnO <sub>3</sub> "				
10:30-10:45	A.A. Ivanov "Kinetics of methane hydrate formation by NMR"				
10:45-11:00	M.V. Sundukova "Inhibition of water transport across cell membranes by dimephosphon"				
11:00-11:30	COFFEE BREAK				
11:30-11:45	D.S. Irisov "Magnetic properties of dielectric Van Vleck paramagnet PrF <sub>3</sub> "				
11:45-12.00	V.V. Kuzmin "Enhanced <sup>169</sup> Tm NMR and magnetization measurements in study of anisotropic magnetic properties of crystal LiTmF <sub>4</sub> "				
12:00-12:15	I.E. Lyubin "Binding energy of a Cooper pairs with non-zero center of mass momentum in d-wave superconductors"				
12:15-12:30	A.A. Rodionov "The surface effects influence on magnetic resonance in carbonizate"				
12:30-12:45	I.V. Romanova "Magnetoelastic effects and magnetization in LiDyF <sub>4</sub> and LiHoF <sub>4</sub> single crystals"				
12:45-13:00	N.V. Shkalikov "Solid-like component in the spin-spin NMR-relaxation of heavy oils"				
13:00-14:00	LUNCH				
14:00-14:15	I.S. Abornev "The peculiarities of the of Ni nanoparticles formation in supramolecular system [LiAl <sub>2</sub> (OH) <sub>6</sub> ] <sub>2</sub> [Niedta]•4H <sub>2</sub> O studied by Ferromagnetic Resonance Method (FMR)"				
14:15-14:30	M.V. Burova "Electron-acceptor centers of alkali metal modified alumina studied by the anthraquinone as a probe molecule"				
14:30-14:45	D.V. Guseinov "Spin relaxation of electrons localized on shallow and deep donor centers in silicon with different isotopic composition"				
14:45-15:00	D.M. Druzhnov "Ferromagnetism in thin films of germanium and silicon supersaturated by manganese or iron impurities"				
15:00-15:15	K.A. Kozhanov "An EPR monitoring of isomerism and coordination sphere dynamics in five-coordinated pincer nickel complexes"				
15:15-15:30	E.I. Kuznetsova "Multiple quantum NMR dynamics in spin systems in dypolar ordered state"				
15:30:15:45	K.S. Okhotnikov "NMR study of quasi-1D magnetic chain in cuprates LiCu <sub>2</sub> O <sub>2</sub> and NaCu <sub>2</sub> O <sub>2</sub> "				

15:45-16:15	COFFEE BREAK					
16:15-16:30	A.N. Pyrkov "Entanglement in one-dimensional open spin chains s=1/2 with XY-Hamiltonian"					
16:30-16:45	L.L. Rapatskiy "CW EPR study of the molecular dynamics of nitronil nitroxide on LB films"					
16:45-17:00	A.V. Sinicin "EPR of transition metal ions in micro-plasma coatings on the aluminum alloy D16"					
17:00-17:15	M.N. Uvarov "Triplet state dynamics of fullerene C <sub>60</sub> studied by pulse EPR"					
17:15-17:30	I.V. Fokina "Structure of anthraquinone and fluorenone complexes on the surface of metal oxides (CaO, Al <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub> )"					
17:30-17:45	Д.О. Толмачев "Исследования спин-зависимых рекомбинационных процессов в системах с квантовыми точками методом оптической регистрации ЭПР по послесвечению"					
17:45-18:00	С.Р. Шакиров "Химическая поляризация ядер мицеллизованных радикальных пар в присутствии нитроксильных радикалов"					

## 1 November

10:00-10:10	OPENING OF THE SYMPOSIUM "MODERN PROBLEMS OF CHEMICAL PHYSICS"				
10:10-10:40	HW. Spiess "Magnetic resonance, a powerful tool for studying supramolecular systems"				
10:40-11:10	S.A. Dzuba "Supramolecular structure and dynamics of spin-labeled biomembrane-peptide systems"				
11:10-11:35	S.B. Orlinskiy "From monocrystal to nanocrystal ZnO by high-frequency EPR/ENDOR"				
11:35-12:00	COFFEE BREAK				
12:00-12:30	V.A. Atsarkin "Electron spin resonance and relaxation in nanoparticles: between para- and ferromagnetism"				
12:30-13:00	G. Buntkowsky "NMR Spectroscopy on the mesoscopic length scale"				
13:00-14:30	LUNCH				
14:30-15:00	M. Bowman "The semiquinone intermediate in ubiquinol oxidation by cytochrome bc1"				
·					
15:00-15-25	I.A. Garifullin "The superconductor/ferromagnet proximity effect and its				
15:00-15-25 15:25-15:50	I.A. Garifullin "The superconductor/ferromagnet proximity effect and its potential application in spintronics" E.G. Bagryanskaya "Phase transitions and exchange interaction in molecular magnetics studied by EPR"				
15:00-15-25 15:25-15:50 15:50-16:20	I.A. Garifullin "The superconductor/ferromagnet proximity effect and its potential application in spintronics" E.G. Bagryanskaya "Phase transitions and exchange interaction in molecular magnetics studied by EPR" COFFEE BREAK				
15:00-15-25 15:25-15:50 15:50-16:20 16:20-16:45	I.A. Garifullin "The superconductor/ferromagnet proximity effect and its potential application in spintronics" E.G. Bagryanskaya "Phase transitions and exchange interaction in molecular magnetics studied by EPR" <b>COFFEE BREAK</b> R.M. Rakhmatullin "Rare-earth clusters in SiO <sub>2</sub> and GeO <sub>2</sub> glasses. Study by the EPR spectroscopy"				
15:00-15-25 15:25-15:50 15:50-16:20 16:20-16:45 16:45-17:05	I.A. Garifullin "The superconductor/ferromagnet proximity effect and its potential application in spintronics" E.G. Bagryanskaya "Phase transitions and exchange interaction in molecular magnetics studied by EPR" <b>COFFEE BREAK</b> R.M. Rakhmatullin "Rare-earth clusters in SiO <sub>2</sub> and GeO <sub>2</sub> glasses. Study by the EPR spectroscopy" S. Marque "Persilylated phosphoranyl radicals: The first persistent phosphoranyl radicals. An EPR Study"				
15:00-15-25 15:25-15:50 15:50-16:20 16:20-16:45 16:45-17:05 17:05-17:25	I.A. Garifullin "The superconductor/ferromagnet proximity effect and its potential application in spintronics" E.G. Bagryanskaya "Phase transitions and exchange interaction in molecular magnetics studied by EPR" <b>COFFEE BREAK</b> R.M. Rakhmatullin "Rare-earth clusters in SiO <sub>2</sub> and GeO <sub>2</sub> glasses. Study by the EPR spectroscopy" S. Marque "Persilylated phosphoranyl radicals: The first persistent phosphoranyl radicals. An EPR Study" R.T. Galeev "EPR of clusters containing non-Kramers ions"				

## 2 November

9:00-9:30	D. Stehlik "Control of function in photosynthetic reaction centers by electron acceptor-protein interactions as studied by transient EPR spectroscopy"				
9:30-9:55	D.V. Stass "Effect of low magnetic fields and MARY spectroscopy"				
9:55-10:20	P.A. Purtov "Spin catalysis theory"				
10:20-10:50	COFFEE BREAK				
10:50-11:20	HM. Vieth "Dynamic polarization and relaxation in systems of coupled nuclear spins"				
11:20-11:45	K.M. Salikhov "Quantum teleportation across a biological membrane by means of correlated spin pair dynamics in photosynthetic reaction centers"				
11:45-12:10	A.G. Maryasov "Dipole-dipole interactions of high-spin paramagnetic centers in disordred systems"				
12:10-12:30	A.E. Mambetov "Calculations of rate constants of electron spin polarisation of triplet excitons in molecular crystals due to triplet-triplet annihilation"				
12:30-13:00	K. Mubius "Combining light, microwaves and magnetic fields to reveal electron-transfer characteristics in photosynthesis by high-field EPR"				
13:00-14:30	LUNCH				
	W. Lubitz "Spectroscopic investigations to elucidate the function of hydrogenase: basis for a biological hydrogen production"				
14:30-15:00	hydrogenase: basis for a biological hydrogen production"				
14:30-15:00 15:00-15:25	w. Edubiz       Spectroscopic investigations to endedate the function of hydrogenase: basis for a biological hydrogen production"         T.V. Leshina "Spin chemistry application to modelling of ligand – receptor interaction"				
14:30-15:00 15:00-15:25 15:25-15:50	<ul> <li>W. EdotZ Spectroscopic investigations to endedate the function of hydrogenase: basis for a biological hydrogen production"</li> <li>T.V. Leshina "Spin chemistry application to modelling of ligand – receptor interaction"</li> <li>A.I. Kruppa "Investigation of guest-host complexes of beta-cyclodextrin by spin chemistry"</li> </ul>				
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14:30-15:00 15:00-15:25 15:25-15:50 15:50-16:20 16:20-16:50	<ul> <li>W. EdotZ Spectroscopic investigations to endedate the function of hydrogenase: basis for a biological hydrogen production"</li> <li>T.V. Leshina "Spin chemistry application to modelling of ligand – receptor interaction"</li> <li>A.I. Kruppa "Investigation of guest-host complexes of beta-cyclodextrin by spin chemistry"</li> <li>COFEE BREAK</li> <li>A. van der Est "Electron spin polarization in coupled spin systems"</li> </ul>				
14:30-15:00 15:00-15:25 15:25-15:50 15:50-16:20 16:20-16:50 16:50-17:10	<ul> <li>W. EdotZ Spectroscopic investigations to endedate the function of hydrogenase: basis for a biological hydrogen production"</li> <li>T.V. Leshina "Spin chemistry application to modelling of ligand – receptor interaction"</li> <li>A.I. Kruppa "Investigation of guest-host complexes of beta-cyclodextrin by spin chemistry"</li> <li>COFEE BREAK</li> <li>A. van der Est "Electron spin polarization in coupled spin systems"</li> <li>V.R. Gorelik "CIDEP in micellised radical pairs in the presence of stable nitroxide radicals"</li> </ul>				
14:30-15:00 15:00-15:25 15:25-15:50 15:50-16:20 16:20-16:50 16:50-17:10 17:10-17:30	<ul> <li>W. EdotZ Spectroscopic investigations to endedate the function of hydrogenase: basis for a biological hydrogen production"</li> <li>T.V. Leshina "Spin chemistry application to modelling of ligand – receptor interaction"</li> <li>A.I. Kruppa "Investigation of guest-host complexes of beta-cyclodextrin by spin chemistry"</li> <li>COFEE BREAK</li> <li>A. van der Est "Electron spin polarization in coupled spin systems"</li> <li>V.R. Gorelik "CIDEP in micellised radical pairs in the presence of stable nitroxide radicals"</li> <li>S.R. Shakirov "CIDNP of micellised radical pairs and short-lived biradicals in presence of stable nitroxides"</li> </ul>				

## 3 November

9:00-9:25	U. Eichhoff "Recent life science applications of NMR and EPR"			
9:25-9:50	M.V. Eremin "On interplay between the magnetic susceptibilities of localized and itinerant electrons in HTSCs"			
9:50-10:15	V.F. Tarasov "Tunable high-frequency low-field EPR spectroscopy of EPR- silent ions"			

10:15-10:35	M. P. Tseitlin "Comparison of maximum entropy methods to reconstruct EPR images from rapid scan spectra"				
10:35-10:55	R.G. Gatiiatov "Atomic and magnetic force microscopy of nanostructures obtained by laser and ion etching"				
10:55-11:25	COFEE BREAK				
11:25-11:50	N. Fatkullin "Intermolecular contribution into spin-lattice relaxation rate and relative intermolecular displacents in polymer systems"				
11:50-12:15	B.Z. Malkin "Experimental and theoretical studies of <sup>19</sup> F nuclear relaxation in LiYF <sub>4</sub> :Ho <sup>3+</sup> single crystals"				
12:15-12:40	S.A. Moiseev "Photon echo quantum memory for arbitrary light pulses and quantum manipulations of time-qubit states"				
12:40-13:00	S. Lijewski "Electron Spin Relaxation in Fluorite Type Crystals"				
13:00-13:20	Yu.E. Kandrashkin "Spin `Algebra` package for general analysis of magnetic resonance problems in Mathematica"				
13:20-13:40	L.I. Savostina "Quantum-mechanical calculations of dynamic processes in the bimolecular reactions including phosphorus atom"				
13:40	CLOSING OF THE SYMPOSIUM AND YOUNG SCIENTISTS SCHOOL'2006				

#### **ESEEM** study of dipole-dipole interaction in nitroxide biradicals

R.B. Zaripov<sup>1</sup>, K.M. Salikhov<sup>1</sup>, L.V. Kulik<sup>2</sup>, S.A. Dzuba<sup>2</sup>

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The spin labels are widely utilized to study the structure and dynamic features of polymers and biological samples. EPR spectroscopy has good potentials in these studies. However, CW (continues wave) spectroscopy does not allow to get information about weak spin-spin interactions like the weak dipole-dipole interaction between two paramagnetic species separated more than about 1 nm distances. At larger distances the contribution of the dipoledipole interaction is masked by inhomogeneous broadening of the EPR lines and by the contribution of the hyperfine interaction with nuclei. This masking effect can be avoided using pulse EPR methods [1]. In pulse EPR experiments the dipole-dipole interaction can produce the echo signal modulation. Note there is another important source for the echo modulation, namely, hyperfine interaction causes a periodic oscillation in the echo height superimposed on the normal echo decay. Fortunately, by varying the protocol of the pulse experiment we can suppress the contribution of the hyperfine interaction to the ESEEM and highlight the contribution of the weak dipole-dipole interaction between paramagnetic centers.

In this report we have compared the potentials of the two-pulse, three-pulse and fourpulse ESEEM methods for studying the weak dipole-dipole interaction between two unpaired electrons of imidazoline biradical (fig. 1)



Fig.1. Chemical structure of imidazoline biradical. (Adapted from [2])

The investigations were carried out on the EPR spectrometer ELEXSYS E580 at the liquid nitrogen temperature.

In the two-pulse ESEEM we used primary echo sequence  $\pi/2-\tau$ -  $\pi$ - $\tau$ -echo, where  $\tau$  is variable (fig.2).

The three-pulse stimulated echo sequence  $\pi/2-\tau - \pi/2-\tau$ -echo is used with fixed T and variable  $\tau$  (Fig. 3).

And the four-pulse sequence which we have used in our experiment consists of  $\pi/2-\tau_1-\pi/2-\tau_2-\pi-\tau_1$ -echo, where T is fixed and  $\tau_1$ ,  $\tau_2$  are variable (Fig. 4). This four-pulse



Fig. 2. Schematic representation of the two-pulse ESEEM



Fig. 3. Schematic representation of the three-pulse ESEEM experiment.



Fig.4. Schematic representation of the four-pulse ESEEM experiment.

sequence with time spacing  $\tau_2 > \tau_1$  and  $T >> T_m$  creates refocused stimulated echo after  $\pi$  pulse [3].

The results obtained demonstrate that the four-pulse ESEEM has definite advantage compared to two-pulse and three-pulse ESEEM for extracting relatively weak dipole-dipole interaction between two paramagnetic centers. The distance between spins in this sample is  $\sim 2$  nm.

This work is supported by the Russian Foundation of Basic Research grants № 06-03 - 32175 and Scientific School 6213.2006.2.

- [1] K. M. Salikhov, A. G. Semenov, Yu. D. Tsvetkov. Electron spin echo and its application. Nauka, M. 1976.
- [2] L. V. Kulik, S. A. Dzuba, I. A. Grigoryev, Yu. D. Tsvetkov, Chem. Phys. Lett. 343 (2001) 315-324.
- [3] A. Schweiger, G. Jeschke, Principles of pulse electron paramagnetic resonance, Oxford University Press, Oxford (2001).

#### EPR investigation of spin architectures built on a basis of chromium dimers

R. Galeev<sup>1</sup>, L. Mingalieva<sup>1</sup>, A. Sukhanov<sup>1</sup>, V. Voronkova<sup>1</sup>, Gh. Novitchi<sup>2</sup>, V. Ciornea<sup>3</sup>

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Design of new spin architectures with pre-established properties is currently of interest in molecular magnetism and quantum informatics. The dimer fragment can be successfully used as building blocks in constructing multinuclear clusters and extended structures with useful properties. We report EPR study of new heteronuclear systems built up of Cr-Cr dimer fragments:  $[Me_1(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2]\cdot7H_2O$  (where  $Me_1 = Zn(II)$ , Ni(II), Co(II)),  $[Me_2(H_2O)_6][Cr_2(OH)_2(nta)_2]\cdot4H_2O$  (where  $Me_2 = Mg(II)$ , Ca(II)),  $[Mn(H_2O)_2(bpy)Cr_2(OH)_2(nta)_2]$  (bpy) 5H<sub>2</sub>O. These compounds contain the chromium dimer fragment and mononuclear complexes with transition metal ions. EPR investigations were carried out on polycrystalline samples in X-and Q-bands (Figs.1 and 2).

 $[Me_1(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2]\cdot 7H_2O$  and  $[Me_2(H_2O)_6][Cr_2(OH)_2(nta)_2]\cdot 4H_2O$  compounds with diamagnetic metal ions in mononuclear complexes are chosen for detailed research of the exchange interaction in dimer fragments. Isotropic exchange interaction JS<sub>1</sub>S<sub>2</sub> between ions chromium results in the formation of spin states with a total spin S=0, 1, 2, 3. Anisotropic spin-spin interaction causes splitting of spin multiplets into sublevels and the fine structure of EPR spectra due to transitions between sublevels in multiplets.



 $7H_2O$  in X-band, where:  $Me_1=Zn - (a)$  and  $Me_1=Co - (b)$ .

The spectra of chromium dimers (Fig.1a) are a superposition of spectra from spin multiplets with S=1, S=2, S=3 and the temperature dependence of EPR spectra is determined by the change of the ratio of intensities of spectra from different multiplets. The detailed

analysis of the temperature dependence of EPR spectra has allowed us to attribute spectral lines to transitions in definite multiplets.

The analysis of the experimental temperature dependence of the EPR spectrum of  $[Me_1(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2]$  7H<sub>2</sub>O (where Me<sub>1</sub> = Zn(II)) (Fig.1a) has shown that the interaction between chromium ions in dimer has an antiferromagnetic character and J<sub>Cr1 Cr2</sub> = 25 cm<sup>-1</sup>. For  $[Me_2(H_2O)_6][Cr_2(OH)_2(nta)_2]$ ·4H<sub>2</sub>O compounds the antiferromagnetic exchange interaction between chromium ions also is realized.



It was established that the exchange interaction between chromium dimers and mononuclear complexes is realized only for  $[Mn(H_2O)_2(bpy)Cr_2(OH)_2(nta)_2]$  (bpy) 5H<sub>2</sub>O compound. Analysis of temperature dependences of magnetic susceptibility indicates the ferromagnetic interaction between the manganese and chromium ions.

This work is supported by the Russian Foundation for Basic Research grants №04-02-17163, № 06-03 -32175 and Scientific School 6213.2006.2.

## Monte Carlo simulations of the EPR spectra of charge separated states in photosynthetic reaction centers

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Photosynthetic reaction centers represent the large theoretical and practical interest. This interest is caused by desire to create artificial systems which will effectively transform light energy into chemical energy. Quantum yield of an electron in such systems is close to 100 %. Such high performance of transformation of light energy is achieved because of the specific structure of single molecules and protein complexes involved in photoreaction. The strictly ordered rigid structure of the reaction center as a whole is also very important for high efficiency. To obtain information about the structure of the photosynthetic reaction center and the intramolecular processes it is necessary to interpret correctly experimental EPR spectra of the electron-hole pairs.

The EPR spectrum of the electron-hole pair reflects non-equilibrium processes that take place in photoreaction center.

There are many factors which influence on the shape of the EPR spectrum of the electron-hole pairs. The hyperfine interaction of the electron spin with the magnetic nuclei is one of the important factors. In experimental EPR spectra of the electron - hole pairs the inhomogeneous broadening of resonant spectral lines is observed as result of unresolved hyperfine structure.

Previously the influence of the magnetic nuclei was introduced in spectra simulations by convolution procedure [1]. It was done as follows.

Let's consider the photosynthesis reaction center to be in the strong magnetic field. Then the local magnetic fields created by nuclei are much less than an external magnetic field. For each orientation of the reaction center relative to an external magnetic field the effective gfactor and the corresponding Zeeman frequency are calculated. With the spin-spin interaction taking into account the spin polarization and the shape of EPR spectrum of the sub-ensemble of the reaction centers are calculated for a given orientation. Thus, we obtain the EPR spectrum in a form of  $J_0(B_0, \Omega)$ , where  $B_0$  is the induction of an external magnetic field, and  $\Omega$  is parameter, which defines a sub-ensemble of the reaction centers.

At a convolution procedure the unresolved hyperfine structure of lines EPR is supposed to have Gaussian distribution of the local magnetic fields:

$$J(B_0,\Omega) = \frac{1}{\sqrt{2\pi\sigma^2}} \int J(B_0',\Omega) e^{-\frac{(B_0-B_0')^2}{2\sigma^2}} dB_0'.$$

The convolution procedure for the equilibrium systems might be good approach. But the convolution procedure for charge separated states in reaction center can lead to serious mistakes. Let's see the reasons for these mistakes to occur. Suppose that resonance frequencies of donor  $\omega(1)$  and acceptor  $\omega(2)$  are close to each other and their difference is positive  $\omega(1)$ - $\omega(2)>0$ . Let's assume that due to chemical polarization of electron - hole pair

the EPR spectrum of type A/E/A/E is formed. Local magnetic fields from nuclei will shift of resonance frequencies of donor  $\omega$ `(1)= $\omega$ (1)+ $\delta$ (1) and acceptor  $\omega$ `(2)= $\omega$ (2)+ $\delta$ (2). In this case the difference of resonance frequencies  $\omega$ `(1)- $\omega$ `(2) can become negative that will lead to formation of EPR spectrum of type E/A/E/A. However, when convolution procedure is applying, this replacement of EPR spectrum of type A/E/A/E by EPR spectrum of type E/A/E/A is not considered.

In this work hyperfine interaction with magnetic nuclei was considered at a stage of formation of chemical polarization of electron-hole pair. The distribution of resonance frequencies of the donor and an acceptor due to hyperfine interaction with nuclei was simulated by means of a Monte Carlo method for each orientation of the reaction center relative to external magnetic field. We suppose the Gaussian distribution. The kinetic equation for spin density matrix of electron-hole pairs was solved for each random value of resonance frequency of the donor and the acceptor. By averaging of all orientations of the reaction, EPR spectrum of the charge separated states in the photosynthetic reaction center was calculated.

On a personal computer, using the convolution procedure, EPR spectrum of the charge separated states is calculated about ten hours. The suggested sequential account of interaction with magnetic nuclei demands on the orders of magnitude large time at calculation of EPR spectra of the charge separated states, than at a convolution procedure. As for obtaining of comprehensible accuracy of each point of calculated EPR spectrum it is necessary to consider not less than 1000 orientations of the reaction centres relative to an external magnetic field and more than 100 000 random values of resonance frequencies of the donor and the acceptor.



**Fig.1**. Simulated EPR spectra of RP state, donor P<sup>+</sup> and acceptor Q<sup>-</sup> with taking into account an unresolved hyperfine structure by convolution procedure (solid line) and Monte-Carlo method (dotted line).

This problem can be solved if one uses multiprocessing computers and parallel algorithms and programs which efficiently work on these devices. It increases productivity of calculations and has made possible to calculate spectra by the suggested method.

#### Results

Figure 1 shows simulated EPR spectra of RP state, donor  $P^+$  and acceptor Q<sup>-</sup> with taking into account an unresolved hyperfine structure by convolution procedure and Monte-Carlo method. The simulation parameters, collected in table 1, have been obtained from several independent sources [1-3].

<b>Table 1</b> . Simulation parameters.g-tensors						
P <sup>+</sup> Q <sup>-</sup>	g <sub>x</sub> 2.00308 2.00622	g <sub>y</sub> 2.00264 2.00507	g <sub>z</sub> 2.00226 2.00218			
A-tensors (in MHz)		•				
Q	A <sub>x</sub> 9.0	A <sub>y</sub> 12.8	A <sub>z</sub> 9.0			
Spin-spin-coupling						
P <sup>+</sup> Q <sup>-</sup>	D -170 r	nT 1.0 m <sup>°</sup>	Т			
Geometrical parameters <sup>1</sup>						
g( <b>P</b> <sup>+</sup> )	$\alpha_p$ 171°	$\beta_{p}$ 107°	γ <sub>p</sub> 215°			
A(CH <sub>3</sub> )	$\alpha_A$ -25°	${\beta_A \atop 0^o}$	$ \overset{\gamma_A}{0^o} $			
$\begin{array}{ccc} \theta_{D} & \phi_{D} \\ 101^{\circ} & 177^{\circ} \end{array}$ <sup>1</sup> The Euler angles describe the relative orientation of g(P <sup>+</sup> ) to g(Q <sup>-</sup> ). The polar and azimuthal angles, $\theta$ and $\phi$ , respectively, describe the orientation of Z <sub>D</sub> relative to g(Q <sup>-</sup> ): Z <sub>D</sub> =(-sin $\theta \cos \phi$ , sin $\theta \sin \phi$ , cos $\theta$ ). Ref. [1-3].						

#### Conclusion

Monte Carlo method is to be used when analyzing the effect of the unresolved hyperfine structure on the electron spin polarization pattern of the charge separated states in photosynthetic reaction centres.

This work was supported by RFBR grant 06-03-32175, NIOKR RT 06-6.3-349.

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#### The analysis of the polycrystalline EPR spectra of Cu-Gd dimers

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Magnetism of the molecular complexes including ions of iron group (3d ions) and rare-earth ions (f ions), is an object of research of last years since the mixed compounds with rare-earth ions can be perspective for creation of new functional materials with operated properties for molecular electronics and information systems. The most part of researches is fulfilled for compounds in which interaction between copper and gadolinium ions is realized but EPR investigations of clusters constructed of these ions are absent. We present the first example of experimental EPR study of Cu-Gd dimer fragments and analysis of the polycrystalline EPR spectra of these dimers. Main aim of this report to establish the possibilities of EPR study to obtain the information about spin-spin interaction in the Cu-Gd dimer fragments.

EPR investigations are carried on polycrystalline sample of  $[LCu(OH_2)Gd(NO_3)_3]$  built up of Cu-Gd dimmers in the temperature range of 293-4.2 K in the X-band and at T=293 and 4,2 K in the Q-band (Figs. 1, 2).





**Fig.2**. EPR spectrum of [LCu(OH<sub>2</sub>)Gd(NO<sub>3</sub>)<sub>3</sub>] in Q-band at room temperature.

The spin states of Cu-Gd dimer can be characterized total spins S=3,4 due to exchange interaction between copper (S<sub>1</sub>=1/2) and gadolinium (S<sub>2</sub>=7/2) ions. The spin Hamiltonian described the interactions in the Cu-Gd fragment can be written in a form:

$$\begin{split} \mathsf{H} &= \sum \beta (\mathsf{H} \cdot \mathsf{g} \cdot \mathsf{S}_{j}) + \beta^{2} r^{-3} \{ (\mathsf{g}_{1} \cdot \mathsf{S}_{1}) (\mathsf{g}_{2} \cdot \mathsf{S}_{2}) - 3 r^{-2} (\mathsf{g}_{1} \cdot \mathsf{S}_{1} \cdot \mathsf{r}) (\mathsf{g}_{2} \cdot \mathsf{S}_{2} \cdot \mathsf{r}) \} + (\mathsf{S}_{1} \cdot \mathsf{J}_{12} \cdot \mathsf{S}_{2}) + \mathsf{D}[\mathsf{S}_{1z}^{2} - \frac{1}{3}\mathsf{S}_{1}(\mathsf{S}_{1} + 1)] + \mathsf{E}[\mathsf{S}_{1x}^{2} - \mathsf{S}_{1y}^{2}], \end{split}$$

where  $J_{12}$  – tensor of the exchange interaction which include isotropic and anisotropic contributions, r-radius-vector between ions, D,E- fine structure parameters of a gadolinium ion [2].





**Fig.4**. Angular dependence of single crystal EPR spectra of Cu-Gd dimer for xz plane,  $D=0.07 \text{ cm}^{-1}$ ,  $E = 0.04 \text{ cm}^{-1}$ .

It is necessary to note several facts in result of which investigation of this system by EPR method can be ineffective: the spectrum is the sum of spectra from two spin multiplets with S=3 and S=4, and polycrystalline samples were investigated.

Program of simulation of EPR spectra of single crystal and polycrystalline samples of the given dimer has been created. Numerical experiment of EPR spectra has been made to analysis frequency, temperature dependences of EPR spectra and dependence on the values of exchange and fine structure parameters.



Fig.5. Simulated EPR spectra of Cu-Gd dimer, D=0,07  $\text{cm}^{-1}$ ,E=-0,04 cm<sup>-1</sup>,J= -10 cm<sup>-1</sup>.

Comparison of calculated angular dependence of single crystal EPR spectra of Cu-Gd dimmer concerning a magnetic field (fig.3,4, principal direction of  $\{g_{Cu}\},\$  $\{g_{Gd}\}$ and  $\{D_{Gd}\}$ tensors are coincided,  $\theta$ -angel between the z axis and direction of the magnetic field, o-angel between the x axis and magnetic field) and polycrystalline spectra (fig.5) to show that in polycrystalline EPR spectra the basic contribution is brought with perpendicular orientation.

Calculations of polycrystalline EPR spectra at various parameters Hamiltonian (fig.6,7) have shown, that the form of a spectrum for the dimer with  $S_1=1/2$  and  $S_2=7/2$  depends not only on parameters of a crystal field of the nearest environment, but also from of sign of exchange interaction.



Research of the form of the spectrum of such compounds it is very complicated, but it is possible to receive the necessary information. In particular by consideration of temperature dependence of EPR spectra in Q-band(fig. 8) we have established, that small change of signal intensity in zero fields specifies ferromagnetic character of interaction in dimer.

Fit of experimental and calculated spectra allows to estimate the parameter of fine structure of the Gd center. The result of calculation EPR spectra at temperature T=275K with these parameters is shown in fig. 9.



temperature 275K

in Q-band. D=0,07 cm<sup>-1</sup> E=-0,04 cm<sup>-1</sup> J= -10 cm<sup>-1</sup>.

This research shows that analysis of the temperature and frequency dependences of fine structure of polycrystalline spectrum for Cu-Gd dimer in detail allows to determine ferromagnetic interaction between the centres and parameters of a crystal field.

This work is supported by the Russian Foundation of Basic Research grants №04-02-17163, № 06-03 -32175 and Scientific School 6213.2006.2.

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#### Observation of a Griffiths Phase in Paramagnetic La<sub>1-x</sub>Ba<sub>x</sub>MnO<sub>3</sub>

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Recently, a Griffith phase was observed in crystals  $La_{1-x}Sr_xMnO_3$  [1]. Within the context of quenched disorder scenarios, the existence of a Griffiths-like [2] temperature scale  $T_G$  above the magnetic ordering temperature  $T_C$  has been predicted and linked to CMR [3–5]. Moreover, the competition between charge-ordered antiferromagnetic (AFM) and metallic ferromagnetic (FM) phases appears to be a significant factor for the rich phase diagrams of these systems [4], and the persistence of nanoscale inhomogeneities in the paramagnetic (PM) regime has been reported early on [6].

Below  $T_G$ , the quenched disordered system is in between the completely disordered PM high-temperature regime and the magnetically ordered state. This phase regime is usually referred to as the *Griffiths phase* (GP) [7], based on Griffiths' seminal treatment of the effects of quenched randomness on the magnetization of a dilute Ising ferromagnet [2]. Griffiths showed that essential singularities would develop in a temperature region  $T_C(p) < T < T_G$ , where *p* denotes the disorder parameter,  $T_C(p)$  the disorder-dependent FM ordering temperature [Fig. 1(a)], and  $T_G$  a new temperature scale corresponding to  $T_C(1)$ , the Curie temperature of the undiluted system



**Fig.1**. (a) *T-p* diagram for the dilute FM Ising model [2]. (b) Conjectured schematic *T-p* diagram of the GP arising in a *J* random Ising model due to the competition of FM/AFM clusters.

with p=1.

Further studies showed the importance of correlated disorder in generating and enhancing the new singularities [8–10], but a systematic study of the Griffiths phenomenon in a competing 3D twophase situation (e.g., AFM/FM) is still not available at present. To date, however, an entire GP, i.e., a globally PM regime characterized by the temperature boundaries  $T_G$  and  $T_C$  and a well-defined disorder parameter p, has not been identified experimentally.

Here we report the discovery of an entire GP in single crystals of the paradigm system La<sub>1-x</sub>Ba<sub>x</sub>MnO<sub>3</sub> (LBMO), demonstrating the impact of quenched disorder in manganites. Using electron spin resonance

(ESR) and magnetic susceptibility measurements, we clearly identify a triangular phase regime limited by the Ba concentration  $x_c \sim 0.1$ , the Griffiths temperature scale  $T_{G}$ ~340 K, and the FM transition temperature up to a maximal Ba concentration  $x_{max}\sim 0.20$ . Furthermore, we propose that the appearance of Griffiths-phase regimes can be expected for many other manganite systems and mapped out by ESR, which is a local magnetic probe and particularly sensitive in the PM regime.

ESR measurements were performed with a Bruker and Varian E-12 spectrometers at 9.4 and 34 GHz. Susceptibilities were measured with a SQUID magnetometer (Quantum Design).

ESR spectra in La<sub>1-x</sub>Ba<sub>x</sub>MnO<sub>3</sub> in the PM regime above  $T_C$ =200 K not only consist of a PM signal due to the majority of Mn<sup>3+</sup> and Mn<sup>4+</sup> spins [11] but also exhibit an intriguing FM resonance (FMR) signal at lower resonance fields. A rough estimate obtained by comparing the FMR and PM signals shows that the fraction of spins contributing to the FMR is  $\leq 1\%$ . The PM resonance signal and its anisotropy in the orbitally ordered phase have been analyzed in detail previously [12, 13]. Here the focus is on the FMR signal, which emerges from the signal of the PM Mn<sup>3+</sup>/Mn<sup>4+</sup> background (g=2) at T $\approx$ 290 K, far above T<sub>C</sub>=200 K [14], and then shifts towards lower resonance fields, indicating an increase of the local magnetic fields in the sample. This shift corresponds to the T dependence of the FM magnetization [15]. Concomitantly, the intensity of the FMR (estimated via its peak-to-peak linewidth  $\Delta H_{pp}$  and its amplitude A as  $\Delta H_{pp}^2 \cdot A$ ) first clearly increases and then saturates with decreasing temperatures. This behavior excludes a superparamagnetic origin of the signal, which would result in a T dependence according to the Langevin function [for temperatures under consideration, a Curie-Weiss (CW)-like increase] instead of a saturation.

These FMR signals were observed in the PM regime above  $T_C$  in single crystals with Ba concentrations x=0.1, 0.12, 0.15, and 0.2. They all separate from the PM signal below 340 K, indicating a temperature scale  $T_G$  above  $T_C$  which is almost independent of x, and they all exhibit the same anisotropy ~ 6000 Oe. Remarkably, no such additional FMR signals could be identified above  $T_C$  for samples with x > 0.2, which already exhibit a FM metallic ground state. Moreover,



Fig.2. T dependence of the magnetic susceptibility and the inverse susceptibility at 10 Oe and 1 kOe in La<sub>0.9</sub>Ba<sub>0.1</sub>MnO<sub>3</sub>. The external magnetic field was applied within the easy ac plane.

for  $x \le 0.05$  no FMR was observed in the PM regime.

In Fig. 2, we show susceptibility data for a sample with x=0.1. For a large applied magnetic field (3 kOe), the FM component is hidden in the PM contribution and a CW law is found throughout the PM regime, while in small magnetic fields (10 Oe), clear deviations from a CW behavior are observed below  $T_G=340 K$  [Fig. 2].

Having identified the new phase regime in low doped LBMO, we will now discuss its interpretation in the context of quenched disorder as an enhanced GP becoming observable due to the competition of two ordering phases [3]. The source of disorder is the random substitution of  $La^{3+}$ by ions with different size and valence, such as Ba or Sr. The probability p(x) for the existence of a FM bond increases with x, because the increasing number of  $Mn^{3+}$ -Mn<sup>4+</sup> pairs enhances the double-exchange (DE) driven FM interaction. Because of the static Jahn-Teller (JT) distortion of the Mn<sup>3+</sup> ions, the non-JT active Mn<sup>4+</sup> ions and the FM bonds can be regarded as fixed within the lattice (quenched disorder).

The lower bound  $T_G$  for the nonanalyticity of the magnetization is identified with the appearance of the FMR signals at  $T\approx 340$  K. From the intersection of the  $T_G$  boundary with the magnetic ordering boundary, the regular ferromagnet corresponding to p=1 is found to be at  $x\sim0.2$ . In Bray's generalization of Griffiths' concept to FM systems with an arbitrary distribution of bond strengths, the Griffiths temperature scale  $T_G$  is no longer the critical temperature of the pure FM system with p=1 but the maximal critical temperature among all configurations compatible with the static nature of disorder [17].

Keeping in mind that the disorder in LBMO is quenched within the JT-distorted structure, it becomes clear that the disorder must be of a correlated nature as assumed in the argument above. In the case of theoretical models which include correlated disorder, it was found that Griffiths effects are enhanced [8,10]. Additionally, the existence of AFM bonds in the system and the resulting two-phase competition have to be considered and, indeed, Burgy *et al.* [3] argue on theoretical grounds that the existence of competing phases stabilizes and enhances FM Griffithslike effects. In the presence of AFM clusters, the GP should be confined to a restricted region of the T-p phase diagram.

The existence of such a novel phase regime characterized by the FMR features is not restricted to weakly doped LBMO but rather represents a generic feature of manganite systems where the structural distortions are sufficiently strong to allow for the bond disorder to be completely quenched: The coexistence of PM and FMR signals above  $T_C$  has already been reported for some samples of the layered La<sub>2-2x</sub>Sr<sub>1+2x</sub>Mn<sub>2</sub>O<sub>7</sub> [31,32] manganites and La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>[1].

In conclusion, we have experimentally identified, to the best of our knowledge, for the first time an entire Griffiths phase in the T-x phase diagram of LBMO by means of ESR and susceptibility measurements. This phase regime arises as a result of the strong quenching of the randomly diluted locations of the FM bonds in the cooperatively JT-distorted structure and can be expected to be a generic feature in manganites.

This work was supported by RFBR 06-02-17401.

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#### Kinetics of methane hydrate formation by NMR

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#### Sample preparation and research method

Methane hydrate [1] was prepared in a quartz glass cell filled with water approximately up to 50% vol. Then the cell was cooled down to the desired temperature  $(7\pm0.1^{\circ}C)$  in our experiments), it was purged with methane gas at pressure 100 bar. Two samples of methane hydrate were prepared: for the first sample distilled normal water was used, for the second one – deuterated water was used. Experimental studies of methane hydrate formation kinetics were performed on <sup>1</sup>H NMR spectrometer with resonance frequency 19.08 MHz, duration of 90° RF pulse – 2 µs and receiver dead time – 8 µs.

#### **Results and discussion**

Typical transverse relaxation decays in solid-echo experiment are shown on fig. 1.1 and 1.2. Fig.1.1 presents relaxation decays of sample with normal water and fig.1.2 – sample with deuterated water. Data set before methane hydrate formation occurs is marked as 1, data set after methane hydrate appeared – as 2.







**Fig.1.2**. A typical shape of solid-echo decays (sample with deuterated water) before hydrate formation (curve 1) and after 130 hours of hydrate growth (curve 2).

Relaxation decay of sample with normal water during the process of methane hydrate formation is characterized by 3 relaxation times. The slow relaxing component corresponds to protons of methane gas, and the fast relaxing components correspond to protons of methane and water in hydrate state. Transverse relaxation times of methane and water in hydrate state are  $65\pm15\mu$ s and  $13\pm4\mu$ s and their amplitudes related to overall signal (so called populations) are  $0.3\pm0.1$  and  $0.7\pm0.1$ . Fast relaxing component of sample with deuterated water has transverse relaxation time  $70\pm15\mu$ s and corresponds to protons of methane in hydrate state, that proves our components' decomposition in the first sample.

It should be noted that theoretical value for relaxation time of methane solid lattice is about 9  $\mu$ s [2]. Thus our results could be an evidence of significant rotation motion of

methane molecules in solid lattice of methane hydrate. Correlation time of methane molecule rotation motion can be evaluated at  $10^{-7}$  s.

Fast component's population is directly proportional to amount of formed methane hydrate. Therefore in order to obtain the methane hydrate formation kinetic behavior time dependence of fast component's population was investigated.

Obtained kinetic curves are shown in figs. 1.3, 1.4 at three characteristic periods. During first period (induction time, lasts about 7-12 hours) any signal of methane hydrate wasn't registered by NMR. Next period is a period when intensive methane hydrate growth begins. This period lasts 11-12 hours and after that period the growth rate of methane hydrate decreases. Populations of fast components for studied samples were equal 5-6% of overall signal at this period.







As it seen from fig.1.3 and fig.1.4 growth rate of methane hydrate was decreased with time. Apparently it's concerned with formation of hydrate film at liquid – gas interface. Hydrate film hinders infiltration of gas molecules to liquid water in the area where hydrate growth can occur and hence slows down further hydrate formation. To be convinced of this version after 90 hours from the beginning of hydrate formation the cell with a sample with normal water has been subjected to easy mechanical stirring. On fig. 1.3 it is visible, that after destruction of hydrate film, growth rate was increased again.

Fig.1.4 presents kinetic of hydrate growth obtained for system deuterated water – methane within 160 hours. From comparison of the data on fig. 1.3 and 1.4 it is obvious, that for not destroyed film by time about 160 hours appreciably smaller amount of a hydrate is achieved in comparison with a situation shown on fig.1.3. Thus, the film at liquid – gas interface substantially limits growth rate. This implies that hydrate permeability for molecules of methane is not high. Now if one accept, that hydrate was formed as a film, from the geometrical sizes of the cell (internal diameter of 5 mm) thickness of a film d can be calculated. Then the estimation of diffusion coefficient of methane through hydrate can be made using a kinetic curve data. Considering value of a hydrate amount at time about 100 hours from the beginning of hydrate formation thickness of a film is estimated at a level 0.3 mm, and diffusion coefficient – about  $10^{-13}$  m<sup>2</sup>/s.

On the example of sample 2 we made a try to study hydrate stability. After 160 hours from the beginning of growth process we made following: at the pressure 100 atm. Temperature was decreased to  $-18^{\circ}$ C. Then at the constant temperature pressure was dropped off by steps. As one can see from Fig.1.5, decreasing of hydrate content was insufficient up to

pressure about 20 atm. Subsequent decreasing of the pressure leaded to more intensive hydrate degradation. In the pressure interval from 20 atm. to 1 atm. the hydrate contend decreased in two times. Note that under that step-by-step pressure change hydrate riches the equilibrium state quite fast (some tens of minutes).

It was unexpectedly found also the relaxation time of methane in hydrate sufficiently decreases (twice!) with hydrate degradation. Note that it happened in agreement with hydrate amount in the sample.



**Fig.1.5**. Signal intensity and transverse relaxation time dependences on applied pressure for methane in hydrate.

This not trivial result could indicate about presence of different types of hydrate crystal structures in which methane molecule has different relaxation times. Note that we didn't observe any direct change of methane relaxation in hydrate during hydrate formation.

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#### Inhibition of water transport across cell membranes by dimephosphon

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#### Introduction

1,1-Dimethyl-3-hydroxybutyl phosphonic acid ethers synthesized at the A. E. Arbuzov Institute of Organic and Physical Chemistry (Kazan Research Center) are organophosphorus compounds with a variety of pharmacological effects.

The dimethyl ether of 3- hydroxybutyl phosphonic acid (dimephosphon, fig.1) like a majority of drugs is an amphiphile one, with octanol – water partition coefficient of  $1.09\pm0.09$  [1]. It is widely used in metabolic therapy with wide application spectrum, but the molecular mechanism of its medical effect is not clear yet.



Recent investigations of effect of dimephosphon and other acid derivatives on synaptic transmission in neuromuscular junction [1] suggest dual-effect model (blockade and modulation) of channel-blocking action. The modulation model of protein blocking is also associated with interactions through lipid bilayer. It's well recognized that action of membrane proteins, transporters and enzymes is strongly affected by their local environment, including membrane lipid bilayer. Therefore it seems interesting to study the effect of 1,1-Dimethyl-3-hydroxybutyl phosphonic acid derivatives (dimethyl, diethyl, diproyl and dibytil ethers) on

of dimephosphon der biological membranes properties.

The red blood cell (RBC) suits ideally for investigating of many physiological processes in cells including water transport across cell membranes because of its simple structure (no internal membranes) and availability. As there are two water transport pathways: across the lipid bilayer and through transmembrane specific water-channels aquaporins, effect of pharmacological reagents on the water exchange rate in RBCs can provide more information about molecular mechanisms of water transport and drug – membrane interaction.

#### Materials and methods

Venous blood was drawn from healthy male volunteers into sample tubes with heparin (15 IU/ml). The RBCs were isolated by centrifugation and washed three times in medium S (150 mM NaCl, 5.5 mM glucose, 5 mm HEPES (4-(2-hydroxyethyl)-1-piperazine ethanesulphonic acid), pH 7.4. Samples for NMR measurements were prepared by carefully mixing 0.2 ml RBC suspension, 0.1 ml doping solution (30 mM  $MnCl_2$ , 110 mM NaCl, pH 7.4) and 0.1 ml of medium S or pharmacological agent solution of appropriate concentration.

Studies of proton T<sub>2</sub> relaxation in paramagnetically doped RBC suspensions is focused on extracting the intracellular water residence time  $\tau_a$  [2]. Fitting experimental relaxation data from doped cell suspensions to biexponential functions supplies the parameters from which  $\tau_a$  is calculated using expression (1):

$$\tau_a = \frac{(A^2 + B^2 + 2ABC)}{(A^2 - B^2)(B + AC)} \tag{1}$$

where  $A = \frac{1}{2}(\frac{1}{T_a'} - \frac{1}{T_b'}); B = \frac{1}{T_a} - \frac{1}{2}(\frac{1}{T_a'} + \frac{1}{T_b'}); C = 1 - 2P_a'; T_a', T_b', P_a'$  - apparent relaxation times and relative populations of intra- and extracellular water measured in depend PRC suspension. The

relative populations of intra- and extracellular water, measured in doped RBC suspension. The intrinsic relaxation time of the intracellular water  $T_a$  measurements were carried out on packed cell samples (whole blood centrifuged at 5000 g for 30 min.)

NMR relaxation data were obtained with home-built NMR spectrometer at a Larmor frequency of 19 MHz with Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. All experiments, including drug exposure were performed at  $37^{0}$  C on samples with 26-28 % hematocrit in medium S.

#### **Results and discussion**

No significant erythrocyte volume changes were observed. Intrinsic relaxation time of intracellular water without or with dimephosphon was typically within 140-150 ms.

All used concentrations of dimephosphon (0.0015 - 2 % v/v) caused an increase of mean residence time of intracellular water molecules  $\tau_a$  above the control value  $9.2 \pm 0.4$  ms in a concentration-dependent manner.



**Fig.2**. Relative increase of intracellular water residence time in human RBC by dimephosphon.

The relative increase of  $\tau_a$  for different concentrations is represented on fig.2. As one can see from the figure, residence time increases with the dimephosphon concentration increasing. It indicates that one (or both) of the water transport pathways are inhibited. It is significant to note that aquaporin water channels can be specifically blocked by organomercuric SH-reagents, especially pCMB and pCMBS, reaching the maximal inhibition of water transport (increasing of  $\tau_a$  at 50 %) in ~60 min [3].

It should be noted that exposure of dimephosphon to RBC suspension produced faster water transport

inhibition (in  $\approx$ 5 min), but less efficient than pCMB. Further experiments will be held in order to get detail understanding of the molecular mechanism of the found effect.

The work was supported by RFBR projects № 04-03-32861, № 06-04-48160, RNP 2.1.1.3222.

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#### Magnetic properties of dielectric Van Vleck paramagnet PrF<sub>3</sub>

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#### Abstract

For dynamic polarization of liquid <sup>3</sup>He nuclei in our previous researches we suggested using of dielectric Van Vleck paramagnet PrF<sub>3</sub>. In present work the magnetic properties of PrF<sub>3</sub> single crystal and crystal powders were studied in details to clarify this proposal.

Experimental magnetic susceptibility data of  $PrF_3$  shows unusual temperature dependence (in temperature region 2-14 K and 20-65K) in comparison with the majority of other Van Vleck paramagnets. Such anomalous dependence at 20-65K comes from the peculiar structure of wave functions and needs the detailed experimental investigation.

The magnetic susceptibility in the  $PrF_3$  single crystal was measured by use dc-SQUID magnetometer MPSM-2 (Quantum design) at temperatures 2÷300 K for two directions of the applied magnetic field 0.01 T (along and perpendicular to *c*-axis). Experimental results allowed us to find out crystal field parameters in the framework of the crystal field theory. A rather good agreement between observed temperature dependence of magnetic susceptibility and the calculated one was obtained. The calculated structure of the Stark energy levels for ground multiplet  ${}^{3}H_{4}$  describes experimental data much better than any previous proposed structures. Using obtained crystal field parameters we calculated the magnetic field dependences of Stark energy levels. Such dependencies should help us to find an optimal condition for dynamic polarization and to predict the behaviour of  $PrF_3$  in ultra low temperatures.

#### Introduction

We suggested using dielectric Van Vleck paramagnet PrF<sub>3</sub> for dynamic polarization of liquid <sup>3</sup>He nuclei in our previous investigations [1]. Therefore, studying of magnetic properties both PrF<sub>3</sub> single crystal and PrF<sub>3</sub> fine-dispersed crystal powders attracts great interest.

Earlier, dielectric Van Vleck paramagnet magnetic properties research was carried out in case of single crystals and crystal powders which was in contact with liquid <sup>3</sup>He. For example, systems contains LiTmF<sub>4</sub> and TmES Van Vleck paramagnets was investigated extensively [2,3]. But on practice surface quality of crystal powder particles doesn't allow the nuclear dynamic polarization of <sup>3</sup>He, or experiments are not reproduced. During single crystal grinding mechanical stress arises and leads to nanocavities on the powder particles surface. As a result, defect paramagnetic centers appear on this surface. That is why magnetization transfer from Van Vleck paramagnet nuclei to nuclei liquid <sup>3</sup>He becomes complicated because of strong local heterogeneous magnetic fields on nuclei <sup>3</sup>He. Cleavage plains are present at PrF<sub>3</sub> and, therefore, atomic-smooth surface of crystal powders is quite possible. This fact favorably distinguishes PrF<sub>3</sub> from other Van Vleck paramagnets. Another remarcable feature of this cristal is that according to Bleaney [5] the temperature at which the nuclei of the single stable isotope <sup>141</sup>Pr, I=5/2, enter an

ordered state is estimated to be 0.1 mK, smaller than the overall nuclear electric quadrupole splitting 1.2 mK.

In the present work the magnetic properties of PrF<sub>3</sub> single crystal and fine-dispersed crystal powders were studied in details.

#### Magnetic properties of PrF<sub>3</sub>

The  $PrF_3$  single crystal was grown by the Bridgman-Stockbarger method from the  $PrF_3$  powder at the melting temperature of 1400  $^{0}$ C. The EPR measurements have shown that the paramagnetic admixture content ( $Er^{3+}$ ,  $Dy^{3+}$ ,  $Nd^{3+}$ ,  $Gd^{3+}$  and  $Sm^{3+}$  ions) totally is much less than 0.01% from the number of  $Pr^{3+}$  ions.

The magnetic susceptibility in the  $PrF_3$  single crystal was measured by use dc-SQUID magnetometer MPSM (Quantum design) at temperatures 2÷300 K for two directions of the applied magnetic field 0.01 T (along and perpendicular to *c*-axis). Also was measured magnetic susceptibility in the  $PrF_3$  crystal powder with character size of particles about 45-75 mkm as function of temperature (see fig. 1).



**Fig.1**. Magnetic susceptibilities of PrF<sub>3</sub> measured in the external magnetic field 0.01T directed across (solid circles) and along (open circles) the c-axis. Solid curves represent results of simulations.

Peculiar structure of wave functions leads to unusual temperature dependence of magnetic susceptibility of  $PrF_3$  among the majority of Van Vleck paramagnets. Susceptibility arises with temperature at 20-65 K when external magnetic field direction is along symmetry *c*-axis.

Also unusual result at the temperatures 2-14 K attracts great interest. This anomalous Curielike behavior exists along with temperature independent Van Vleck contribution into susceptibility. Experiment showed that this effect doesn't depend on orientation of single crystal in external magnetic field and become weaker at high fields above 5 T. So we suggest that this anomaly arises from intrinsic lattice defects in PrF<sub>3</sub>. Local crystal fields in the region of the defects differ from the crystal field in the "bulk". As a result, a quasi-doublet crystal field state may appear as the ground state of a  $Pr^{3+}$  ion. The resembling behaviour was observed by Bucher [4] on monocrystal Rb<sub>2</sub>NaHoF<sub>6</sub>.

Received experimental results allow us to find out crystal field parameters in the framework of the crystal field theory.

The magnetic susceptibility of the paramagnetic crystal  $PrF_3$  was computed in the same framework. The Hamiltonian of the  $Pr^{3+}$  ion in the external magnetic field  $H_0$ , acting within the space of 91 states of the ground  $4f^2$  electronic configuration,

$$H = H_{fi} + H_{cf} + H_Z \tag{1}$$

contains the free ion Hamiltonian  $H_{fi}$  which involves energies of electrostatic and spin-orbit interactions, the crystal-field Hamiltonian  $H_{CF}$  and the Zeeman Hamiltonian  $H_Z$ . In the local coordinate system with the z-axis parallel to the corresponding symmetry axis of monoclinic site symmetry, the crystal-field Hamiltonian is given by an expression

$$H_{cf} = \sum_{k,q} B_{kq} C_{kq}; \quad k=2,4,6; q=-k,..,k$$
(2)

where  $C_{kq}$  are the components of a spherical tensor of rank k,  $B_{kq}$  are the complex crystal-field parameters which describe the effect of the crystal field on the free-ion energy levels.



**Fig.2**. Magnetic susceptibilities of PrF<sub>3</sub> crystal powder measured in the external magnetic field 0.01 T. Solid curves represent results of simulations.

The calculated structure of the Stark energy levels for ground multiplet  ${}^{3}H_{4}$  describes experimental data much better than any previous proposed structure. Using obtained crystal field parameters we calculated the magnetic field dependences of Stark energy levels.

Magnetic susceptibility of undirected  $PrF_3$  crystal powder was calculated by using averaging method of any directions of crystal particles in external magnetic field. In this case we obtained rather good agreement between observed temperature dependence of magnetic susceptibility and the calculated one (see fig. 2).

#### Conclusion

Experimental and theoretical investigations of  $PrF_3$  magnetic susceptibility were carried out. Obtained wave functions are in good agreement with all measurement data both  $PrF_3$  single crystal and  $PrF_3$  fine-dispersed crystal powders.

Investigations of magnetic properties of  $PrF_3$  in this work and recent NMR investigations of magnetic coupling between the <sup>141</sup>Pr and <sup>3</sup>He in the system of "solid  $PrF_3$  – liquid <sup>3</sup>He" and studies of surface quality of  $PrF_3$  particles with different size in powders suggest this Van Vleck paramagnet as a perspective material for the dynamic polarization of <sup>3</sup>He nuclei.

#### Acknowledgment

This work was supported by the Russian Fund for Basic Researches (project 06-02-17241-a) and the Research Educational Center REC-007.

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# Enhanced <sup>169</sup>Tm NMR and magnetization measurements in study of anisotropic magnetic properties of crystal LiTmF<sub>4</sub>

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The double fluoride LiTmF<sub>4</sub> is the Van Vleck dielectric paramagnet with singlet Stark ground state of Tm<sup>3+</sup>. This crystal has a scheelite structure with the space group  $C_{4h}^6$ . The Tm<sup>3+</sup> positions have the S<sub>4</sub> point symmetry. The Tm<sup>3+</sup> ground electron configuration is 4f<sup>12</sup>, the ground multiplet <sup>3</sup>H<sub>6</sub>. Giant magnetostriction in LiTmF<sub>4</sub> in (001) plane was first observed in [1]. As has been reported there, the lattice deformations in magnetic field of 30 kOe oriented in the basal plane achieve the values of  $-1.1 \cdot 10^{-3}$ . The effect of magnetostriction on magnetic properties of LiTmF<sub>4</sub> in (001) plane is the subject of present work.

The experiments on <sup>169</sup>Tm NMR in LiTmF<sub>4</sub> have been performed on specially designed high frequency magnetic resonance spectrometer [2, 3] and rotary device of sample in the superconducting solenoid at frequencies 372.7 MHz at 15 kOe and 653 MHz at 25 kOe at temperature 4.2 K. Spherical–shaped 4 mm in diameter oriented crystal of LiTmF<sub>4</sub> has been used as a sample. The resonance field dependences on magnetic field direction in basal plane (001) have been measured (figure 1).







**Fig.2.** The measured dependences of the magnetization on the magnetic field strength and direction (circles). Dashed lines are fits using equation (1) and table 1. Sample has been deeply embedded in epoxy glass.  $H \perp [001]$ , T=4.2K. The increments of *H* are 4 kOe everywhere.

In <sup>169</sup>Tm NMR experiment we have failed to determine the absolute value of the angle between magnetic field direction and crystallographic axis [100] of the sample, but it can be determined from the experimental dependences on magnetization. Since the paramagnetic shift of <sup>169</sup>Tm NMR line in LiTmF<sub>4</sub> is greatly exceeds 1, the variation of <sup>169</sup>Tm effective gyromagnetic ratio is reproduced by the LiTmF<sub>4</sub> magnetization dependence rather precisely.

Experimental results give mean value of  $\varphi_0 = 12.5^\circ$  for the angle of a maximum magnetization (see table 1 and figure 3). This value should correspond to the direction of minimum resonance magnetic field of <sup>169</sup>Tm. Figure 1 shows the <sup>169</sup>Tm NMR field dependences where the absolute angle values were defined by this way. The value of  $\varphi_0$  is in good agreement with the corresponding value defined in [4] as 11° as a direction of the maximum effective gyromagnetic ratio of <sup>169</sup>Tm in LiTmF<sub>4</sub> at 160 MHz.

The experiments on LiTmF<sub>4</sub> magnetization have been performed on Quantum Design SQUID MPMS setup. The magnetic field strength and direction dependences in basal plane (001) have been measured at magnetic fields up to 55 kOe at temperature 4.2 K (figures 2, 3). The sample has been oriented relative to (100) axis by means of X-ray diffractometer and shaped as a parallelepiped of  $1.5 \times 1.5 \times 0.9$  mm in size with the faces parallel to crystallographic axes (*c* axis was normal to larger face). The magnetization in (001) plane was substantially anisotropic, therefore it was necessary to fix the sample reliably as the torque of value as much as  $\approx 4 \cdot 10^{-3}$  N·m was supposed to act on sample on some directions in 55 kOe magnetic field. Two types of experiments have been performed: first, with sample, deeply embedded into low temperature epoxy glass (Stycast 1266) (figure 2) and second with sample only glued by epoxy glass to the capsule bottom (figure 3). It has been clearly seen that the variation of magnetization in first case, when the sample couldn't change its size freely under the action of magnetic field, was about two times smaller than in second case (see table 1). The experimental dependences of magnetization *M* can be fitted by the expression

$$M = \left[a^{2}H^{2} + b^{2}H^{4}\left(1 + \cos 4\left(\varphi - \varphi_{0}\right)\right)\right]^{1/2},$$
(1)

where parameters *a* and *b* are constant at small magnetic fields (below  $\approx 20$  kOe), though at high magnetic fields they tend to decrease (see table 1).



**Fig.3.** The calculated (solid lines) and experimental (circles) dependences of the magnetization on the magnetic field strength and direction.  $H \perp [001]$ , T=4.2K. H=31 kOe for (a) and H=55 kOe for (b). Dashed lines are fits using equation (1) and table 1. About a quarter of sample has been embedded in epoxy glass.

	<i>H</i> , kOe	$a, \frac{\text{emu}}{\text{g} \cdot \text{kOe}}$	$b, \times 10^{-2} \frac{\text{emu}}{\text{g} \cdot \text{kOe}^2}$	$\varphi_0,{}^{\circ}$
Theory	55	1.30	1.67	8.1
Theory	31	1.48	2.27	7.9
Experiment on	55	$1.39 \pm 0.02$	$1.66 \pm 0.05$	13.6±0.8
figure 3	31	$1.61 \pm 0.01$	$2.26 \pm 0.09$	$11.4{\pm}1.1$
	55	$1.37 \pm 0.01$	$1.20 \pm 0.04$	_
Experiment on	31	$1.60 \pm 0.01$	$1.55 \pm 0.07$	_
figure 2	19	$1.69 \pm 0.01$	$1.68 \pm 0.17$	_
	15	$1.71 \pm 0.01$	$1.70\pm0.27$	_

**Table 1.** Parameters of the equation (1) to fit the LiTmF<sub>4</sub> magnetization dependences.  $H \perp [001], T=4.2$ K.

According to [5, 6], the energy levels and wave functions of  $\text{Tm}^{3+}$  in LiTmF<sub>4</sub> can be determined by the single ion Hamiltonian

$$H_e = H_{cr} + H_{eZ} + H_{e-d} , (2)$$

where

$$H_{cr} = \alpha B_2^0 O_2^0 + \beta \left( B_4^0 O_4^0 + B_4^4 O_4^4 + B_4^{-4} \Omega_4^4 \right) + \gamma \left( B_6^0 O_6^0 + B_6^4 O_6^4 + B_6^{-4} \Omega_6^4 \right), \ H_{eZ} = g_J \mu_{\rm B} H J .$$
(3)

 $\alpha$ ,  $\beta$ ,  $\gamma$  are the Stevens coefficients,  $O_p^k$ ,  $\Omega_p^k$  – Stevens operators and  $B_p^k$  are the crystal field parameters published in [7] and corrected in [5, 6]:

$B_2^0$	$B_4^0$	$B_4^4$	$B_4^{-4}$	$B_6^0$	$B_6^4$	$B_6^{-4}$
184	-90	-4.06	-669	-578	-328	-284

 $g_J = 7/6$  is the Lande factor,  $\mu_B$  is the Bohr magneton and J is the operator of total angular momentum. The third term in (2) equals to

$$H_{e-d} = Ve(H) + V'' \Delta w(H) .$$
<sup>(4)</sup>

These two terms define linear interactions of rare earth ions with the homogeneous macro– (deformations of whole crystal) and microdeformations (sublattice displacements), respectively. e(H) is characterizing the crystal deformations of rhombic symmetry defined by irreducible representation  $B_g$  of the Tm<sup>3+</sup> point group  $C_{4h}$ ,  $\Delta w(H)$  is the vector, which components equal to linear combinations of sublattice displacements. V and V'' are the vectors of linear combinations of Stevens operators.

The final Hamiltonian has been calculated by the manner reported in [5], eigenvectors of the Hamiltonian matrix was obtained by its numerical diagonalization in the  ${}^{3}H_{6}$  manifold, the magnetic field strength and orientation dependences of LiTmF<sub>4</sub> crystal magnetization have been calculated (figure 1). Calculated dependences are in good agreement with experimental ones when the LiTmF<sub>4</sub> sample was fixed so that it could change its shape freely due to magnetostriction.

At rather high magnetic fields (*H*>30 kOe), the energy of electron Zeeman interaction become comparable with the values of Stark splittings. For Tm<sup>3+</sup> in LiTmF<sub>4</sub> in lowest  $\Gamma_2^1$ ,  $\Gamma_{34}^1$ and  $\Gamma_1^1$  states the energy shifts approximately equal to 1.5 cm<sup>-1</sup> at 30 kOe and 5 cm<sup>-1</sup> at 55 kOe, while the initial energy gaps between these states are about 30 cm<sup>-1</sup>. Thus, in order to calculate the splitting of electron–nuclear sublevels of ground  $\Gamma_2^1({}^{3}H_6)$  state it is necessary to

do an exact diagonalization of Hamiltonian by numerical means the same way as it has been performed for thulium ethyl sulphate (TmES) in [8, 2 and 3]. The following modification has been introduced to Hamiltonian to take into account the interactions with <sup>169</sup>Tm nucleus:

$$H_{en} = H_e + H_{nZ} + H_{hf} = H_e - \gamma_I \hbar H I + A_J J I , \qquad (5)$$

where  $\gamma_I = -2\pi \times 352$  Hz/Oe is the <sup>169</sup>Tm nucleus gyromagnetic ratio,  $A_J/h = -393.5$  MHz is the hyperfine interaction constant. As an initial basis for the wave functions 26 wave functions were taken in the form of a direct product of the electronic and nuclear wave functions:

$$|J,M_J\rangle \cdot |I,M_I\rangle.$$
 (6)

The energies of electron–nuclear states were obtained by numerical diagonalization of Hamiltonian (5), NMR frequencies of <sup>169</sup>Tm in ground state of Tm<sup>3+</sup> were found. Calculated by this manner <sup>169</sup>Tm NMR field dependences on magnetic field orientation and resonance frequency are shown on figure 3 and agree well with experimental dependences.

#### Acknowledgements

The authors are grateful to V.A. Shustov for performing the sample orientation and to B.Z. Malkin for valuable comments.

This study was done with the support of the research and educational center REC–007 (BHRE).

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### Binding energy of a Cooper pairs with non-zero center of mass momentum in d-wave superconductors

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#### Abstract

The binding energy of a Cooper pairs has been calculated for the case of d-wave symmetry of the superconducting gap in layered cuprate structures. If one assumes that Cooper pairs are formed by short range potential then the binding energy is given by  $\Delta(\mathbf{k},\mathbf{q})=\Delta_x(\mathbf{q})\cos k_x a + \Delta_y(\mathbf{q})\cos k_y a + \Omega_x(\mathbf{q})\sin k_x a + \Omega_y(\mathbf{q})\sin k_y a$  where **q** is a total momentum of the pair. Numerical solutions of the self-consistent system of the integral equations for quantities  $\Delta_x(\mathbf{q})$ ,  $\Delta_y(\mathbf{q})$  and  $\Omega_x(\mathbf{q})$ ,  $\Omega_y(\mathbf{q})$  along different lines in  $q_x$ ,  $q_y$  plane have been obtained. The origin of the high order harmonics in energy gap function, discovered recently experimentally, will be discussed.

#### Main text

The binding energy of a Cooper pairs has been calculated for the case of d- wave symmetry superconducting gap in layered structures. If one assumes that Cooper pairs are formed by short range potential then the binding energy is given by

$$\Delta(k,q) = \Delta_x(q)\cos k_x a + \Delta_y(q)\cos k_y a + \Omega_x(q)\sin k_x a + \Omega_y(q)\sin k_y a \tag{1}$$

where q is total momentum of the pair. Numerical solutions of the self-consistent system of the integral equations for quantities  $\Delta_x(q)$ ,  $\Delta_y(q)$ ,  $\Omega_x(q)$  and  $\Omega_y(q)$  along different lines in the  $q_x$ ,  $q_y$  plane have been obtained. The problem of the binding energy of a Cooper pair in the BCS model (phonon pairing mechanism) was discussed by Cooper in his pioneering paper [1] and later on by Casas at al. [2]. It was founded that  $\Delta(q)=\Delta(0)-cq$ , i.e. cooper pairs are distorted very fast when they start to move. This future in strong contrast with respect to usual bosons behavior.

In our calculations we start from integral equation for the binding energy

$$\Delta(k,q) = \frac{1}{N} \sum_{k'} J(k-k') \frac{\Delta(k',q) \left[ f(E_{2k'q}) - f(E_{1k'q}) \right]}{E_{1k'q} - E_{2k'q}}$$
(2)

where q is total momentum of cooper pair,

$$f(E) = 1/(1 + \exp(E/k_B T))$$

is Fermi function, k is relative momentum of quasiparticles in pair. Energy of Bogoliubov type quasiparticles are given by

$$E_{1kq} = \frac{1}{2} \left( \varepsilon_k - \varepsilon_{-k+q} \right) + \frac{1}{2} \sqrt{\left( \varepsilon_k + \varepsilon_{-k+q} - 2\mu \right)^2 + 4 \left| \Delta(k,q) \right|^2}$$

$$E_{2kq} = \frac{1}{2} \left( \varepsilon_k - \varepsilon_{-k+q} \right) - \frac{1}{2} \sqrt{\left( \varepsilon_k + \varepsilon_{-k+q} - 2\mu \right)^2 + 4 \left| \Delta(k,q) \right|^2}$$
(3)

The energy dispersion of quasiparticles we take in the form

$$\varepsilon_k = 2t_1 \left(\cos k_x a + \cos k_y a\right) + 4t_2 \cos k_x a \cos k_y a + \dots$$
(4)

where hopping integrals  $t_1$ ,  $t_2$ ... and chemical potential  $\mu$  are taken according experiment data based on photoemission [3] for layered cuprates. The Fourier-transform of the pairing potential is written as:

$$J(k-k') = 2J_1[\cos(k_x - k_x')a + \cos(k_y - k_y')a)] = 2J_1\cos k_x a \cos k_x'a + \dots$$
(5)

This form is valid for any short-range interaction. As an example one may assume the superexchange interaction between of copper spin, then  $J_1 \approx 100 \text{meV}$ . The case with q=0 was described earlier [4].

Equation (2) is belonging to the separable type of integral equations. It is easily seen that its general solution may be written in the form (1).

After substitution (1) in the equation (2) one arrives to the systems:

$$\begin{split} \Delta_{x}(q) &= \frac{2J_{1}}{N} \sum_{k'} \Big[ f(E_{2k'q}) - f(E_{1k'q}) \Big] \frac{\Delta(k',q) \cos k'_{x}}{(E_{1k'q} - E_{2k'q})} \\ \Delta_{y}(q) &= \frac{2J_{1}}{N} \sum_{k'} \Big[ f(E_{2k'q}) - f(E_{1k'q}) \Big] \frac{\Delta(k',q) \cos k'_{y}}{(E_{1k'q} - E_{2k'q})} \\ \Omega_{x}(q) &= \frac{2J_{1}}{N} \sum_{k'} \Big[ f(E_{2k'q}) - f(E_{1k'q}) \Big] \frac{\Delta(k',q) \sin k'_{x}}{(E_{1k'q} - E_{2k'q})} \\ \Omega_{y}(q) &= \frac{2J_{1}}{N} \sum_{k'} \Big[ f(E_{2k'q}) - f(E_{1k'q}) \Big] \frac{\Delta(k',q) \sin k'_{y}}{(E_{1k'q} - E_{2k'q})} \end{split}$$
(6)

This equation system is solved numerically. Resulting dependence of a binding energy on total momentum q (with  $q_x=q_y$ ) is shown in Fig.1 at T=1K. Dependences  $\Delta_x$ ,  $\Delta_y$ ,  $\Omega_x$ ,  $\Omega_y$ 



**Fig.1**. Dependences  $\Delta_x$ ,  $\Delta_y$ ,  $\Omega_x$ ,  $\Omega_y$  on total momentum q along axis  $q_x = q_y$  with T = IK.

versus  $q_x$  and  $q_y$  are presented in Fig. 2 and 3.

Fig. 4 gives an idea about parameters changes with temperature change.

Work was partially supported by the National Science Foundation, Grant # IB7420-



**Fig.2**. Dependences  $\Delta_x$ ,  $\Delta_y$ ,  $\Omega_x$ ,  $\Omega_y$  on total momentum q along axis  $q_x$  ( $q_y=0$ ) with T=1K.



**Fig.3**. Dependences  $\Delta_x$ ,  $\Delta_y$ ,  $\Omega_x$ ,  $\Omega_y$  on total momentum q along axis  $q_y$  ( $q_x=2\pi$ ) with T=1K.



**Fig.4**. Dependences  $\Delta_x$ ,  $\Delta_y$ ,  $\Omega_x$ ,  $\Omega_y$  on temperature with q=0.

110784 and the Russian Foundation of basic researches, Grant # 06-0217197-a.

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## The surface effects influence on magnetic resonance in carbonizate

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One of the main problems in medicine today is diagnostic of human lungs illnesses at the early stage of their evolution. When the NMR tomography is used, lungs cavities are filled up with noble gas (usually <sup>3</sup>He or <sup>129</sup>Xe) mixtured with oxygen. But for good resolution of NMR-image the gas should be hyperpolarized. There are several methods of hyperpolarized noble gas production (laser-pumping, brute-force polarization). The first method have low efficiency, the second one is high expensive.

One of the perspective methods of noble gas production can be the dynamic polarization of the noble gas. Solid substance with developed surface and big quantity of absorbed noble gas atoms need for the realization of the method. In this case the polarization can transfer from the electron subsystem of the solid substance to the nuclear subsystem of the gas. The main problem now is finding of solid substance with best properties to the method of dynamic polarization of the gas.

The sample prepared from the tree called «astronium» has been studied. This tree wood characterize high porous structure. The wood transformed to the coal by pyrolysis and the coal was mill for increasing of area of the surface interacting with the gas. In previous works, the behaviors of paramagnetic centers on the coal surface from dimension of powder particle were established[1–4].



 $\begin{array}{ccc} 125\text{-}150\ \mu\text{m} & 50\text{-}75\ \mu\text{m} & \text{less 10}\ \mu\text{m} \\ \textbf{Fig.1} \text{ Images of powder surfaces of carbonizate "astronium" with three different characteristic particle dimensions.} \end{array}$ 

The images of the surfaces of samples with three characteristic dimensions were obtained by electron scanning microscope Philips XL30ESEM (Fig.1). One can see, that the samples with particle dimensions 50-75  $\mu$ m and 125-150  $\mu$ m have porous structure, while pores are destroyed in the sample with particle dimensions less then 10  $\mu$ m. The rate between pore's surfaces and common surface's areas differ for each sample and the behaviors of surface's paramagnetic centers can be change.

The behaviors of paramagnetic centers were investigated by EPR. All measurements were made on the X-band commercial spectrometer ESP-300 Bruker at room temperature. Samples are pumping for remove oxygen molecules from surface (the residual pressure less  $10^{-4}$  torr). Asymmetric EPR signal with g-factor 2.0023 was observed in each sample (Fig.2).

The EPR line is narrow and linewidth is near 0.4 gauss. The line narrowing is caused by exchange interaction between paramagnetic centers on the surfaces of coal [4,5]. The shape of line can be approximated by two Lorentz lines with different intensities, linewidths and g-factors. Linewidths of both lines are nearly similar for all three samples. But the ratio of line's intensities and consequently the ratio of concentrations of paramagnetic centers is different for samples with different dimension of powder particle. Accordingly two kinds of paramagnetic centers were observed on the surfaces of such coal. Also the ratio of areas of two types of surface is estimated on the images. There is the good correlation between these parameters (Fig.3). Hence the types of paramagnetic centers can be attached to types of surfaces. The narrow line correspond to paramagnetic centers on the pores surface, while wide line correspond to paramagnetic centers on surface of break powder particle.



Fig.2 Approximation EPR spectra by two Lorentz curve



**Fig.3** Correlation of two line intensities rate and two surface types areas: the area of break  $(s_1)$  and the area of pores $(s_2)$ 

The concentrations of paramagnetic centers were measured for each sample by the comparison EPR signal intensities of investigated sample to signal of the calibrated sample (DFPG). In all measured samples this concentrations of paramagnetic centers is near 1% of all

carbon's atoms. The largest concentration has been obtained from the sample with the particle's dimension 50-75  $\mu$ m.



concentration of surface paramagnetic centers

The obtained values are in agreement with the <sup>3</sup>He NMR relaxation, when <sup>3</sup>He gas filled carbonizate powder. The correlation of spin-lattice relaxation time of <sup>3</sup>He nuclei and concentration of paramagnetic centers on the coal's surface (Fig.4) show, that the paramagnetic centers on the surface of such coal are the main channel of <sup>3</sup>He nuclear relaxation.

The research is supported by program BRHE-CRDF (REC-007), RFBR-N06-02-17241.

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# Magnetoelastic effects and magnetization in LiDyF<sub>4</sub> and LiHoF<sub>4</sub> single crystals

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#### Abstract

Temperature and magnetic field dependences of the magnetization of LiHoF<sub>4</sub> and LiDyF<sub>4</sub> single crystals were measured with a dc-SQUID magnetometer MPSM-2 (Quantum Design) with the magnetic field applied along and perpendicular to the *c* axis. Experimental data are well reproduced by simulations based on the microscopic model of the crystal field and magnetoelastic interactions.

#### Introduction

Double lithium-rare earth fluorides which crystallize in the tetragonal scheelite  $C_{4h}^6$  structure attract much interest as model objects in physics of dipolar magnets and quantum phase transitions [1]. The unit cell of LiRF<sub>4</sub> contains two magnetically equivalent lanthanide R<sup>3+</sup> ions at sites with the S<sub>4</sub> point symmetry. LiDyF<sub>4</sub> is a dipolar antiferromagnet with Dy<sup>3+</sup> magnetic moments normal to the crystal symmetry axis (T<sub>N</sub>=0.62 K), LiHoF<sub>4</sub> is a dipolar Ising-like ferromagnet with T<sub>c</sub>=1.53 K [1]. The main goal of the present study was to elucidate the role of magnetoelastic interactions in formation of the magnetization and the energy level pattern of LiRF<sub>4</sub> crystals in the external magnetic fields.

#### **Experimental results and discussion**

Single crystals of LiDyF<sub>4</sub> and LiHoF<sub>4</sub> were grown by Bridgeman-Stockbarger method. After X-Rays orientation they were shaped as spheres to acquire a definite demagnetizing factor. To prevent the samples from rotation in the strong magnetic field, they were fixed in Stycast 1266 epoxy resin. The temperature dependences of the magnetization of all single crystals in the temperature range of 2-300 K and the dependences of the magnetization on the magnetic field in the interval 0-5 T applied along and perpendicular to the *c* axis were measured with a dc-SQUID.

In the presence of an applied magnetic field *B* (below a direction of *B* relative to the [001] and [100] axes is specified by spherical coordinates  $\theta$  and  $\varphi$ ), we write the Hamiltonian of a single R<sup>3+</sup> ion in the following form (the nuclear Zeeman energy is neglected):

$$H = H_{cf} - g_J \mu_B B J + A J I + \sum_{\alpha \beta} V'_{\alpha \beta} e_{\alpha \beta} + \sum_{\alpha, s} V''_{\alpha} (s) w_{\alpha} (s).$$
(1)

Here the first term is the crystal field Hamiltonian:

$$H_{cf} = \alpha B_2^0 O_2^0 + \beta (B_4^0 O_4^0 + B_4^4 O_4^4 + B_4^{-4} \Omega_4^4) + \gamma (B_6^0 O_6^0 + B_6^4 O_6^4 + B_6^{-4} \Omega_6^4)$$
(2)

determined in the crystallographic system of coordinates by the set of seven crystal field parameters  $B_p^{\ k}$  ( $O_p^{\ k}$  and  $\Omega_p^{\ k}$  are the Stevens operators,  $\alpha$ ,  $\beta$ ,  $\gamma$  are the reduced matrix elements). The second term in Eq. (1) is the electronic Zeeman energy ( $\mu_B$  is the Bohr

magneton,  $g_J$  is the Lande factor, J is the total angular momentum). The third term represents the magnetic hyperfine interaction, and the last two terms define linear interactions of rare earth ions with the homogeneous macro- and microdeformations, respectively, where e is the deformation tensor, and w(s) is the vector of the *s*-sublattice displacement. The electronic operators  $V'_{\alpha\beta}$  and  $V''_{\alpha}(s)$  can be presented, similar to the crystal field energy, through the linear combinations of Stevens operators with the parameters which have been calculated earlier in the framework of the exchange charge model [2,3].

Taking into account a linear coupling between the lattice macro- and micro-deformations and the equilibrium conditions for the coupled paramagnetic ions and the elastic lattice, we obtain the lattice macrodeformation induced by the magnetic field

$$\boldsymbol{e}(\boldsymbol{B}) = -\frac{n}{v_0} \boldsymbol{S}[\langle \boldsymbol{V} \rangle_B - \langle \boldsymbol{V} \rangle_0]$$
(3)

and the sublattice displacements, which define the internal magnetostriction,

$$\boldsymbol{w}(\boldsymbol{B}) = -\frac{n}{v_0} \boldsymbol{a}^{-1} [\langle \boldsymbol{V}'' \rangle_{\boldsymbol{B}} - \langle \boldsymbol{V}'' \rangle_0].$$
(4)

Here n = 2 is the number of rare earth ions in the unit cell, **S** is the compliance tensor of the lattice,  $v_0$  is the volume of the unit cell, **a** is the dynamic matrix of the lattice at the Brillouin zone centre, and angular brackets  $<...>_B$ ,  $<...>_0$  indicate thermal averages over the eigenstates of the rare earth ion Hamiltonian (1) for  $B \neq 0$  and B=0, respectively. Operators V in Eq.(3) equal to operators V' renormalized due to linear coupling of macro- and microdeformations.

To take into account magnetic dipole-dipole interactions between the rare earth ions, we use the mean field approximation. The local field  $B_{loc}=B+(Q-N)M$  in the spherical sample (Q is the tensor of dipole lattice sums,  $N=4\pi/3$ , M is the magnetization) is substituted for B in the Hamiltonian (1), and the expressions (3) and (4) are substituted for e and w, respectively. Thus we obtain the effective self-consistent single-ion Hamiltonian parametrically dependent on the magnetization. When studying magnetic properties of the system, it is enough to consider the matrix of this Hamiltonian in the subspace of states of the ground multiplet of a rare earth ion. The magnetic moment of an ion satisfies to the self-consistent equations

$$m_{\alpha} = \frac{\sum_{i} g_{J} \mu_{B} < i | J_{\alpha} | i > e^{-E_{i}(M) / kT}}{\sum_{i} e^{-E_{i}(M) / kT}},$$
(5)

where  $E_i(M)$  are the energy levels of a rare earth ion (eigenvalues of the Hamiltonian (1)), T-temperature, k is the Boltzman constant. To obtain energies of sublevels of the ground multiplet and the magnetization  $M = nm / v_0$ , the following actions are performed: the matrix of the effective Hamiltonian with M=e=w=0 is diagonalized, and the macro- (e(B)) and microdeformations (w(B)), and the magnetic moment (5) are calculated. At the next step the obtained values of M, e, w are substituted into the Hamiltonian, and the procedure is repeated (up to five times) to get a steady solution.

The calculations are essentially simplified when making use of symmetry properties of a system. Really we worked with linear combinations of the deformation tensor and the sublattice displacements corresponding to irreducible representations  $A_g$ ,  $B_g$ ,  $E_g$  of the lattice factor group C<sub>4h</sub>. In particular, the magnetic field directed along the crystal symmetry axis *c* brings about only totally symmetric  $A_g$  deformations, and the field in the basal plane induces only  $A_g$  and rhombic ( $B_g$ ) deformations. The corresponding internal  $A_g$  and  $B_g$  deformations are described by three and five independent linear combinations of sublattice displacements, respectively. We used in calculations the low-temperature compliance constants of LiErF<sub>4</sub>

 $(10^{-12}\text{m}^2/\text{H})$ :  $S(A_g11)=7.79$ ;  $S(A_g12)=-2.5$ ;  $S(A_g22)=3.26$ ;  $S(B_g11)=63.2$ ;  $S(B_g12)=24.2$ ;  $S(B_g22)=29.4$ ; and the parameters of a rigid ion model of the lattice dynamics [1–3].



**Fig.1**. Magnetic field dependences of LiHoF<sub>4</sub> magnetization. Solid lines – theory, points– experiment.



**Fig.2**. Temperature dependences of LiHoF<sub>4</sub> magnetization. Solid lines – theory ( $\theta$ =83<sup>0</sup>,  $\varphi$ = –15<sup>0</sup>), points – experiment.

The measured temperature and field dependences of the magnetization in  $LiHoF_4$  and  $LiDyF_4$  single-crystals are compared with results of simulations in Figs.1-3. The calculated angular dependences of the magnetization in the basal plane of  $LiDyF_4$  are shown in Fig. 4.



**Fig.3**. Field dependences of LiDyF<sub>4</sub> magnetization. Solid lines – theory ( $\theta$ =90<sup>0</sup>,  $\phi$ =-5<sup>0</sup>), points – experiment.

Mixing of the ground multiplet with the excited multiplets of a rare earth ion due to spinorbit coupling was taken into account by making use of slightly renormalized matrix elements of Stevens operators and values of Lande factors  $g_J$  (1.22 and 1.3133 instead of 5/4 and 4/3 for pure <sup>5</sup>I<sub>8</sub> and <sup>6</sup>H<sub>15/2</sub> multiplets of Ho<sup>3+</sup> and Dy<sup>3+</sup>, respectively). From fitting the calculated dependences to the experimental data, small corrections for the published earlier crystal field parameters in diluted isomorphic crystals LiYF<sub>4</sub>:Dy and LiYF<sub>4</sub>:Ho were determined (Table 1).



**Fig.4**. Angular dependences of magnetization in the basal plane of LiDyF<sub>4</sub> (T=2 K). The dashed curves correspond to zero magneto-elastic coupling.

p k		Dy <sup>3+</sup> (41	<sup>9</sup> ) <sup>6</sup> H <sub>15/2</sub>	$Ho^{3+} (4f^{10}) {}^{5}I_{8}$		
		This work	Ref. [4]	This work	Ref. [5]	
2	0	170	165	219.7	190.35	
4	0	-85	-88	-87.3	-78.25	
6	0	-4.2	-4.4	-3.55	-3.25	
4	4	-721	-980	-710	-657.2	
4	-4	-661	0	-612	-568.6	
6	4	-390	-427	-387	-364	
6	-4	-248	-65	-253.7	-222.3	

**Table 1**. Crystal field parameters  $B_p^{k}$  (cm<sup>-1</sup>) for LiHoF<sub>4</sub> and LiDyF<sub>4</sub> single-crystals

### Conclusion

As it is seen in Figs.1-3, simulated temperature and magnetic field dependences of the magnetization are in good agreement with experimental results. It follows from calculations that magnetoelastic interactions in double lithium-rare earth fluorides bring about essential contributions to the magnetization in external magnetic fields at liquid helium temperatures. In particular, theory predicts a large anisotropy of the magnetization in the basal plane of  $LiDyF_4$  (see Fig.4) at temperatures lower than 5 K in magnetic fields larger than 0.7 T.

A possible reason for some discrepancies between the calculated and experimental data is the neglect of dependences of compliance constants on temperature and magnetic field and of the interaction between the paramagnetic ions induced by the phonon exchange.

Results of this work are very important for the correct interpretation of the magnetization measurements in very large pulsed magnetic fields [6].

#### Acknowledgements

The work was supported by RFBR (the project 06-02-17241), by Ministry of education and science of Russian Federation (the project RNP 2.1.1.7348) and CRDF (BRHE REC-007).

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### Solid-like component in the spin-spin NMR-relaxation of heavy oils

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At the present time, because of light oil reserve depletion rising attention to production of heavy hydrocarbon raw materials — heavy oil and bitumen. However, size of it production as now remain low all over the world. Few reason of this: high costs on the production and transportation, imperfection of hardware and technological difficulties of such oilfield development. That mainly determined by high viscosity of heavy hydrocarbon raw materials. It's considered to be the case, that oil content of high-molecular asphaltenes [1] and paraffin due to oil viscosity. At the same time, molecules of asphaltenes can be able to aggregate with each other to form supramolecular structures [2], which have characteristics of crystalline state. Also it is well known, that paraffin molecules can be able to form steady supramolecular crystalline structures in the oil.

Since <sup>1</sup>H NMR signals of solids and liquids differ in form of free induction decay (FID) and spin-spin relaxation times  $T_2$ , it's possible to determinate part  $P_S$  of <sup>1</sup>H NMR signal related to oil solids.

It can be assume, that correlation between content of solids in the oil and oil viscosity be exist. The purpose of present work is examination of this assumption.

#### Samples and experimental methods

The investigations of density  $\rho$ , "zero" viscosity  $\eta_0$ , content of asphaltenes and part  $P_S$  of <sup>1</sup>H NMR signal of solid was performed for row of Tatarstan and Vietnamese heavy oil samples. The oil viscosity was measured by capillary viscosimeter under temperature 303 K. Value of "zero" viscosity  $\eta_0$  was determined by approximation of dynamic viscosity value on the zero value of displacement velocity. The content of asphaltenes in the oil was determined by using method of asphaltenes precipitation from oil solution in heptane, in this method we had thirty part of heptane on the one part of oil.

The part  $P_s$  of <sup>1</sup>H NMR signal of solid in the oil was measured by pulse NMR-relaxometer with resonance frequency 19,08 MHz and dead time  $\tau_p = 13 \mu s$  reception channel. It was found that for the all studied oil samples short relaxation time component ("short



component" further) with the FID signal shape of solid exists. This component has relaxation time about 10  $\mu$ s and could not be registered by classical liquid-state NMR approaches and by logging. In order to study this component we use Solid-Echo two-pulse sequence [3] (see Fig.1.). The aim was to determine the population of solid component  $P_S$  for different oils.

In the Table 1 T<sub>2</sub> values and the populations  $P_S$  of the solid component are shown for Tatarstan and Vietnamese oils. As one can see from the table, solid component was found in the all oils. Relaxation time varies in the range from 10 to 30 µs. This is a sufficient difference that could mean different origin of the solid component in the different oils.

Nº well	$\rho, kg/m^{3}$ (T=293 K)	η <sub>0</sub> , Pa·s (T=303K)	P <sub>S</sub> , %	T <sub>2s</sub> , μs
Well 3509 (Tatarstan oil)	904,9	0,105	0,6±0,4	23,9±3
Well 3205 (Tatarstan oil)	923,11	0,108	0,95±0,3	30,2±4
Well 435 (Tatarstan oil)	931,71	0,103	1,4±0,5	13,6±2
Well 3196 (Tatarstan oil)	921,89	0,135	1,65±0,3	12,1±2
Well 3473 (Tatarstan oil)	926,03	0,359	1,9±0,3	17,1±3
Well 3195 (Tatarstan oil)	919,87	0,149	2,1±0,2	25,9±4
Well 4612 (Tatarstan oil)	937,59	0,278	2,4±0,5	13,2±3
Well 3609 (Tatarstan oil)	928,42	0,188	<i>3,4</i> ± <i>0,3</i>	31,2±5
Well 4290 (Tatarstan oil)	939,55	0,343	3,9±0,5	14,6±4
Well 69 (Tatarstan oil)	966,44	1,39	5,3±0,5	19,8±4
"White tiger", well 136 (Vietnamese oil)	898,64	>3	6,6±0,8	12,1±3
"Safonov oil" (Vietnamese oil)	923,8	>>10	45,9±5	9,8±2



Since part  $P_S$  of <sup>1</sup>H signal of NMR solid amount characterize of crystalline formations in the oil, which mainly containing hydrocarbon compound. But it's well known, that most of crystals have more compact packing of molecules in compare with liquid in the nature, and as sequense, more high density. Then we assume correlation can between part  $P_S$  of <sup>1</sup>H NMR signal of solid and density  $\rho$ . The data on the Fig.2 confirms correlation between



density  $\rho$  and  $P_S$  for all samples of Tatarstan heavy oil.

One could assume correlation between population of solid component P<sub>s</sub> both and with viscosity and the amount of asphaltene (fraction with the highest density) in the oil. One can see in Figure 3 that there correlation is no asphaltene between content and  $P_{S}$ . (Note: asphaltene amount was determined as heptane-insoluble fraction). Figure 4 shows that there is no direct correlation between asphaltene amount and viscosity. Hence, we can assert, that asphaltenes are not single molecules, that can be able to crystalline form supramolecular structures., Although, it's presence in the oil have an essential influence on the oil viscosity, other solidstate formations have

a strong influence on the oil viscosity. In particular, oils with a high content of paraffin have a high viscosity under room temperature. For example, Vietnamese oil (well 136), which containing a large amount of crystalline paraffin (up to 6-7%). For this oil, part  $P_S$  of <sup>1</sup>H NMR signal of solid in the oil due to mainly crystalline paraffin and not asphaltenes, it was confirmed by NMR investigations of deasphaltened oils.

At the same time it was found that  $P_s$  correlate quite strong with "zero" viscosity of oil (Fig. 5). This well correlation bringing us to the conclusion that viscosity of heavy oil, which being a colloidal system, mainly determined by content of solid-state formations, independent from nature – asphaltenes or paraffins.



#### **Summary**

Thus, we found correlation between oil viscosity and the amount of the solid-like structures in it. At the same time, absence of the correlation between Ps and asphaltene amount forces us to assume that solid component is determined by the presence of other oil components, more likely paraffin.

Note that the shape of Solid Echo signal and  $T_2$  values were different for different oils, but we are not able to discuss this differences on this stage of the study, because they are small and the signal shape is very complicated. Nevertheless we can say that even small amount of solid component leads to the viscosity change.

Work performed by support of projects CRDF GAP № RUP 1331, РЦКП КГУ and ПВНШ-108.

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# The peculiarities of the of Ni nanoparticles formation in supramolecular system [LiAl<sub>2</sub>(OH)<sub>6</sub>]<sub>2</sub>[Niedta]•4H<sub>2</sub>O studied by Ferromagnetic Resonance Method (FMR)

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#### Annotation

The attention to the dispersed nanomagnets is constantly growing due to its possible applications in biotechnology including usage as drug supports. Application of dispersed nanomagnets in medicine requires a strict set of properties: luck of toxicity, chemical and magnetic stability, monodispersion and nanosize of the particles. The layered double hydroxides (LDH) with intercalated particles of Ni and Co can be used as an appropriate biocompatible material.

In the present work the peculiarities of the behavior of the Ni, Co nanoparticles in layered double hydroxides were investigated using ferromagnetic resonance (FMR) method in the in situ regime under reduction conditions.

#### Theoretical and experimental background

Much of the current study in the field of "physics and chemistry of a solid state" is focused on studying the structure and properties of the magnetic lowsized and nanostructured heterogeneous materials. The trend has clear fundamental and applied motivation as the electronic and magnetic properties of such systems essentially differs from those of massive substance and that allows the creation of new systems for prospective use in high technology fields such as tool making, microelectronics and the chemical industry. Highly dispersed ferromagnetic systems consisting of nanoparticles of ferromagnetic substances are of a great



interest either as catalyst, special magnetic materials, or magnetic carriers for therapeutic products etc.

The surface of a biocompatible material has special functional groups, which are capable of binding therapeutic molecules of medical products (Fig.1). The relatively low active surface area of the existing systems leads to the low binding capacity of the carriers. This results in the binding of larger amounts of such carrier material to the medical product being required in order to achieve the desired therapeutic effects in the human body. Therefore, the development of new systems to carry therapeutic molecules not only on the surface of the biocompatible material, but also in its entire volume would allow the total amount of the ferromagnetic carrier introduced into the organism to be minimized. One such biocompatible material could be layered double hydroxides (LDH).

Layered double hydroxides represent a wide group of inorganic compounds. Quite a large number of LDH contain lithium and aluminium in their structure with a common formula  $[\text{LiAl}_2(\text{OH})_6]_n\text{A}\cdot\text{mH}_2\text{O}$ . The structure of the compounds consists of positively charged bidimentional metal hydroxide layers  $[M^{2+}_{(1-X)}M^{3+}_X(\text{OH})_2]^{Y+}$  or  $[\text{LiAl}_2(\text{OH})_6]^+$  separated with the layers containing both anions  $A^{n-}$  and molecules of water. The layered structure of these compounds is large enough to allow the introduction of both inorganic and organic molecules into the interlayer space. The mass fraction of the interlayered molecules in such compounds can reach over ten percent. It gives an opportunity to use double hydroxides as effective carriers, which allow the binding of therapeutic molecules not only to the surface of a firm body, but also within its entire volume.

During the thermolysis  $[LiAl_2(OH)_6]n[M(edta)] \cdot mH_2O$ , where  $[M(edta)]^{2-}$  (M = Ni, Co) is transition metal complex with ethylenediamminetetraacetic acid (edta), the transition metallic nanoparticles is formed. The metal hydroxide layers transformed to the amorphous lithium aluminate and aluminate oxide.

The Hydroxide matrix  $[LiAl_2(OH)_6]$  restores the layered structure, whose interlayer space can contain various anions after treatment with water solutions. Nitrate ions, which enter the interlayer space during the interaction of the spread out sample with lithium nitrate (LiNO<sub>3</sub>), could be easily substituted with organic ions (in this case on phtalat ions). There is a high probability, that nickel particles will remain stable after all these procedures.



To study the conditions of nickel ferromagnetic particles during the interaction of the thermolyse products with lithium nitrate, we carried out in-situ experiments using the resonator cavity of a EPR spectrometer. For this purpose, the product of the thermal decomposition of Li-Al-Niedta obtained at  $400^{\circ}$ C, was placed in a quartz ampoule in the resonator of the EPR spectrometer followed by the addition of a small amount of a concentrated solution of lithium nitrate.

Fig. 2 shows that the FMR spectrum of nickel for the initial composite represents a symmetric lane with a width of ~ 910G. The addition of a lithium nitrate solution to the substance results in a quick shift (within 1-2 minutes) of the resonant frequency by 250 G aside the strong fields, and also in the decrease of the lane width by 90 G. Increasing the interaction time leads to further changes in both the resonant frequency and the width of the lane. After 15-20 minutes of interaction the changes in the parameters of FMR spectrum are insignificant (Fig.3). The changes in FMR spectrum, most likely, indicate that during this time the restoration of the hydroxide matrixes layered structure is completed. However, it is notable, that the most significant changes in FMR spectrum occur within the ~ 1-5 minutes, indicating that the restoration of a major portion of the hydroxide matrixes occurs during this interval of time.



It was also shown that the influence of water solutions leads to a formation of a hydroxide form of layered double hydroxide  $[LiAl_2(OH)_6](OH)$ , and followed by (OH)-group being substituted with the nitrate ions.

# Electron-acceptor centers of alkali metal modified alumina studied by the anthraquinone as a probe molecule

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Alkali metals are often used for the modification of alumina catalysts, and also of  $Al_2O_3$ based catalysts [1-2]. Their presence on the surface could strongly affect on the acid-base properties and, hence, the catalytic properties. The main goal of this work was to study how a modifying with alkali Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> cations can influence the electron-acceptor sites on the surface of alumina. We applied the method of paramagnetic complexes of probe molecules for investigation. As a probe molecule we chose 9,10-anthraquinone.

After the adsorption of anthraquinone on the surface of studied samples the EPR spectra appeared (Fig. 1). Three different types of spectra have been found:

- 1. The 11-component spectrum with line intensities 1:2:3:4:5:6:5:4:3:2:1, g = 2.0036,  $a = 7.4\pm0.2$  G. This spectrum was analogous to those observed previously on the alumina [3] and alumina modified by LiAl<sub>5</sub>O<sub>8</sub>, MgAl<sub>2</sub>O<sub>4</sub> and boric acid [4, 5], and corresponded to the paramagnetic anthraquinone complex with two equivalent aluminum ions (spin of <sup>27</sup>Al is 5/2).
- 2. The 6-component spectrum with equal intensities, g = 2.0036,  $a = 9.0\pm0.2$  G. This spectrum was analogous to those observed previously on the various aluminas [3, 4], Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> system [6], and corresponded to the paramagnetic anthraquinone complex with one aluminum ion.
- 3. The narrow spectrum, g = 2.0036, peak to peak line width  $8.0\pm0.2$  G. The nature of this spectrum was not clear before because of the absence of hyperfine splitting (h.f.s). In the present investigation the nature of this spectrum for the studied samples is discussed.

In the raw of modifying cations  $Li^+$ ,  $Na^+$ ,  $K^+$  in the equal concentration (0.9 mmol/g Al<sub>2</sub>O<sub>3</sub>) the shape of the spectra noticeably changed. The contribution of 11-component spectrum decreased in this raw, when the contribution of narrow spectrum increased. Thus, the spectra of complexes on the surface of  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> and of Li-modified samples were mainly similar and exhibit h.f.s. of 11-component, for a samples with Na the contribution of the 6component spectrum and of narrow spectrum in the middle appeared, and for K-modified samples these two spectra became dominate. The same changes in the spectra shapes took place, when the Li<sup>+</sup> concentration increased to the 4 mmol/g [7]. Taking into account the mechanism of formation of the paramagnetic anthraquinone complex [4], the appearance of the 6-component EPR spectrum is explained, most likely by a considerable enhancement of the basicity of alkali metal modified alumina. In this case, it can be assumed that the interaction of anthraquinone with Lewis acid sites (LAS) affords only a complex with one coordinatively unsaturated Al<sup>3+</sup> cation, because the strength of electron-acceptor sites is not strong enough for this complex to react with an additional Al<sup>3+</sup> cation. The decrease of the strength of the LAS is also responsible, most likely, for the appearance of a narrow spectrum, which should be attributed to anthrasemiquinone weakly bound with the LAS.

The ENDOR spectra of the anthraquinone complexes of the samples, modified with ions of alkali metals were in good agreement with EPR spectra (Fig. 2). The two broad lines,

denoted by <sup>27</sup>Al<sub>a</sub>, split by twice the <sup>27</sup>Al Zeeman frequency  $2v_1 = 7.8$  MHz in the applied magnetic field and centered at 10.5 MHz, attributed to the 11-line EPR spectra and were observed for complexes with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and with Li<sup>+</sup>/Al<sub>2</sub>O<sub>3</sub>. In the same raw of modifiers (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>) the intensity of lines corresponded to the large proton coupling (8-9 MHz) of the anthraquinone protons (two broad lines centered at 14,9 MHz – Zeeman frequency of <sup>1</sup>H) increased. As it was shown early [5] this pair of lines attributed to the anthraquinone radical, which gave narrow spectrum. According to the obtained data it has been shown that modification with alkali metal led to decrease of the strength of electron-acceptor sites because of their inductive effect (electronic influence) and did not block the acid centers.



**Fig.1**. EPR spectra of anthraquinone adsorbed on the surface of the:  $1-\gamma$ -Al<sub>2</sub>O<sub>3</sub>;  $2-Li^+/Al_2O_3$ ;  $3-Na^+/Al_2O_3$ ;  $4-K^+/Al_2O_3$ .



**Fig.2**. ENDOR spectra of anthraquinone adsorbed on the surface of the:  $1-\gamma$ -Al<sub>2</sub>O<sub>3</sub>;  $2-Li^+/Al_2O_3$ ;  $3-Na^+/Al_2O_3$ ;  $4-K^+/Al_2O_3$ .

For the more detailed investigation of the alkali metal influence on the electron-acceptor centers we studied aluminates LiAl<sub>5</sub>O<sub>8</sub> and α-LiAlO<sub>2</sub>, as a model compounds with desired structure. LiAl<sub>5</sub>O<sub>8</sub> has a spinel-like structure with aluminum ions distributed between octahedral and tetrahedral positions. The three-coordinated aluminum ions formation is possible after the removal of the terminal OH-groups from tetrahedral coordinated aluminum ions (they seems to play a role of Lewis acid Sites on the alumina surface). In the structure of  $\alpha$ -LiAlO<sub>2</sub> there are no three-coordinated aluminum ions, there are only octahedral ions. The spectra of the complexes with the systems with big concentration of lithium (4 mmol/g) were similar to the spectra of the complexes on the surface with aluminates and consisted of 6component spectrum and of a narrow spectrum (Fig. 3). When the temperature of anthraquinone adsorption increased from 120°C to 200°C the concentration of single line decreased and the contribution of 6-component spectrum rose. This fact means that narrow spectrum is less stable, than the spectrum from complex with one aluminum. In the ENDOR spectra of aluminates (Fig. 4) a matrix line from lithium revealed. The intensity of this line was higher for the complexes with  $\alpha$ -LiAlO<sub>2</sub> samples due to higher lithium content. With the help of Q-band EPR it was shown, that narrow spectrum on aluminates was a superposition of

two spectra, one of them should be attributed to anthrasemiquinone weakly bound with the LAS and another was supposed to be concerned with anthrasemiquinone ion pair with lithium cation.



**Fig.3**.EPR spectra of anthraquinone adsorbed on the surface of the:

1 -  $LiAl_5O_8$  at  $120^{\circ}C$ ;

2 - LiAl<sub>5</sub>O<sub>8</sub> at 200°C; 3 -  $\alpha$ -LiAlO<sub>2</sub> at 120°C;

4-  $\alpha$ -LiAlO<sub>2</sub> at 200°C.



**Fig.4**.ENDOR spectra of anthraquinone adsorbed on the surface of the:

1 -  $LiAl_5O_8$  at  $120^{\circ}C$ ;

2 - LiAl<sub>5</sub>O<sub>8</sub> at 200°C; 3-  $\alpha$ -LiAlO<sub>2</sub> at 120°C;

4- 
$$\alpha$$
-LiAlO<sub>2</sub> at 200°C.

We managed to obtain distinct HYSCORE spectra of anthraquinone complexes on the surface of lithium aluminates. The HYSCORE spectra of anthraquinone adsorbed on  $\alpha$ -LiAlO<sub>2</sub> are depicted on the Fig. 5-6. They both clearly showed the presence of the pair of cross-peaks, centered on the Zeeman frequency of <sup>7</sup>Li, equal 5.7 MHz in the field of 3450 G). Thus with the help of HYSCORE technique we showed the presence of h.f.s. from the lithium in the spectra, that was not revealed in the X-band EPR. Thus in the case of aluminates one of the narrow spectra could be also attributed to the anthrasemiquinone ion pair with lithium.

It has been shown that alkali metal ions decreased the strength of electron-acceptor centers due to the inductive effect. As a result the concentration of anthraquinone complex with two Lewis acid sites (LAS) decreased, when the concentration of complex with one LAS increased with the increasing of alkali metal content. At large alkali metal concentration other kind of anthraquinone paramagnetic complexes are formed, that are anthrasemiquinone weakly bonded with LAS as well as anthrasemiquinone ion pair with alkali metal cation (lithium).



**Fig.5**. HYSCORE spectra of anthraquinone adsorbed on  $\alpha$ -LiAlO<sub>2</sub>, obtained at the maximum of the EPR signal at  $\tau$ =180 ns.

**Fig.6**. HYSCORE spectra of anthraquinone adsorbed on  $\alpha$ -LiAlO<sub>2</sub>, obtained at the maximum of the EPR signal at  $\tau$ =200 ns.

This work was supported by the Federal Agency on the Science and Innovations (State Contract 02.451.11.7012 of August 29, 2005), the Concil on Grants of the President Of the Russian Federation (Program of State Support for Leading Scientific Schools of the Russian Federation, Grant RI-112/001/056) and the Russian Foundation for Basic Research (Project No. 06-03-32830a).

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# Spin relaxation of electrons localized on shallow and deep donor centers in silicon with different isotopic composition

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At present there is again a great interest in the relaxation processes in spin systems since it is connected with developing of spintronics and perspectives of building quantum computers on the basis of <sup>28</sup>Si:P or GaAs quantum dots [1]. Silicon differs advantageously from GaAs by the fact that the enrichment of silicon by the <sup>28</sup>Si isotopes makes it a spinless material. Therefore in case of silicon quantum computer models the condition of spin coherency at quantum operations can be realized easier than for GaAs which is caused by a significant increasing of spin relaxation time and spin dephasing time at the isotopic enrichment. An appearance of opportunity to work with the isotopical enriched crystals give us a possibility to investigate a series of new effects in relaxation processes. One of them is a predicted by us [2] linear dependence of the superhyperfine interaction contribution of the electron localized on the intrinsic vacancy defect (V<sup>-</sup>) and the iron impurity (Fe<sup>+</sup>) in silicon to the EPR line width on the concentration of <sup>29</sup>Si nuclei having nonzero spin. It is well known that interaction of electron spins with nuclear spins gives most significant contribution to the spin relaxation rate at low temperatures. The enrichment of silicon by isotopes with zero nuclear spin and taking into account the linear contribution of superhyperfine interaction to the line width will give less contribution to the spin relaxation rate compared to other relaxation processes.

There is an opinion in the literature that the contribution of the ligand superhyperfine interactions to the line width for paramagnetic centers in solids has a square- root behavior. In Ref. [3] we suggest such a behavior for phosphorus shallow donors in silicon in contradiction to deep centers reported in Ref. [2]. Using the methods described in Ref. [2] we calculated the contribution of the ligand superhyperfine interactions to the line width for the phosphorus donor electron in silicon. For calculations the superhyperfine constants for the phosphorus center in silicon obtained by electron-nuclear double resonance (ENDOR) in Ref. [4] were used. For improvement of the results we have taken into account the changing of the line shape with changing of nuclei concentration by applying the deconvolution methods for finding the inhomogeneous contribution of the superhyperfine interaction to the calculated line shape. As can be seen from Fig.1 the calculated dependence become linear at concentrations of magnetic nuclei below 3%. Hence, in case of shallow donor center the deviation from square root law can be also obtained, but at a lower concentration in comparison with the deep centers. More rapid linear behavior of this dependence leads to longer times of spin system dephasing at isotopic enrichment with zero spin isotope of silicon. The line widths so far measured for phosphorus in monoisotopic silicon-28 samples have a great dispersion of values (0.022 mT [4], 0.008 mT [5], 0.045 mT [3]). It means that measured values depend on the history of samples and therefore on the action of additional relaxation mechanisms. Among them could be combined spin-spin and spin-lattice relaxation with participation of other defects. We studied spin-lattice relaxation processes in chromium doped silicon samples enriched by <sup>28</sup>Si isotope and with natural isotopic abundances.



**Fig.1**. Dependence of the full width at half maximum (FWHM) of EPR lines of P and Fe<sup>+</sup> centers in silicon on magnetic nuclear <sup>29</sup>Si concentration.

From the temperature dependencies of the EPR line width and continuous saturation experiments we obtained spin-lattice relaxation rates in the wide temperature range for silicon samples with different isotopic composition doped by chromium. We investigated samples of monoisotopic silicon ( $^{28}$ Si-99.873%, FZ-grown) doped by chromium at the range of concentrations  $2.5 \cdot 10^{15} - 1.5 \cdot 10^{16}$  cm<sup>-3</sup>, and samples of natural silicon (Chohralsky grown) with chromium ions concentration  $2 \cdot 10^{15} - 8 \cdot 10^{15}$  cm<sup>-3</sup>. The dependences of spin-lattice relaxation rate ( $T_1^{-1}$  (T)) are shown in Fig.2.



**Fig.2**. Dependencies of spin-lattice relaxation rate for chromium ions Cr<sup>+</sup> on temperature in silicon with different isotopic composition.

To explain the obtained temperature dependencies of the spin-lattice relaxation rate for silicon doped by chromium we have considered spin-relaxation model represented in Fig.3. For monoisotopic silicon-28 sample for investigated temperature range the obtained dependence can be described by Bloum-Orbach relaxation process [6] (Fig. 3a). In this case it is enough to take in account only the relaxation channel "Spin A – phonons – thermostat" and neglect "phonons – thermostat" energy transfer time to fit the dependence ( $T_1^{-1}$  (T)). But for



Fig.3. Model of spin relaxation processes in silicon.

samples with natural isotopic composition the dependencies couldn't be correctly described by only one relaxation process. For less chemically and isotopically purified samples one need to additional consider relaxation channels, such as "Spin A – Spin B phonons – thermostat". The second channel may be more effective than the first one only if spins "B" transfer their energy to the phonon subsystem faster than "A" spins. However, as the "Spin A

– Spin B" interaction is a dipolar one and has characteristic time of interaction, the mentioned relaxation channel is effective only in definite temperature range, when dipole-dipole interaction time is shorter than "Spin B – phonons" energy transfer time. In this case, the spin-lattice relaxation rate can be expressed as:

$$(T_A)^{-1} = \left(\frac{(T_{12}' + T_{12}'')^{-1}}{\gamma'(2\pi)^2 \Delta v_{dip}^2} + \frac{1}{(T_{12}' + T_{12}'')^{-1}}\right)^{-1} + (T_1 + T_1')^{-1}$$

where  $(T_{12})$ ,  $(T_1)^{-1} \sim \alpha T$  – phonons transfer rates,  $(T_{12})^{-1}$ ,  $(T_1)^{-1}$  – spin-phonon energy transfer rate,  $\gamma$  – gyro-magnetic ratio,  $\Delta v_{dip}^2$  – dipole-dipole contribution to the line width. For the samples of natural isotopic composition for which dependence of spin-lattice relaxation rate at T higher than 77 K has a linear behavior. The relaxation rate at high temperatures is defined mostly by phonons transfer rate and in the quasidiffusion regime leads to linear law [7]. The results of fitting are shown in Fig.3b. For low temperature range the parallel channel of relaxation via dipole interaction with spins "B" becomes more effective. To explain the value of relaxation rate at 10K it was necessary to take in account Orbach processes that can be evidence of complicated multilevel electronic structure of center B.



**Fig.4**. Dependencies of spin-lattice relaxation rate for chromium ions Cr<sup>+</sup> on temperature in isotopically enriched (a) and natural (b) silicon. The solid line represents the results of fitting.

One can believe that parallel channel of relaxation could be a cause of obtained spinlattice relaxation rate dependence on the concentration of chromium ions in the monoisotopic silicon samples (insert in Fig.2), for which the concentration of chromium ions is comparable with that one of "B" spins. The interaction of chromium ions with these centers increases the effectiveness of spin-lattice relaxation. In that case when concentration of "B" spins is lower than that one of chromium ions only small part of them relaxes effectively that is negligible in comparison with more durable spin-lattice relaxation of major part of ions which don't interact with impurity. Oxygen concentration in investigated sample of natural silicon is 10<sup>18</sup> cm<sup>-3</sup>, and 10<sup>15</sup> cm<sup>-3</sup> in monoisotopic one, thus we suppose that "B" spin is a center bound with oxygen, spin-lattice relaxation rate of which is higher than that one of chromium ions.

This work was supported in part by RFBR, grant № 05-02-16449.

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# Ferromagnetism in thin films of germanium and silicon supersaturated by manganese or iron impurities

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Diluted magnetic semiconductors (DMS) based on diamond-like crystals doped with 3d irongroup impurities with ferromagnetic ordering of the spins of 3d ions are promising materials for spintronics. Previously Danilov et al. [1, 2] demonstrated the possibility of the laser synthesis of 30-100 nm in thickness epitaxial layers of DMS GaSb:Mn and InSb:Mn with the Curie temperature  $T_c$  above 500 K and of InAs:Mn with  $T_c$  no lower than 77 K. DMS based on elementary Ge and Si semiconductors doped with 3d-impurities are of particular interest for spintronics, due to compatibility with the most wide-spread silicon solid electronics. Epitaxial Ge:Mn layers with 5% manganese were obtained by Park et al by the molecularbeam epitaxy method [3]. The ferromagnetism was manifested in nonlinear and hysteresis dependence of the magnetization and anomalous Hall effect (AHE) on the magnetic field up to a temperature 116 K. In [4] the ferromagnetism in thin silicon layers with 0.8 at % of the ion implanted manganese was observed up to temperature 400 K.

In the present work we report first successful application of laser deposition for synthesis of 50-100 nm Ge and Si layers, supersaturated with manganese or iron. The iron and manganese concentrations were up 10-15 at % and the samples manifested considerably more high-temperature ferromagnetic spin ordering than previously reported. The ferromagnetism of films has been confirmed by the observation AHE, ferromagnetic resonance (FMR) and Magnitooptic Kerr effect (MOKE) at temperatures 77-500 K.

Iron and manganese as dopants were chosen on the basis of our previous investigation of regularities in recharge levels of 3d-atoms in diamond-like semiconductors [5]. Analysis of the similar regularities for the 3-d impurities in the  $A^3B^5$  the semiconductors shows, that GaSb, InSb and InAs are favorably over, e.g., GaAs as a base of the DMS, due to a lower electron work function in the first case [2, 3]. Manganese substituted for Ga or In in these compounds has high spin state favorable for ferromagnetism. It also have high acceptor activity even at low temperatures and is efficient source of holes for valence band of a crystal. It is important for the Ruderman-Kittel-Kasuya-Yosida (RKKY) ferromagnetic exchange interaction between magnetic ions. According to the family of levels for 3d substitution ions in Ge and Si, the most preferable situation for maximal spin S=5/2 and S=4 and ferromagnetic spin ordering occurs for iron and manganese.

Ge:Mn, Si:Mn, and Si:Fe layers were deposited on single crystal wafers of semiinsulating gallium arsenide or sapphire by laser sputtering. The substrate was heated to 200-480°C. A pulsed AYG:Nd laser was used for sputtering of the semiconductor and metallic (Mn or Fe) targets. The laser radiation wavelength is 1.06  $\mu$ m, a pulse energy is 0.2 J, and a pulse duration is 12 ns. The DMS layer thickness was ranged from 30 to 200 nm. The content of 3d-impurity was controlled by the x-ray spectrum analysis with electron excitation. A He-Ne laser with a wavelength 0.63  $\mu$ m was used for MOKE investigations at 293 K. The FMR was studied at a frequency of 9.3 GHz in the temperature range 77-500 K for various orientations of the external magnetic field. Field value was up to 0.66 T. The differential Hall effect was measured at 77-293 K in a weak alternating magnetic field with amplitude of  $5 \cdot 10^{-3}$  T and a frequency of 50 Hz in combination with a magnetic field slowly varying within  $\pm 0.4$  T, both fields are perpendicularly oriented to a sample plane.

Both MOKE, and AHE, and FMR measurements have demonstrated the ferromagnetic behavior of Si:Mn layers on GaAs substrate at room temperature. The films of Ge:Mn on GaAs substrate revealed the ferromagnetism in AHE and FMR. In these two DMS the introduction of a 3d-impurity leads to significantly high hole conductivity. The hysteresis of AHE in Ge:Mn, Si:Mn and Si:Fe at 77 K, non-linear dependencies of Hall effect at room temperature was observed in magnitotransport measurements. The concentration of holes p and their mobility  $\mu$  at 293 K was determined by measurements of resistivity  $\rho$  and Hall factor at the maximal field. We obtained the following data: for Ge:Mn (with the x-ray spectral content of manganese  $N_{Mn}$ =13 at %) p=6.6·10<sup>19</sup> cm<sup>-3</sup>,  $\mu$  =23 cm<sup>2</sup>/V·s,  $\rho$ =0.004  $\Omega$ ·cm, for Si:Mn with  $N_{Mn}$ =15 at % p=7.5·10<sup>20</sup> cm<sup>-3</sup>,  $\mu$  =33 cm<sup>2</sup>/V·s,  $\rho$ =0.00025  $\Omega$ ·cm. Evidently in the both cases manganese exhibits a surprising high electric activity as a shallow acceptor with an inserted concentration of holes up to 10 % of Mn content. The acceptor action with low activation energy is consistent with the expected behavior of manganese in substitution site of Ge or Si. Hence, embedding of a 3d-impurity in a crystal lattice during laser deposition of nanometer layers is significantly different from that in the case of bulk crystal doping. Previously [6] it was established that in the case of silicon matrix such impurities is mainly dissolved in the interstitial crystal positions with limiting solubility  $\approx 10^{16}$  cm<sup>-3</sup> and basically shows the donor properties. In our Si:Mn films the concentration of holes  $(7.5 \cdot 10^{20} \text{ cm}^{-3})$  is particularly great, and their mobility is one and half time higher than in Ge:Mn films where p is less by one order of value. In both cases the mobility of current carriers is much higher than that in metals.

The observed strong anisotropy of the spectra FMR for Ge:Mn and Si:Mn films (Fig.1) indicates the presence of an inner magnetic field comparable with external magnetic field and



**Fig.1.** The first derivatives of FMR absorption spectra for Si:Mn 50 nm thick films and for Ge:Mn 75 nm thick film at room temperature. The numbers above the lines are the angles (in degrees) between the sample plane and the magnetic field.

caused by geometry of a flat sample. The spectra for normal orientation are shown in Fig.2 for different temperatures. The single line with smooth temperature transition (up to  $\approx$ 420 K) from FMR to electronic paramagnetic resonance was observed in the case of Ge:Mn. Such transition is a consequence of the thermal destruction of spin ordering of manganese magnetic ions. As well as in the case of GaSb:Mn the shift FMR field is non-monotonic with the temperature. It have a maximum at 256 K for the case of Ge:Mn. The line amplitude falls down below 256 K.



**Fig.2** The FMR spectra of the samples Si:Mn and Ge:Mn (same as in Fig.1), oriented perpendicularly to the magnetic field for different temperatures. The numbers at the right are the temperature in K.

In the case of the Si:Mn the FMR spectrum consists of two or more resonant peaks. It is not the of spin waves resonance spectrum, because in the case of spin wave resonance the amplitudes of the lines have the opposite order with the increase of the external field. The variation of the content of manganese and the thickness of a film lead to the change of the ratio of amplitudes of peaks, but do not change their position. The peaks cannot be due to ferromagnetic inclusions. Only one weak ferromagnetic manganese silicide with the Curie point 29 K is known [7, 8] and metal Mn is antiferromagnet. So, most likely, the observable FMR peaks in our Si:Mn samples are caused by the presence of domain structure in DMS films. The FMR of Si:Mn layers take place up to temperatures ≈500 K. As in the case of Ge:Mn, there is a temperature shift of FMR lines to smaller fields and a reduction of their intensity. Supposing that each Mn ion has spin 5/2, one can calculate the manganese concentration  $(N_{Mn})$  using the data in Fig.2, as it had been done in [2]. So we estimate the concentration of magnetic ions of manganese as  $2.6 \cdot 10^{21}$  cm<sup>-3</sup> or 5.9 at % in relation to germanium in Ge:Mn at 256 K. That is that 45% of Mn atoms K show the magnetic activity at 293. Similar estimations for Si:Mn (Fig.3) give  $N_{Mn}=1.8\cdot10^{21}$  cm<sup>-3</sup> for the first FMR peak and 2.8·10<sup>21</sup> cm<sup>-3</sup> for the second one. The part of magnetically active manganese ( $\approx$ 9 at %) is much higher, than in layers Ge:Mn and constitutes 3/5 from x-ray spectral contents of this impurity (15 at %). The shift of FMR lines to the right with a decrease of temperature shows, that, practically all manganese is probably magnetically active (Fig.2).

Promising results were obtained for Ge:Fe and Si:Fe layers deposited on single crystal sapphire substrates. AHE and FMR are pronounced at 77 K, the FMR of Si:Fe was observed up to 220 K. The ferromagnetism of Si:Fe layers on the same substrates is stronger than that for Ge:Fe layers. The amplitude of FMR spectrum for Si:Fe/Al<sub>2</sub>O<sub>3</sub> was five times more intensive, than that for Ge:Mn/Al<sub>2</sub>O<sub>3</sub> at thickness about 50 nanometers. Fig.3 shows the strong anisotropy of the spectrum for Si:Fe/Al<sub>2</sub>O<sub>3</sub> at 77 K. The concentration of magnetically active iron atoms in silicon is near  $10^{21}$  cm<sup>-3</sup> at 77 K. The layers have a high hole



**Fig.3.** The angle dependencies of FMR for the Si:Fe/Al<sub>2</sub>O<sub>3</sub> films at 77 K. The numbers above the curves are the angles (in degrees) between the sample plane and the direction of the magnetic field

conductivity, the resistivity of Si:Fe layers does not exceed the value  $10^{-3} \Omega$ ·cm at 77 and 300 K.

Thus, we demonstrated the possibility of laser synthesis of thin layers of elementary semiconductors supersaturated by 3d-impurities Ge:Mn and Si:Mn with the Curie point much higher than room temperature as well as Ge:Fe and Si:Fe with the Curie point not below 77 K and 220 K, respectively. In the nonequilibrium thermodynamics terms laser formation of the supersaturated solid solution of the 3d-impurity in Ge and Si elementary semiconductors is no worse than the ion beam doping used in [4] to form Si:Mn ferromagnetic layers.

This work was supported by the State Program "Universities of Russia", grant No.513 (UR01.01.174), and the Russian Foundation for Basic Research, grant 05-02-17362, RAS Program "Spin-dependent effects in solids and spintronics" and grant ISTC G1335.

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### An EPR monitoring of isomerism and coordination sphere dynamics in fivecoordinated pincer nickel complexes

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Pincer complexes consist of a metal center and a pincer skeleton. The pincer skeleton is a tridentate ligand which is connected to the metal *via* a metal–carbon  $\sigma$ -bond and two coordinative bonds. The most common type of pincer skeleton is an aryl fragment having two arms as substituents in aryl 2,6-positions. Due to the rigid chelating skeleton providing excess electron density on the metal, this class of complexes determines its specific properties. First discovered in the early 1970s, the chemistry of pincer complexes has been extensively developed over the last ten years. This class of compounds has found application in wide range of organic syntheses as catalysts [1, 2] and is fundamental to the creation of new materials such as gas sensors, switches, self assembling dendrimers, *etc.*[3].

o-Semiquinone ligand is a radical anion of o-quinone containing an unpaired electron in  $\pi$ -aromatic system. It coordinates to metal through two oxygen atoms forming five-membered chelate ring. It has already been used as a spin label for EPR spectroscopy [4]. In many cases it has allowed us to study structural features and dynamic processes occurring in the inner coordination sphere of complexes in solution [4, 5]. It is also a useful tool to investigate thermodynamic and kinetic parameters of inner-sphere dynamics [6]. Tautomeric interconversions of o-semiquinonic complexes were studied as well [7].

Here we report a new five-coordinated spin-labeled *o*-semiquinonic, *o*-iminosemiquinonic, catecholate and di-halogen PCP- and NCN-pincer nickel complexes.

*o*-Semiquinonic and catecholate nickel complexes with different pincer ligands have been obtained using exchange reaction of nickel organohalogenides with corresponding thallium salts:



Complex	ER <sub>2</sub>	SQ	Complex	ER <sub>2</sub>	SQ	Complex	ER <sub>2</sub>	SQ
1	PPh <sub>2</sub>	O O Bu <sup>t</sup>	7	PPh <sub>2</sub>	O O Bu <sup>t</sup> Bu <sup>t</sup>	13	N	O O Bu <sup>t</sup>
2	PPh <sub>2</sub>	$O$ $F$ $F$ $Bu^{t}$ $F$ $Bu^{t}$	8	PPh <sub>2</sub>	O O $Br$ $Bu^t$	14	N	O O Bu <sup>t</sup> Bu <sup>t</sup>
3	PPh <sub>2</sub>	O = OMe O = OMe $Bu^{t}$	9	PPh <sub>2</sub>	O NO <sub>2</sub> Bu <sup>t</sup>	15	N	O O Bu <sup>t</sup> OMe

Table 1. The notation of complexes 1-18.


It was found using EPR spectroscopy and X-ray diffractometry that complexes 1-17 have a structure of square pyramid [8, 9]. Complexes 4, 5, 7 - 11, 14 with asymmetrical *o*-semiquinones exist in solution in a form of two interconverting geometry isomers:



Isomers equilibrium is controlled by entropy factor. For 7, 8, 10, 11 an activation parameters ( $\Delta H^{\#}$  and  $\Delta S^{\#}$ ) have been estimated [9].

In the case of NCN complexes 13 - 17 [10] the spin density is shifted from *o*-semiquinone to the metal fragment in a great extent that this one in 1, 7, 4, 6, 5. Also, the mesomeric donor groups in 2 - 5, 15, 17 decrease such shift whereas withdrawal substituent in 6 and 16 increase this shift [8-10]. In complex 16 spin density is even localized on metal forming catecholate of nickel(III) [10].

Complex **18** have a square plane structure with bidentate coordination mode of pincer fragment. Most probably, it is caused by sterical reasons.

The mixed halogen NCN-pincer complexes **19** and **20** have been obtained by oxidation of monohalogen precursor by appropriate compounds:



It was found by X-ray diffractometry that complex **19** have a square pyramid structure. It was shown by EPR that this complex exists in solution as a mixture of two isomers as the *o*-semiquinonic complexes:



In opposite site, complex 20 exists in a form of only one of isomers, with apical iodine atom. Most probably, it is caused by sterical reasons.

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## Multiple quantum NMR dynamics in spin systems in dipolar ordered state

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Multipe-quantum (MQ) NMR spin dynamics in solids [1] is a powerful tool for the investigation of structure and dynamical processes in solids, counting the number of spins in impurity clusters [2] and the simplification of ordinary NMR spectra [3]. Although MQ NMR was successful in a lot of applications and experimental methods of MQ NMR have been developed adequately, the theoretical interpretation of many-spin MQ NMR dynamics is restricted by the phenomenological approach [1]. A systematic quantum-mechanical approach was developed [4]-[6] only for onedimensional systems in the approximation of nearest neighbor dipolar interactions. Up to now the thermodynamycal equilibrium density matrix in a strong external magnetic field has been considered as the initial condition for these experiments and theoretical interpretations. Recently, it has been suggested [7] to consider the dipolar ordered state as the initial state for such experiments. It is well known that the dipolar ordered state can be prepared using the method of adiabatic demagnetization in a rotating frame (ADRF) [8,9] or with the Jeener-Brokaert (JB) twopulse sequence [8,10]. As a result of such initial condition, many-spin correlations appear faster than in the ordinary MQ NMR experiments in solids [1] and some peculiarities of MQ dynamics can be investigated with these experiments. Of course, it is necessary to make some changes in the scheme of the standard experiment in order to obtain non-zero signals of MQ coherences.

In the present work we consider MQ NMR dynamics when the initial condition is determined by the dipolar ordered state. However, the observable is the longitudinal magnetization as in the usual MQ experiments. MQ NMR dynamics in the suggested experiment is strongly different from the standard one [1]. In particular, the sum of intensities of MQ coherences of arbitrary opposite orders equals zero in contrast to the usual MQ NMR experiments where these intensities are equal. It is interesting to underline that the phases of signals of MQ coherences are shifted over  $\pi/2$  in comparison with the signals of the standard experiments [1]. Computer simulations of such experiments for linear chains containing up to eight spins are presented in this paper.

We consider a system of nuclear spins (s = 1/2) coupled by the dipole-dipole interaction (DDI) in a strong external magnetic field. The secular part of the DDI Hamiltonian [8] has the following form

$$\boldsymbol{H}_{dz} = \sum_{j < k} \boldsymbol{D}_{ik} \left[ \boldsymbol{I}_{jz} \boldsymbol{I}_{kz} - \frac{1}{4} (\boldsymbol{I}_{j}^{+} \boldsymbol{I}_{k}^{-} + \boldsymbol{I}_{k}^{-} \boldsymbol{I}_{j}^{+}) \right]$$
(1)

where

$$\boldsymbol{D}_{jk} = \frac{\boldsymbol{\gamma}^2 \hbar}{\boldsymbol{r}_{jk}^3} (1 - 3\cos^2 \boldsymbol{\theta}_{jk})$$

is the coupling constant between spins j and k,  $r_{jk}$  is the distance between spins j and k,  $\gamma$  is the gyromagnetic ratio,  $\theta_{jk}$  is the angle between the internuclear vector  $r_{jk}$  and the external magnetic field  $\overrightarrow{H_0}$  is directed along the axis z.  $I_{j\alpha}$  is the projection of the angular spin momentum operator on the axis  $\alpha$  ( $\alpha = x, y, z$ );  $I_j^+$  and  $I_j^-$  are the raising and lowering operators of spin j.

The basics scheme of MQ NMR experiments consists of four distinct periods: the preparation, free evolution, mixing and detection [1]. MQ coherences are created by the multipulse sequence consisting of eight-pulse cycles on the preparation period [1]. In the rotating reference frame [8] the average Hamiltonian, describing spin dynamics in the preparation period can be written as [1]:

$$H_{MO} = H^{(2)} + H^{(-2)}, \qquad (2)$$

where

$$\boldsymbol{H}^{(\pm 2)} = -\frac{1}{4} \sum_{j < k} \boldsymbol{D}_{jk} \boldsymbol{I}_{j}^{\pm} \boldsymbol{I}_{k}^{\pm}$$

The density matrix of the spin system at the end of the preparation period is

$$\rho(\tau) = U(\tau)\rho(0)U^+(\tau),$$

where

$$\boldsymbol{U}(\boldsymbol{\tau}) = \exp(-i\boldsymbol{\tau}(\boldsymbol{H}^{(2)} + \boldsymbol{H}^{(-2)}))$$

and  $\rho(0)$  is the initial density matrix of the system. Usually the thermodynamic equilibrium density matrix is used as the initial one for MQ NMR experiments. Here we consider MQ NMR dynamics with the initial dipolar ordered state when the Hamiltonian of the system is determined by Eq.(1).

We introduce  $\varphi_y$ -pulse turning spins around the axis y on the angle  $\pi/4$  after the preparation period. Without this additional pulse it is not possible to obtain a nonzero signal at the end of the MQ NMR experiment. As a result, we have the following expression for the observable signal

$$\boldsymbol{I}_{z}(\tau,t) = \boldsymbol{T}\boldsymbol{r} \left\{ \boldsymbol{e}^{-i\boldsymbol{\varphi} \ \boldsymbol{I}_{y}} \boldsymbol{U}(\tau) \boldsymbol{H}_{dz} \boldsymbol{U}^{+}(\tau) \boldsymbol{e}^{i\boldsymbol{\varphi} \ \boldsymbol{I}_{y}} \boldsymbol{e}^{i\boldsymbol{\delta} \ \boldsymbol{I}_{z}} \boldsymbol{U}(\tau) \boldsymbol{I}_{z} \boldsymbol{U}^{+}(\tau) \boldsymbol{e}^{-i\boldsymbol{\delta} \ \boldsymbol{I}_{z}} \right\}, \quad (3)$$

where  $\delta$  is the frequency offset on the evolution period of the duration t which is a result of applying the TPPI method [1].

Density matrix  $\rho_{MQ}(\tau)$  at the end of the preparation period can be represented as follows:

$$\boldsymbol{\rho}_{MQ}(\tau) = \boldsymbol{U}(\tau)\boldsymbol{I}_{z}\boldsymbol{U}(\tau) = \sum_{n} \boldsymbol{\rho}_{n}(\tau) \,. \tag{4}$$

The term  $\rho_n(\tau)$  is responsible for MQ coherence of the n-th order. The observable signal can be presented as

$$\boldsymbol{I}_{z}(\boldsymbol{\tau},\boldsymbol{t}) = \sum_{n} e^{-in\delta t} \boldsymbol{J}_{n}(\boldsymbol{\tau}) = \sum_{n} e^{in\delta t} \boldsymbol{J}_{n}^{*}(\boldsymbol{\tau}) = \sum_{n} e^{-in\delta t} \boldsymbol{J}_{-n}^{*}(\boldsymbol{\tau}).$$
(5)

The intensity,  $J_n(\tau)$ , of MQ coherence of the n-th order is

$$\boldsymbol{J}_{n}(\boldsymbol{\tau}) = \boldsymbol{T}\boldsymbol{r} \{\boldsymbol{A}(\boldsymbol{\tau})\boldsymbol{\rho}_{n}(\boldsymbol{\tau})\},\$$

where

$$A(\tau) = e^{-i\varphi I_y} U(\tau) H_{dz} U^+(\tau) e^{i\varphi I_y}$$

From (5) follows that

 $\boldsymbol{J}_{n}(\boldsymbol{\tau}) = \boldsymbol{J}_{-n}^{*}(\boldsymbol{\tau})$ 

Expanding the density matrix,  $\rho_{MQ}(\tau)$ , in the Taylor series over the parameter t, one can prove [11] that

$$\boldsymbol{J}_{n}(\boldsymbol{\tau}) + \boldsymbol{J}_{-n}(\boldsymbol{\tau}) = 0 \tag{6}$$

Eq.(6) allow us to conclude that  $J_n(\tau)$  is imaginary for all  $n \neq 0$ . Thus, the phases of the MQ NMR coherences in this experiment are shifted by  $\pi/2$  from the signals of usual MQ NMR [1]. It is well-known that in the usual MQ NMR experiments the sum of the intensities of all MQ



**Fig.1**. (a) time dependence of the intensities of the sixth order MQ coherences in a linear chain of six spins coupled by the DDI: the intensity of MQ coherence of the sixth order (solid) for  $\rho(0) = I_z$ ; Im $(J_{-6})$  (dash) for  $\rho(0) = H_{dz}$ .

(b) time dependence of the intensities of the sixth order MQ coherences in a linear chain of eight spins coupled by the DDI : the intensity of MQ coherence of the sixth order (solid) for  $\rho(0) = I_z$ ; Im $(J_{-6})$  (dash) for  $\rho(0) = H_{dz}$ . The intensity of MQ coherence of the eighth order is equal to 0. The insets show that the MQ coherence appears little earlier than in the usual MQ NMR.

coherences does not depend on time [12]. Here this law has a specific form. According to Eq.(6) the sum of intensities of orders –n and n is equal to zero for all n.

The numerical calculations are performed for MQ dynamics of linear chains consisting of 6 and 8 spins. The DDI constant of the nearest neighbors is chosen to be  $D=1c^{-1}$ . Then the DDI constant of spins j and k is  $D_{jk} = D/|j-k|^3$ . We introduce normalized intensities of MQ coherences  $\text{Im}\{J_n\}/\{Tr(I_z)^2 Tr(H_{dz})^2\}^{1/2}$ . The dependence of normalized intensities of MQ coherences on dimensionless time in spin chains containing six and eight spins is presented in Fig.1. It is clear that MQ coherence of the sixth order in a linear chain of six spins appears little earlier than in the usual MQ NMR. This can be seen in the inset of Fig.1a. An analogous tendency takes place for the linear chain containing eight spins (Fig.1b). This peculiarity is connected with the initial dipolar ordered state. The numerical calculations confirm the results obtained in the previous section. In particular, the computer simulations yield the following: i) all intensities,  $J_n(n \neq 0)$ , are imaginary, ii)  $J_0 \equiv 0$ ,  $J_n + J_{-n} = 0$ . The growth of MQ coherences in time occurs in accordance with the condition  $J_n + J_{-n} = 0$  for all n.

Thus, the growth of MQ coherences in the systems with dipolar ordered state has some peculiarities which are related to the initial spin correlations. The spin-lattice dipolar relaxation in such systems is slower than the Zeeman one and it does not hamper the investigations of the MQ NMR coherences of high orders.

We are grateful for financial support for this work through a grant from the Russian Foundation for Basic Research (grant no. 04-03-32528).

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# NMR study of quasi-1D magnetic chain in cuprates LiCu<sub>2</sub>O<sub>2</sub> and NaCu<sub>2</sub>O<sub>2</sub>

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## Abstract

NMR investigation of magnetic structure and phase transitions in two isostructural quasi-onedimensional cuprates  $LiCu_2O_2$  and  $NaCu_2O_2$  has been performed. While  $LiCu_2O_2$  exhibits a magnetic phase transition at  $T_c = 24$  K,  $NaCu_2O_2$  orders magnetically at around 13 K.<sup>6,7</sup>Li and <sup>23</sup>Na NMR spectra in  $LiCu_2O_2$  and  $NaCu_2O_2$ , respectively, provide an unambiguous experimental evidence that below  $T_c$  an incommensurate in-chain helical spin structure is established in both compounds. However, the features of the observed low temperature NMR are different pointing to different properties of the helical magnetic structure.

## Introduction

The quasi-1D spin chain cuprate LiCu<sub>2</sub>O<sub>2</sub> exhibits a unique sequence of phase transitions at T = 24, 22.5 and 9 K [1,2] resembling the "Devil's staircase" type behaviour. Recently we have obtained the first NMR evidence for a low temperature incommensurate (IC) in-chain spin structure in LiCu<sub>2</sub>O<sub>2</sub> [3]. It was shown that below the magnetic ordering temperature T<sub>c</sub> = 24 K the <sup>7</sup>Li NMR lineshape is determined by a IC static modulation of the local magnetic field caused by spin structure of Cu magnetic moments twisted along the chain axis [3]. This result was confirmed by NMR spectra measurements on the <sup>6</sup>Li isotope as well as by neutron diffraction study [4].

The larger ionic radius of Na<sup>1+</sup> (0.97 Å against 0.68 Å of Li<sup>1+</sup>) favors the higher degree of in-chain crystallographic order and hence increasing one-dimensionality of magnetic properties in NaCu<sub>2</sub>O<sub>2</sub>. This results in lower magnetic ordering temperature  $T_c = 12.6$  K [5] and lower values of local magnetic fields in the ordered state. In this paper we report first <sup>23</sup>Na NMR measurements which confirm the existence of incommensurate magnetic structure in NaCu<sub>2</sub>O<sub>2</sub> at 3 K also seen by  $\mu$ SR [5]. The unusual magnetic properties of 1D chain cuprates LiCu<sub>2</sub>O<sub>2</sub> and NaCu<sub>2</sub>O<sub>2</sub> are discussed in terms of strong in-chain frustration and intrinsic incommensurability.

## Experiment

Single crystals of LiCu<sub>2</sub>O<sub>2</sub> and NaCu<sub>2</sub>O<sub>2</sub> were synthesized according to the procedure described in Ref. [4]. The quality of the new NaCu<sub>2</sub>O<sub>2</sub> crystal was much better than that used in our preliminary NMR measurements reported in Ref. [3]. In contrast to LiCu<sub>2</sub>O<sub>2</sub>, the NaCu<sub>2</sub>O<sub>2</sub> single crystal shows no twinning and has no deviation from the ideal stoichiometry as confirmed by X-ray. <sup>23</sup>Na and <sup>7</sup>Li NMR measurements were performed at several temperatures in the paramagnetic and in the ordered phases of both compounds. All three principal orientations of the external magnetic field with respect to the crystallographic axes: H || *a*, *b* and *c* were used. The standard pulsed field-sweep NMR technique was applied at fixed frequency of 33.7 MHz for LiCu<sub>2</sub>O<sub>2</sub> and 46.0 MHz for NaCu<sub>2</sub>O<sub>2</sub>.

#### **Results and discussion**

We present the characteristic NMR spectra of <sup>7</sup>Li in LiCu<sub>2</sub>O<sub>2</sub> and <sup>23</sup>Na in NaCu<sub>2</sub>O<sub>2</sub> measured both above and below magnetic ordering temperature T<sub>c</sub> for orientation of the external magnetic field H || c (Fig.1). To make the comparison more convenient we use the same scaling of magnetic field in both panels. Above T<sub>c</sub> in LiCu<sub>2</sub>O<sub>2</sub> and NaCu<sub>2</sub>O<sub>2</sub> typical first-order quadrupole perturbed NMR spectra for spin I = 3/2 nuclei are observed. The quadrupole splitting between the satellites in NaCu<sub>2</sub>O<sub>2</sub> is about 200 mT, while in LiCu<sub>2</sub>O<sub>2</sub> it is about 10 mT. Since the ratio of quadrupole moments Q(<sup>23</sup>Na)/Q(<sup>7</sup>Li) = 2.7, this large quadrupole splitting ratio means that the electric field gradient (EFG) at Na site in NaCu<sub>2</sub>O<sub>2</sub> is almost an order of magnitude higher than the EFG at Li sites in LiCu<sub>2</sub>O<sub>2</sub>. This result reflects an enhanced role of EFG polarization effect on Na<sup>1+</sup> as compared with Li<sup>1+</sup>, which has only weakly polarizable 1s<sup>2</sup> shell.



Fig.1. <sup>7</sup>Li and <sup>23</sup>Na NMR spectra measured above  $T_c$  (left spectra) and below  $T_c$  (right spectra) for H || c in LiCu<sub>2</sub>O<sub>2</sub> and NaCu<sub>2</sub>O<sub>2</sub> single crystals at 33.7 and 46.0 MHz, respectively.

temperature T<sub>c</sub> the spectra of both compounds exhibit a dramatic change. The spectra are characteristic of IC static modulation of the local magnetic field caused by helical spin structure of Cu moments [6,7,8]. It is worth to mention, that the phase at T<sub>c</sub> is much transition narrower in NaCu<sub>2</sub>O<sub>2</sub> than in LiCu<sub>2</sub>O<sub>2</sub>. The formation of IC field modulation in NaCu<sub>2</sub>O<sub>2</sub> occurs within 0.6 K while in  $LiCu_2O_2$  it takes more than 2 K [6]. The asymmetric van

Hove singularities of <sup>23</sup>Na

NMR central transition line

are very sharp and are clearly

on

satellite

also

visible

Below magnetic ordering

transitions, which in contrast to  $LiCu_2O_2$  are well separated due to the larger EFG. The lineshape of the satellite transitions follows the distribution of the Larmor frequency caused by IC local field modulation. Therefore, in the first-order quadrupole perturbation the satellite lineshape is almost the exact copy of the central transition profile.

The most striking difference between <sup>7</sup>Li and <sup>23</sup>Na spectra is that in NaCu<sub>2</sub>O<sub>2</sub> the doublets (or degenerated quartets) are observed for all three principal orientations of external magnetic field in the magnetically ordered state. For H || a the intensities of both parts of the doublets are equal while for H || c the high field component of the doublet is more intensive. This anisotropy becomes more significant with decreasing temperature. The splitting is almost symmetric with respect to the central field determined as the resonance field of the central transition above T<sub>c</sub>. These results are completely unlike the situation in LiCu<sub>2</sub>O<sub>2</sub> where the <sup>7</sup>Li NMR quartet and sextet are observed for H || c (Fig.1) and H || (a,b) [6]. The possible reason for such dissimilar behavior could be the influence of non-magnetic Li defects in CuO<sub>2</sub> chains of LiCu<sub>2</sub>O<sub>2</sub>. Due to AF character of NNN interaction the both helix phase angles  $\theta$  and  $\phi$  exhibit a step-like change on  $\pi$  in the vicinity of Li defect. This phenomenon will be analyzed in more detail elsewhere.



**Fig.2**. Crystal structure of LiCu<sub>2</sub>O<sub>2</sub> (left panel) and NaCu<sub>2</sub>O<sub>2</sub> (right panel).



**Fig.3**. NQR spectra of NaCu<sub>2</sub>O<sub>2</sub> (black open circles) and LiCu<sub>2</sub>O<sub>2</sub> (red filled squares) measured above  $T_c$  on <sup>63,65</sup>Cu nuclei in Cu(2) site.

The value of the local magnetic field on Na site estimated as the linewidth at the base of the central transition for H || c is only 80 mT, which is a factor of 3 less then that for Li (250 mT). This is quite reasonable since the transition temperature in NaCu<sub>2</sub>O<sub>2</sub> is lower than in LiCu<sub>2</sub>O<sub>2</sub> pointing to a weaker inter-chain interaction in NaCu<sub>2</sub>O<sub>2</sub>.

The difference in crystal structure peculiarities of the two compounds (Fig. 2) is reflected in their NQR properties. Fig.3 shows the NQR spectra of NaCu<sub>2</sub>O<sub>2</sub> and LiCu<sub>2</sub>O<sub>2</sub> measured above  $T_c$  on  $^{63,65}$ Cu nuclei in Cu(2) site. The right and left lines of each pair are assigned to the  $^{63}$ Cu and the  $^{65}$ Cu isotope, respectively. The observed

frequency and intensity ratios correspond to ratios of isotope quadrupole moments and natural abandancies, respectively. In the following, we will concentrate only on <sup>63</sup>Cu isotope NQR lines for convenience. From Fig. 3 it is clearly seen that in NaCu<sub>2</sub>O<sub>2</sub> the NQR linewidth is a factor of 3 smaller than that in LiCu<sub>2</sub>O<sub>2</sub>. This result reflects more homogeneous EFG distribution as a consequence of higher degree of structural order in NaCu<sub>2</sub>O<sub>2</sub>. Probably for the same reason, we succeeded to find another <sup>63</sup>Cu line at 26.8 MHz originated from the Cu(1) position. It should be noted that the <sup>63</sup>Cu line at around 27 MHz has been observed earlier on the polycrystalline LiCu<sub>2</sub>O<sub>2</sub> sample in [9], but it was falsely assigned to the Cu(1) position. In this case, the line should exist also below T<sub>c</sub> which contradicts to our experimental findings described below.

All lines shown in Fig. 3 completely disappear below  $T_c$ . Instead, in LiCu<sub>2</sub>O<sub>2</sub> we observed very complicated <sup>63,65</sup>Cu antiferromagnetic resonance (AFMR) spectrum at 4.2 K. This effect is caused by the space modulated internal magnetic field at the Cu(2) site in the ordered state of LiCu<sub>2</sub>O<sub>2</sub>. For yet unknown reason we did not find any copper AFMR spectrum in NaCu<sub>2</sub>O<sub>2</sub>. At the same time, the Cu(1) NQR line at 26.8 MHz exists even below

 $T_c$ , as expected for non-magnetic  $Cu^+$  ion at the Cu(1) site which is symmetric with respect to magnetic  $Cu^{2+}$  ions in the  $CuO_2$  chains. Therefore, the complete cancellation of local magnetic field occurs at Cu(1) site in the ordered state of  $NaCu_2O_2$ .

In conclusion, <sup>7</sup>Li and <sup>23</sup>Na NMR spectra measured in the magnetically ordered state of the isostructural quasi-1D oxides  $LiCu_2O_2$  and  $NaCu_2O_2$  give unambiguously evidence for static IC modulation of local magnetic fields at the Li and the Na site, respectively. This modulation is caused by a helical spin structure of Cu moments below T<sub>c</sub>. Due to the crystal structure peculiarities the character of the magnetic helix is dissimilar in both compounds reflecting both in NMR and NQR spectra.

## Acknowledgement

We appreciate support by the Grants RFBR 04-03-32876, MK-1212.2005.2.

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# Entanglement in one-dimensional open spin chains s=1/2 with XY-Hamiltonian

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Entanglement of spin pairs in a one-dimension open chain of spins coupled by the dipoledipole interactions (DDI) in the equilibrium state in the external magnetic field is investigated. The reduced density matrix of a spin pair is obtained. Concurrence, the quantitative measure of the entanglement, is estimated with Wootter's criteria. Analytical and numerical methods are used in order to investigate influence of temperature, chain's length and its ends, the space between spins in the pair on the entanglement.

## Introduction

Quantum mechanics and quantum information theory are the theoretical basis for creation of quantum computers. Two types of quantum-mechanical states, separable and entangled, and the application of a quantum-mechanical superposition state as an elementary unit of information (qubit) leads to fantastic advantages of quantum computers in comparison with classical ones [1, 2]. Entangled states are the main resource of quantum computations and communications [3]. Generally, the concurrence [4] is used as a quantitative measure of entanglement. However, the concurrence can be fully investigated only in some simple cases. One of them is the quantum register representing a one-dimension open chain of spins coupled by DDI in a strong external magnetic field. The XY-Hamiltonian of such system can be diagonalized [5-8]. Possibility of exact diagonalization is very important in order to construct the reduced density matrix of any spin pair of the chain which is described by the equilibrium density matrix. Then entanglement is investigated with Wootter's criteria [4]. As a result, one can study an influence of the temperature, the chain length and its ends on the entanglement of any spin pair in the chain. These problems are solved in the present paper by analytical and numerical methods [9-11].

### The reduced density matrix of spin pair in homogeneous chains

We consider a one-dimensional open chain consisting of N spins (s=1/2) coupled by DDI in the external magnetic field. In the rotating reference frame [12], the Hamiltonian of the system (XY-Hamiltonian) is

$$H = D \sum_{n=1}^{N-1} (I_{nx} I_{n+1,x} + I_{ny} I_{n+1,y}), \qquad (1)$$

where  $I_{n\alpha}(\alpha = x, y, z)$  is the projection of the angular momentum operator of spin n on the axis  $\alpha$  and D is the DDI coupling constant. In the thermodynamic equilibrium state the density matrix,  $\rho$ , of the system is

$$\rho = \frac{e^{-\beta H}}{Z},\tag{2}$$

where  $\beta = \hbar/kT$ , T is the temperature and  $Z = Tr\{e^{-\beta H}\}$  the partition function. The density matrix  $\rho$  can be written as

$$\rho = \sum_{\xi_1, \xi_2...\xi_N=0}^{3} \alpha_{12...N}^{\xi_1 \xi_2...\xi_N} x_1^{\xi_1} \otimes ... \otimes x_N^{\xi_N} , \qquad (3)$$

where  $\xi_k$  (k=1,...,N) is one of the values {0, 1, 2, 3},  $x_j^0 = I_j$  is the unit matrix  $2 \times 2$ ,  $x_j^1 = I_{jx}$ ,  $x_j^2 = I_{jy}$ ,  $x_j^3 = I_{jz}$  (j=1...N), and  $\alpha_{12...N}^{\xi_1 \xi_2 \dots \xi_N}$  is the numerical coefficient.

In order to obtain the reduced density matrix for spins i, j we consider the system of the other spins of the chain as the environment. Averaging the density matrix  $\rho$  over the environment and taking into account that  $Tr\{x_j^k\}=0$  (j=1...N; k=1,2,3) we find for the reduced density matrix,  $\rho_{ij}$ , of spins i and j the following expression:

$$\rho_{ij} = \sum_{\xi_i, \xi_j=0}^{3} \alpha_{ij}^{\xi_i \xi_j} x_i^{\xi_i} \otimes x_j^{\xi_j} , \qquad (4)$$

where the coefficient  $\alpha_{ij}^{\xi_i\xi_j}$  is defined as

$$\alpha_{ij}^{\xi_i\xi_j} = \frac{Tr\{\rho x_i^{\xi_i} x_j^{\xi_j}\}}{Tr\{(x_i^{\xi_i})^2 (x_j^{\xi_j})^2\}}.$$
(5)

Using the exactly known diagonal representation of the Hamiltonian of Eq.(1) [6] one obtains after laborious calculations

$$\begin{aligned} \alpha_{ij}^{00} &= 1/4 \,; \, \alpha_{ij}^{03} = \frac{1}{N+1} \sum_{k} \sin^{2}(\frac{j\pi k}{N+1}) \frac{e^{-\nu \varepsilon_{k}}}{1+e^{-\nu \varepsilon_{k}}} - 1/4 \,; \\ \alpha_{ij}^{30} &= \frac{1}{N+1} \sum_{k} \sin^{2}(\frac{i\pi k}{N+1}) \frac{e^{-\nu \varepsilon_{k}}}{1+e^{-\nu \varepsilon_{k}}} - 1/4 \,; \\ \alpha_{ij}^{33} &= \frac{4}{(N+1)^{2}} \{ \sum_{k} \sum_{p \neq k} \sin^{2}(\frac{i\pi k}{N+1}) \sin^{2}(\frac{j\pi p}{N+1}) (\frac{e^{-\nu \varepsilon_{k}}}{1+e^{-\nu \varepsilon_{k}}}) (\frac{e^{-\nu \varepsilon_{p}}}{1+e^{-\nu \varepsilon_{p}}}) - \\ \sum_{k} \sum_{p \neq k} \sin \frac{i\pi k}{N+1} \sin \frac{i\pi p}{N+1} \sin \frac{j\pi k}{N+1} \sin \frac{j\pi p}{N+1} (\frac{e^{-\nu \varepsilon_{k}}}{1+e^{-\nu \varepsilon_{k}}}) (\frac{e^{-\nu \varepsilon_{p}}}{1+e^{-\nu \varepsilon_{p}}}) - \\ &- \frac{1}{N+1} \{ \sum_{k} \sin^{2}(\frac{i\pi k}{N+1}) \frac{e^{-\nu \varepsilon_{k}}}{1+e^{-\nu \varepsilon_{k}}} + \sum_{p} \sin^{2}(\frac{j\pi p}{N+1}) \frac{e^{-\nu \varepsilon_{p}}}{1+e^{-\nu \varepsilon_{p}}} \} + \frac{1}{4} \,; \\ \alpha_{i,i+1}^{12} &= \alpha_{i,i+1}^{21} = 0 \,; \, \alpha_{i,i+1}^{11} = \alpha_{i,i+1}^{22} = \frac{2}{N+1} \sum_{k} \sin \frac{i\pi k}{N+1} \sin \frac{(i+1)\pi k}{N+1} \frac{e^{-\nu \varepsilon_{k}}}{1+e^{-\nu \varepsilon_{k}}} \,, \end{aligned}$$

where  $v = \beta D$  and the one-fermion spectrum  $\varepsilon_k$  is defined as

$$\varepsilon_k = \cos\frac{\pi k}{N+1}, \qquad (k=1, 2, \dots, N)$$
(7)

The other coefficients  $\alpha_{ii}^{\xi_i\xi_j}$  equal zero from reasons of symmetry.

Using expressions of Eqs.(4, 6) we find the matrix representation of the reduced density matrix of nearest-neighbor spins i and j:

$$\rho_{i,i+1} = \begin{pmatrix} \frac{1}{4} + \alpha_{i,i+1}^{03} + \alpha_{i,i+1}^{30} + \alpha_{i,i+1}^{33} & 0 & 0 & 0 \\ 0 & \frac{1}{4} - \alpha_{i,i+1}^{03} + \alpha_{i,i+1}^{30} - \alpha_{i,i+1}^{33} & \alpha_{i,i+1}^{11} & 0 \\ 0 & \alpha_{i,i+1}^{11} & \frac{1}{4} + \alpha_{i,i+1}^{03} - \alpha_{i,i+1}^{30} - \alpha_{i,i+1}^{33} & 0 \\ 0 & 0 & 0 & \frac{1}{4} - \alpha_{i,i+1}^{03} - \alpha_{i,i+1}^{30} + \alpha_{i,i+1}^{33} \end{pmatrix}$$

The concurrence  $C_{i,i+1}$  is defined as [4]

$$C_{i,i+1} = \max\{0, \lambda_1 - \lambda_2 - \lambda_3 - \lambda_4\}, \qquad (8)$$

where  $\lambda_p$  (p=1, 2, 3, 4) are the square roots of the eigenvalues of the product matrix  $R = \rho_{i,i+1} \tilde{\rho}_{i,i+1}$  in the descending order; the matrix  $\tilde{\rho}_{i,i+1}$  is defined as  $\tilde{\rho}_{i,i+1} = 1/16(I_{iy} \otimes I_{iy} \rho_{i,i+1}^* I_{iy} \otimes I_{iy})$ . One can show that  $0 \le C_{i,i+1} \le 1$ . The system is non-entangled ("separable"), if its concurrence equals zero.

## Numerical analysis of the concurrence in spin pairs

Using expressions (6)-(8) the dependence on the temperature and the chain length of the concurrence,  $C_{12}$ , of the first and the second spins is numerically investigated. Figure 1 shows that the entanglement appears at  $\beta D \approx 2$ . This corresponds to the temperature interval  $1 \le T \le 15 \mu K$  at  $D = 2\pi \cdot 10^4 c^{-1}$ . Earlier, ordered states of nuclear spins coupled by DDI in solids were observed at such temperatures [12].



Fig.1. The concurrence of spins 1 and 2 versus the temperature for the number of spins N=3, 4, 6, 7, 100, 105. The behavior of the concurrence  $C_{12}$  is different for chains with even and odd N when the system size increases. When N increases the concurrence  $C_{12}$  decreases at even N and increases at odd N.

Our numerical calculations yield that the concurrence in the nine-spin chain is non-zero for nearest neighbors only when DDI of all spins are taken into account. The pair of qubits 1 and 2, and the one of qubits N-1 and N have the maximal pairwise entanglement. Spin 2 can be entangled both with spin 1 and with spin 3. Since spin 2 is strongly entangled with spin 1, the entanglement of spins 2, 3 is weaker. As a result, spin 3 is strongly entangled with spin 4, etc. This explains the oscillator of behavior the concurrence displayed in Fig. 2. The oscillations decay when the spin pair is far from the ends of the chain.

Analogously it is possible to explain the growth (fall) of the concurrence of the entanglement of spins 1 and 2 in the dependence on the length of the chain consisting of an odd (even) number of spins (Fig. 1). For this purpose it is necessary to take into account the influence of both ends of the chain on the entangled states. As a result, we obtain that the



**Fig.2**. The nearest-neighbor concurrence versus the site number for N=105.

ends of the chain yield opposite contributions to the entanglement at an odd number of spins. For example, one can easily find in the chain consisting of 5 spins that spin 5 leads to a decrease of the entanglement of spins 1 and 2. This effect is diminished when the odd number of spins increases and the entanglement of spins 1, 2 increases also. On the contrary, the second end of the chain increases the entanglement of spins 1 and 2 at an even number of spins. This leads to the calculated decrease of the concurrence (see Fig.1) when the even number of spins increases.

The presented numerical calculations show that the homogeneous open spin chain contains quantum correlations which are necessary to form pairwise entangled states. Thus, homogeneous chains of nuclear spins coupled by DDI can be considered as a model of the quantum register. New perspectives, opened by investigations of spin dynamics of the alternating spin-1/2 chains with XY-Hamiltonian, allow us to solve the qubit addressing problem on the basis of the Larmor frequencies of different spins. The advanced methods of diagonalization of the alternating chains [7,8] enable us to study corresponding quantum registers.

This work was supported by the Russian Foundation for Basic Research (project no. 04-03-32528).

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## CW EPR study of the molecular dynamics of nitronil nitroxide on LB films

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Langmuir-Blodgett (LB) films have attracted considerable interest over the past years. Especially in connection with technological applications, such as devices based on molecular electronics. CW EPR spectrum of nitronil radicals are highly sensitive to molecular motions,



Figure 1. Nitronil radical R1.

which actually does take place in the LB layer, therefore nitronil nitroxide is useful for a spin-probe investigations.

In this study we investigate the temperature dependence of CW EPR spectra of nitronil radical R1 (Fig. 1) in a LB film of heptadecanoic acid  $(C_{16}H_{33}COOH)$ .At rise in temperature, the individual line width of the certain orientations decreases that

results to occurrence of the peak specified by an arrow on Figure 2.



Figure 2. Temperature dependence of EPR spectra of nitronil radical R1.

The program for simulation of EPR spectra has been written, but demands completion. Dynamics of molecules was taken into account in implicit dependence of individual linewidth on temperature. Some models of the account of dependence of individual linewidth from orientation were used. The closest to experimental data model was the case with jump change of individual linewidth.



Figure 3. Comparison of theoretical and experimental EPR spectra.

In Figure 3 it is visible, that it is possible to receive similarity to experimental data qualitatively, however adjustment of parameters is necessary for reception of quantitative characteristics, such as the dependence of the linewidth on the temperature. Now work is directed on improvement of the program to obtain quantitative characteristics that permit to receive some parameters of molecular motion.

# EPR of transition metal ions in micro-plasma coatings on the aluminum alloy D16

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Micro plasma oxidation processes are electrochemical processes and produce oxidation of metal surface in the canals of micro discharges, where is realized high temperature plasma. Micro plasma oxidation coatings containing high temperature phase of aluminum -  $\alpha Al_2O_3$  have many interesting applications. Such coatings can be obtained both from material of aluminum detail and by introducing aluminates into electrolyte. Properties of coatings created depend on a variation in anodic and cathodic regimes, value of current discharge, temperature of electrolyte and its composition. The coatings structure consists of two layers. Outer layer on the boundary of electrolyte contains mainly low temperature phase of Al<sub>2</sub>O<sub>3</sub> – a technological layer. Inner laver close to metal surface containing  $\alpha$ - Al<sub>2</sub>O<sub>3</sub> is responsible for the many interesting macroscopic properties of MPO coatings such as microhardness, friction, wear resistance [1]. In this communication we discussed EPR data for micro plasma oxidation coatings on aluminum alloy D-16. As aluminum alloy D16 contains transition metals - cupper, iron, titanium, manganese and chromium, we hoped to gain an information about peculiarities of MPO processes on the different stages of their growth using the EPR data on oxidizing states of transition metal ions. MPO coatings on the surface of aluminum alloy D16 were obtained with semi-industrial plant, developed in Institute of Inorganic Chemistry SB RAS. Objects of EPR investigations were MPO coatings obtained:

- 1) during the anodic MPO process in aqueous solution of  $KOH + Na_2SiO_3$ ,
- 2) during the anodic cathodic MPO process in water solution of  $KOH + Na_2SiO_3$

EPR spectra were prepared with automatized Varian EPR spectrometer E-109 in X-band at 300 K. Analysis of EPR spectra was performed with WinEPR and Simfonia programs. Table 1 shows data for content of alloying elements.

Aluminum	Mg,	Mn,	Cu, %	Si, %	Zn, %	Fe, %	Ti, %	Cr, %	Ni, %
alloy	%	%							
D-16	1,2-	0,3-	3,8-	0,5	0,3	0,5	0,1	-	-
	1,8	0,9	4,9						

**Table 1**. Content of alloying elements in aluminum alloy D16

For the EPR experiments there were prepared the plates of aluminum alloy D16 of sizes  $0.5 \times 5 \times 10$  mm, oxidized during MPO processes. Thickness was measured with thickness meter "Quanix 5000". EPR spectrum of DPPH (g=2.0036) was used as g-value comparison standard.

# Anodic MPO process in aqueous solution of KOH + Na<sub>2</sub>SiO<sub>3</sub> electrolyte

EPR spectra of MPO coatings obtained by anodic micro plasma process in aqueous solution of KOH + Na<sub>2</sub>SiO<sub>3</sub> are shown in Fig. 1. They are identical of Cu<sup>2+</sup> EPR spectrum in  $\gamma$ -phase of Al<sub>2</sub>O<sub>3</sub> [4]. EPR spectrum of coating appears as an asymmetrical single line with g-value 2.07 and

160 Gauss linewidth. Lack of hyper fine structure (HFS) is due to high concentration of cupper ions and exchange interaction between them. Increasing coating thickness (between 10 and 30 microns) results in decreasing concentration of paramagnetic cupper ions. Hereafter (higher 30 microns) concentration of paramagnetic cupper ions has a valid level (Fig.2). Such a behaviour of cupper ions is due to transformation of hydroxide cupper complex into cupper oxide, having no EPR spectra. On the other hand, an existence of EPR spectrum with g =2.07 says that this anodic MPO coating contains only low temperature Al<sub>2</sub>O<sub>3</sub> phase.







# Anodic – cathodic MPO coatings on the surface of aluminum alloy D16 in aqueous solution of KOH + Na<sub>2</sub>SiO<sub>3</sub> electrolyte

EPR spectra of MPO coating obtained during the anodic – cathodic MPO process differ from spectra of anodic coatings. Fig. 3 shows the dependence of paramagnetic centers concentration on the thickness of coatings obtained. As illustrated this Figure, in the low magnetic field (g = 4.3) EPR spectrum of Fe<sup>3+</sup> is presented. Such a spectrum is known from literature and was observed in  $\gamma$ - phase of Al<sub>2</sub>O<sub>3</sub> [5]. Close to the g=2.00 complicated spectrum consisting of six lines is shown. Deconvolution of experimental spectrum and simulation of individual spectra showed that this complicated spectrum is due to overlapping of EPR spectra Cu<sup>2+</sup> with HFS from ion manganese Mn<sup>2+</sup>.



**Fig.3**. Dependence of cupper ions concentration on thickness of MPO coatings obtained on D16 alloy by anodic- cathodic MPO process in aqueous solution of KOH + Na<sub>2</sub>SiO<sub>3</sub>

Figures 4a - 4c show deconvolution of experimental spectrum into spectra of manganese and cupper ions.



**Fig.4**. EPR spectra of transition metal ions in MPO coatings obtained at anodic – cathodic process in aqueous solution of KOH + Na<sub>2</sub>SiO<sub>3</sub>

- a experimental spectrum,
- b simulated spectrum of  $Cu^{2+}$  ions,

c – difference spectrum (a – b) is due to HFS of  $Mn^{2+}$  ions.

Simulation of Cu<sup>2+</sup> EPR spectrum allows estimate g- value  $g_{\parallel} = 2.2876$ ,  $g_{\perp} = 2.050$  at the linewidth  $\Delta H_{1/2} = 90$ . The similar parameters of spin – hamiltonian were observed for the cupper ions in  $\alpha$ - phase of Al<sub>2</sub>O<sub>3</sub> [4]. Subtraction of cupper ions spectrum from experimental one gives typical EPR spectrum for manganese ions Mn<sup>2+</sup> with g = 2.00 and HFS parameter A = 83.7 Gauss. EPR spectrum with the same parameters was observed for  $\alpha$ - phase of Al<sub>2</sub>O<sub>3</sub> [6].

## **Discussion of results**

As follows from previous results [1] created MPO coatings depending on the conditions of MPO process contain different relations of low and high temperature  $Al_2O_3$  phases. Because the structure of these phases of  $Al_2O_3$  has different symmetry, transition metal ions incorporating into coating serve as paramagnetic probes for the diagnostics of phase types and peculiarities of their distributions in the structure of MPO coatings.

Our data showed that anodic MPO process produced mainly low temperature phases of Al<sub>2</sub>O<sub>3</sub> having no high hardness. In this case a typical EPR spectrum of cupper ions with g = 2.07 is observed. It should be noted that increasing in coating thickness up to 40 microns results in decreased concentration of Cu<sup>2+</sup> paramagnetic centers. But beginning with 40 microns their concentration has stable level. Ions of cupper, manganese and iron among alloy impurities have paramagnetic properties. At the content 5% of cupper in aluminum alloy D16 paramagnetic states of Cu<sup>2+</sup>, Mn<sup>2+</sup> and Fe<sup>3+</sup> give single exchange line with g = 2.07. Decreasing in paramagnetic states concentration as coatings created is due to transformation hydroxide complexes of cupper into CuO, which did not show EPR spectra. But at the large thickness of coatings there is existed equilibrium between two these forms of cupper compounds and beginning with 40 microns concentration of paramagnetic centers are stable. The same situation is observed in anodic-cathodic coatings, but the decay in copper paramagnetic states stops with the more low thickness of coatings (beginning with 20 microns). Differences between EPR spectra of anodic and anodic-cathodic coatings arise from existence in last high temperature  $\alpha$  - phase of Al<sub>2</sub>O<sub>3</sub>. At the same time in anodic- cathodic coatings together with exchange line are

observed individual EPR spectra of cupper, iron and manganese ions. These data say that these resolved EPR spectra are due to isolated parts of coatings with low concentration of cupper ions. Such parts of coatings are related to appearance of polycrystalline  $\alpha$ - phase of Al<sub>2</sub>O<sub>3</sub>. Recrystallization of low temperature phases in high temperature phases produces redistribution of impurities due to different incorporation coefficients into different phases of Al<sub>2</sub>O<sub>3</sub>.

To test our assumptions we removed technological part of coating obtained by anodiccathodic MPO process. EPR data show that at this treatment content of cupper ions drops by 10%, at the same time contents of iron and manganese ions remain invariable. The reason of 10% changing in cupper ions content is due to loose structure and small density of technological layer of coatings.

Obtained EPR data showed that coatings grown by anodic and anodic-cathodic MPO processes differed in states of cupper, iron and manganese ions. It allows using nondestructive EPR method for diagnostics of MPO coatings.

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# Triplet state dynamics of fullerene C<sub>60</sub> studied by pulse EPR

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## Abstract

Spin-polarized EPR spectra of fullerene  $C_{60}$  dissolved in glassy ortho-terphenyl was measured in the temperature range of 80 - 240K. The temperature dependence of the spectra was successfully simulated using the model of fast pseudorotation of  ${}^{3}C_{60}$  in a potential created by the surrounding solvent molecules. The strength of this potential was estimated at different temperatures. Near 240K this potential was found to decrease remarkably.

## Introduction

Since the discovery of fullerenes they attracted much attention because of unusual physical and chemical properties and because of possible technical application of fullerene-based materials. The fullerene  $C_{60}$  can be easily excited by visible light, which leads to the formation of triplet state of  $C_{60}$  with the quantum yield close to unity. This state is characterized by high electron spin polarization. That is why the fullerene-based materials can possibly be used as an active media for masers [1]. To create such materials it is necessary to investigate the dynamics of  $C_{60}$  in triplet state and its dependence on temperature, solvent and the time of delay after light flash.

Previously, the triplet state of  $C_{60}$  was studied by time-resolved EPR [2], OD EPR [3] and electron spin echo [4]. It was found that  ${}^{3}C_{60}$  is characterized by non-zero ZFS parameters D and E, which slightly depends on the solvent. Also, the strong temperature dependence of spin-polarized EPR spectrum of  ${}^{3}C_{60}$  was observed. However, so far the interpretation of this temperature dependence is not clear. In our opinion, the satisfactory numerical simulation of this dependence is lacking, and the convincing simulation was performed only for the case of very low temperatures (1.2 - 7K) [5], for which the dynamics of  ${}^{3}C_{60}$  is probably frozen.

The aim of the present work is to study the  ${}^{3}C_{60}$  dynamics at higher temperatures and to find the reasonable model explaining this dynamics, which would allow the adequate simulation of the temperature dependence of  ${}^{3}C_{60}$  EPR spectrum.

## Theory

## The Triplet Energy Levels.

The hamiltonian of the molecule in triplet particles state consists of two main terms — Zeeman energy and energy of magnetic dipole-dipole interaction of two unpaired electron spins  $(H_D)$ :  $H = g\beta HS + H_D$ , where H is the magnetic field vector, S is triplet spin vector, S=1,  $\beta$  is Borh magneton. For simplicity we assumed here the isotropic g-factor g. We can write  $H_D$  through the tensor  $D_{ij}$  of magnetic dipole-dipole interaction:  $H_D = \frac{1}{2} S_i D_{ij} S_j$ . In the

framework of the principal axes of  $D_{ij}$  tensor (x, y, z)  $\mathcal{H}_{\rm D} = D\left(S_z^2 - \frac{1}{3}S^2\right) + E\left(S_x^2 - S_y^2\right)$ , where D

and *E* are zero-field splitting parameters. In the same coordinate system the magnetic field vector may be written as  $H = H(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$ , where  $\theta$  is polar and  $\varphi$  azimuthal angles of *H* vector, respectively. We can rewrite the  $H_D$  term in a framework of reference (*X*, *Y*, *Z*), which has *Z* axis parallel to magnetic field direction:

$$\mathcal{H}_{\mathrm{D}} = \frac{1}{2} \left( D \left( \frac{1}{3} - \cos^2 \theta \right) - \mathrm{Esin}^2 \theta \cos 2 \varphi \right) \left( \mathbf{S}^2 - 3 \mathbf{S}_z^2 \right).$$
(1)

We assume that  $g\beta H >> D$ , i.e. the high-field approximation is valid. The energy levels  $W_+$ ,  $W_0$  and  $W_-$  of high-field eigenstates  $T_+$ ,  $T_0$  and  $T_-$  are [6]:

$$W_{+} = g\beta H + \frac{D}{2} \left( \cos^{2}\theta - \frac{1}{3} \right) + \frac{E}{2} \sin^{2}\theta \cos 2\varphi; \quad W_{0} = D \left( \frac{1}{3} - \cos^{2}\theta \right) - E \sin^{2}\theta \cos 2\varphi;$$
$$W_{-} = -g\beta H + \frac{D}{2} \left( \cos^{2}\theta - \frac{1}{3} \right) + \frac{E}{2} \sin^{2}\theta \cos 2\varphi. \tag{2}$$

#### The Spin Polarization of Triplet State.

The high-field triplet eigenfunctions  $T_+$ ,  $T_0$  and  $T_-$  can be rewritten trough zero-field eigenfunctions  $T_x$ ,  $T_y$  and  $T_z$  as:

$$T_{+} = T_{x} \frac{i \sin \theta + \cos \theta \cos \varphi}{2} - T_{y} \frac{i \cos \varphi + \cos \theta \sin \varphi}{2} + T_{z} \frac{\sin \theta}{\sqrt{2}};$$

$$T_{0} = i T_{x} \sin \theta \sin \varphi + T_{y} \sin \theta \cos \varphi + T_{z} \cos \theta;$$

$$T_{-} = -T_{x} \frac{i \sin \theta + \cos \theta \cos \varphi}{2} + T_{y} \frac{i \cos \varphi + \cos \theta \sin \varphi}{2} + T_{z} \frac{\sin \theta}{\sqrt{2}}.$$
(3)

According to Eq. (3), the populations of high-field eigenstates  $p_+$ ,  $p_0$ ,  $p_-$  can be expressed via the populations of zero-field eigenstates  $p_x$ ,  $p_y$ ,  $p_z$ .

$$p_0 = p_x \sin^2 \theta \sin^2 \varphi + p_y \sin^2 \theta \cos^2 \varphi + p_z \cos^2 \theta.$$
  

$$p_+ = p_- = \frac{1}{2} p_x (\cos^2 \theta \cos^2 \varphi + \sin^2 \varphi) + \frac{1}{2} p_y (\cos^2 \theta \sin^2 \varphi + \cos^2 \varphi) + \frac{1}{2} p_z \sin^2 \theta.$$
 (4)

Therefore, the polarizations of allowed EPR transitions are:

$$p_{+} - p_{0} = p_{-} - p_{0} = \frac{1}{2} p_{x} (\cos^{2}\theta \cos^{2}\varphi + \sin^{2}\varphi - 2\sin^{2}\theta \sin^{2}\varphi) + \frac{1}{2} p_{y} (\cos^{2}\theta \sin^{2}\varphi + \cos^{2}\varphi - 2\sin^{2}\theta \cos^{2}\varphi) + \frac{1}{2} p_{z} (\sin^{2}\theta - 2\cos^{2}\theta).$$
(5)

## Experiment

Fullerene  $C_{60}$  was dissolved in ortho-terphenyl at concentration of about  $10^{-4}$ M. The solution was put in glass tube with a 4 mm inner diameter. Three freeze-pump-thaw cycles were executed, and then the tube was sealed under high vacuum. Before measurements the samples were quickly cooled in liquid nitrogen to obtain the glassy state of ortho-terphenyl.

Electron spin echo experiments were carried out on Bruker ESP-380E FT EPR spectrometer equipped with a dielectric cavity (Bruker ER 4118 X-MD-5) inside an Oxford Instruments CF 935 liquid cryostat. The temperature was controlled by cold nitrogen flow.

For photoexcitation of the sample the pulses of second harmonic Nd-YAG laser Surelite I-10 were used with the wave-length 532 nm, pulse duration 10 ns, pulse energy 20 mJ and the pulse repetition rate 5 Hz. The microwave pulse sequence  $\pi/2 - \tau - \pi - \tau - echo$  with  $\tau = 120$  ns was used. The whole echo signal in time domain was integrated by a built-up integrator. The delay after laser flash was about 100 ns. The microwave frequency was 9.493 GHz.

#### **Results and discussion.**

The echo detected EPR spectra were observed at different temperatures at the range of 80 - 240 K. They are shown at Fig.1. The spectra are spin-polarized with a low-field absorptive part and high-field emissive part. In Fig. 1 one can see progressive narrowing of the spectrum with temperature increase.



**Fig.1**. Echo-detected EPR spectra of the triplet state of  $C_{60}$  in ortho-terphenyl at different temperatures. The spectra are normalized at the absorptive maximum.

**Fig.2**. Simulations of ED EPR spectra (see Fig. 1) using the model of  ${}^{3}C_{60}$  fast pseudorotation in potential  $U = -V\cos\alpha$  (see text).

For explaining this phenomenon the model of fullerene fast pseudorotation (dynamic Jahn-Teller effect) in a potential  $U = -V\cos\alpha$  [7] was suggested. Here  $\alpha$  is the angle within a range of  $[0,\pi]$  between the *z*-axis of tensor  $D_{ij}$  and the direction determined by local surrounding of C<sub>60</sub> molecule. Previously, the model of pseudorotation was used for explaining the temperature change of  ${}^{3}C_{60}$  EPR spectrum in the range of 4 – 80K [4].

We have simulated the obtained spectra numerically in MATLAB program package in the following way. The total spectrum was obtained by the powder average of the  $T_0$ -> $T_+$  and  $T_0$ -> $T_-$  transitions of the individual triplets, which are characterized by the angles  $\theta$  and  $\varphi$ . The polarization of the spin transitions was calculated according to Eq. (5). The frequencies of the transitions were calculated according to Eq. (2), and the averaging of these frequencies over the  $\alpha$  angle was performed. The probability distribution  $W(\alpha)$  was derived from Boltzmann law:

$$\frac{dW}{d\alpha} = \exp\left(-\frac{V\cos\alpha}{kT}\right) \cdot \sin\alpha \,. \tag{6}$$

During the simulation we kept fixed the parameters D = 110G, E = 3G, g = 2.0002,  $p_x = p_y = 0$ ,  $p_z = 1$ . The only fitting parameter was the strength of the potential V. The simulated spectra are shown on Fig. 2. Very good agreement between the experimental and the simulated spectra can be noticed. The averaging over  $\alpha$  leads to partial averaging of the zero-field splitting, which in turn results in narrowing of the simulated spectra.

The dependence of the obtained V values on the temperature is presented on Fig. 3. In the range 80 - 200K it is nearly temperature-independent with the mean value V  $\approx 600$ K. The severe decrease of V is observed at 240K. This is probably caused by the increasing of the molecular mobility of ortho-terphenyl at higher temperature, which facilitates the pseudorotation of  ${}^{3}C_{60}$ . Note that near 240K in ortho-terphenyl a so-called dynamical transition is observed that is characterized by the onset of large-amplitude stochastic motion [8].

To estimate the rate of the  ${}^{3}C_{60}$  pseudorotation we measured the transverse relaxation time  $T_2$  of  ${}^{3}C_{60}$ . For all temperatures it was found that  $T_2 > 200$  ns, and the decrease of  $T_2$  with temperature increase was observed. At higher temperatures, when the EPR spectrum distortion is substantial, the scale of the frequency change due to pseudorotation  $\Delta \omega$  is in order of D = 110G  $\approx 2000$  MHz. For the fast motion the contribution of the pseudorotation to transverse relaxation rate  $1/T_2$  can be calculated according to the Redfield theory:

 $1/T_2 = \tau_c <\Delta \omega^2 >, \tag{7}$ 

where  $\tau_c$  is the correlation time of the pseudorotation, and  $\langle \Delta \omega^2 \rangle$  is the mean-square value of the fluctuation of the resonance frequency. From the Eq. (7) we can estimate  $\tau_c \leq 10^{-12}$  s, which is in agreement with previous estimations [9].



**Fig.3**. Temperature dependence of the strength of the potential V (see Eq. 6), obtained from the simulation of  ${}^{3}C_{60}$  EPR spectra.

### Acknowledgements

This work was supported by grant of the President of Russian Federation for young scientists MK-7740.2006.3 and the Joint grant of Russian Foundation for Basic Research and Japan Society for Promotion of Science 06-03-91362.

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# Structure of anthraquinone and fluorenone complexes on the surface of metal oxides (CaO, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>)

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Paramagnetic complexes of probe molecules are used to characterize electron acceptor properties of oxide catalysts [1-5]. 9,10-Anthraquinone and 9-fluorenone paramagnetic complexes formed under adsorption on the dehydroxilated surface of several oxides (CaO,  $Al_2O_3$ ,  $ZrO_2$ ) have been studied by EPR and ENDOR (fig. 1-4).



**Fig.1**. EPR spectra of anthraquinone adsorbed on the surface of the: (1) CaO, 120°C; (2) ZrO<sub>2</sub>, 120°C; (3) γ-Al<sub>2</sub>O<sub>3</sub> 120°C; (4) γ-Al<sub>2</sub>O<sub>3</sub>, 200°C 3 h; (5) γ-Al<sub>2</sub>O<sub>3</sub>, 300°C 2 h. **Fig.2**. ENDOR spectra of anthraquinone adsorbed on the surface of the: (1) CaO, 120°C; (2) ZrO<sub>2</sub>, 120°C; (3) γ-Al<sub>2</sub>O<sub>3</sub> 120°C; (4) γ-Al<sub>2</sub>O<sub>3</sub>, 200°C 3 h; (5) γ-Al<sub>2</sub>O<sub>3</sub>, 300°C 2 h.





Fig.3. EPR spectra of fluorenone adsorbed on the surface of the: (1) CaO, 120°C; (2)  $ZrO_2$ , 120°C; (3)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 120°C; (4)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 200°C

**Fig.4.** ENDOR spectra of fluorenone adsorbed on the surface of the: (1) CaO,  $120^{\circ}$ C; (2) ZrO<sub>2</sub>,  $120^{\circ}$ C; (3)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>  $120^{\circ}$ C; (4)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $200^{\circ}$ C

It has been shown that anthraquinone on CaO surface formed anthrasemiquinone as a result of one electron transfer from electron-donor center to anthraquinone molecule (fig. 5).



**Fig.5**. Formation of the anthrasemiquinone on the CaO surface as a result of one electron transfer from electron donor center.

On the alumina surface both electron-acceptor and electron-donor centers take place in the anthraquinone complex formation (fig. 6)



Fig.6. Formation of anthraquinone complexes on the Al<sub>2</sub>O<sub>3</sub> surface.

On first stage the anthraquinone forms diamagnetic complex with electron acceptor center, like Hammett indicator. Interaction with electron acceptor center increases the electron affinity of the adsorbed molecule. This allows the next stage to be possible, that is one electron transfer from near electron donor center to adsorbed molecule. As a result, the complex I is formed. Similar complex is formed on the  $ZrO_2$  surface (with  $Zr^{4+}$  cations). Heating results in the transformation of complex I into complex II, which has h.f.s. from <sup>27</sup>Al nucleus. Next heating results in the complex III formation which consists of one anthrasemiquinone molecule and two electron-acceptor centers.

If the probe molecule has only one carbonyl group (as in the case of fluorenone) then complex III does not form. This means that each carbonyl oxygen interacts with one coordination unsaturated aluminum cation on the surface.

Anthrasemiquinone (like on CaO) can also form on the zirconia and alumina surfaces but its concentration is low. It is possible to detect this species by echo-detected EPR or if we decompose complexes I - III by water vapour adsorption.

This work was supported by the Federal Agency on the Science and Innovations (State Contract 02.451.11.7012 of August 29, 2005), the Concil on Grants of the President Of the Russian Federation (Program of State Support for Leading Scientific Schools of the Russian Federation, Grant RI-112/001/056) and the Russian Foundation for Basic Research (Project No. 06-03-32830a).

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# Исследования спин-зависимых рекомбинационных процессов в системах с квантовыми точками методом оптической регистрации ЭПР по послесвечению

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В настоящее время значительный интерес представляют полупроводниковые наноструктуры, в которых квантовый эффект конфаймента носителей и экситонов, приводит к высокой эффективности излучения [1]. В данной работе рассматриваются две различные системы квантовых точек, в каждой из которых наблюдается длительное послесвечение, обусловленное спин-зависимой туннельной рекомбинацией электронных и дырочных центров.

Первая система представляет собой нанокристаллы CsPbBr<sub>3</sub> внедренные в объёмный кристалл CsBr. Нано- и микро- кристаллы CsPbBr<sub>3</sub> образуются в результате самоорганизованного роста в объемном кристалле CsBr с примесью Pb (0.02-0.2% PbBr<sub>2</sub> в расплаве) выращенного методом Бриджмена. Оптические свойства нанокристаллов CsPbBr<sub>3</sub> были исследованы в работе [2]. Там же обсуждалась возможность оценки размеров нано- и микро- кристаллов по сдвигу экситонной люминесценции относительно люминесценции связанных экситонов в объемном кристалле CsPbBr<sub>3</sub>. Исходя из сдвига энергии излучения в сторону высоких энергий относительно объемных кристаллов CsPbBr<sub>3</sub> [2,5] мы оцениваем размер нанокристаллов в рассматриваемом образце CsPbBr<sub>3</sub> равным примерно 3 nm. В этих системах длительное туннельное послесвечение наблюдается при низких температурах (1.5-80 K) после рентгеновского облучения при 77 K.

При рентгеновском облучении номинально чистого кристалла CsBr при низкой температуре в первую очередь образуются автолокализованные дырки (Br<sub>2</sub><sup>-</sup> или V<sub>K</sub> центры) и электронные центры окраски типа F - центров. В активированных примесями кристаллах образуются также электронные и дырочные центры, связанные с примесями. Рекомбинация между наведенными рентгеновским облучением центрами, происходящая при низкой температуре, при которой термоактивационные процессы заморожены, приводит к спин-зависимому туннельному послесвечению. В результате, в сильных магнитных полях и при низких температурах из-за поляризации центров в соответствии электронных спинов электронных и дырочных с Больцмана наблюдается магнитное распределением тушение туннельного послесвечения. Этот эффект позволил по возрастанию интенсивности ТП в момент резонанса вследствие переориентации спина одного из рекомбинирующих партнеров регистрировать ЭПР электронных и дырочных центров, участвующих в рекомбинации и тем самым идентифицировать эти дефекты. Длинноволновое оптическое возбуждение в полосах поглощения отдельных радиационных дефектов, например центров окраски типа F - центров, приводит к фотостимулированной люминесценции (ФСЛ) (photostimulated luminescence - PSL) с более короткими длинами волн, которая обусловлена различными рекомбинационными процессами, включая рекомбинацию экситонов. Именно ФСЛ используется в компьютерной рентгеновской радиографии. Благодаря спиновой зависимости ТП и ФСЛ были разработаны методы оптической регистрации магнитных резонансов (ОДМР) рекомбинирующих центров и экситонов по ТП и ФСЛ [3,4].

На Рис.1а показано уменьшение интенсивности *I* ТП кристалла CsBr:CsPbBr<sub>3</sub> в магнитном поле при температуре 1.8 К. Характер тушения соответствует рекомбинации двух центров с электронными g-факторами ~2.0 и спинами S = 1/2 в соответствии с выражением  $I=I_0(1-P_eP_h)$ , где  $I_0$  - интенсивность ТП в нулевом магнитном поле,  $P_e$  и  $P_h$  - поляризации спинов электронных и дырочных центров в магнитном поле, соответственно (расчетная зависимость показана пунктирной линией). Приложение микроволнового поля (частота 35 GHz) приводит к увеличению интенсивности ТП в магнитных полях, соответствующих ЭПР переходам для электронных и дырочных центров, вследствие переориентации электронного спина и включения режима рекомбинации, то есть имеет место оптическое детектирование магнитного резонанса.

На Рис.1b представлены спектры ОДМР, зарегистрированные в системе CsBr:Pb полному послесвечению (1) и по излучению нанокристаллов (2) (полоса по люминесценции нанокристаллов. Эти спектры имеют одинаковую форму и состоят из сигналов ЭПР F - центров и автолокализованных дырок (V<sub>K</sub> - центров). На Рис. 2 приводятся симулированные сигналы ЭПР F - центров и  $V_K$  - центров для ориентации кристалла в магнитном поле В || [100] с использованием известных параметров для F центров и V<sub>K</sub> - центров в кристалле CsBr [6,7]. Видно, что симулированные спектры экспериментально наблюдаемым. Регистрация сигналов близки к ЭПР рекомбинирующих в матрице F - и V<sub>K</sub> - центров по интенсивности излучения микро- и нанокристаллов, встроенных в решетку матрицы, однозначно свидетельствует о том, что это излучение возбуждается рекомбинационными процессами в матрице. В виду малых размеров нанокристаллов и малых расстояний, на которые переносится энергия, весьма вероятно, что перенос энергии обусловлен взаимодействиями по механизму ближнего поля без излучения фотонов во внешнюю среду (near-field interactions).



Рис.1 а)Зависимость интенсивности ТП от магнитного поля при температуре 1.8 К в кристалле CsBr:Pb, расчетная зависимость для рекомбинации двух центров с S=1/2 и g=2.0 (показана пунктирной линией). На вставке представлен спектр ТП, стрелками отмечены излучение экситонов в нанокристаллах CsPbBr<sub>3</sub> и полоса электронно-дырочной рекомбинации (EHR) в матрице. b) ОДМР на частоте 35 GHz при 1.8 К, зарегистрированный по полному спектру ТП (1) и по узкой линии нанокристаллов CsPbBr<sub>3</sub> с энергией 2.48 eV (2). Внизу показаны симулированные спектры ОДМР F - центров и V<sub>K</sub> - центров в CsBr для ориентации кристалла

Возбуждение послесвечения в микро- и нанокристаллах, встроенных в матрицу, свидетельствует о направленном переносе энергии электронно-дырочной рекомбинации, происходящей в матрице (CsBr) к нанокристаллу через интерфейс.

Другой рассматриваемой системой является порошок из свободных квантовых точек представляющих собой ZnO нанокристаллы, покрытые одним-двумя монослоями Zn(OH)<sub>2</sub>, полученных методами коллоидной химии (методика приготовления образцов описана в работах [9-11]. Нами исследовались нанокристаллы размером 3.5 nm, разброс их размеров составлял не более 10%.

В квантовых точках (нанокристаллах) ZnO, длительное TП наблюдается при низких температурах после кратковременного облучения ультрафиолетовым светом (УФ) с энергией квантов в области межзонного поглощения. Ранее длительное туннельное послесвечение наблюдалось только в объемных кристаллах после рентгеновского облучения и было индуцировано туннельной рекомбинацией между электронными и дырочными центрами, наведенными рентгеновским облучением [8].

На Рис. 2 показано магнитное тушение ТП порошка ZnO при температуре 1.8 К (скорректирована с учетом уменьшения интенсивности ТП за время развертки магнитного поля). В правой части рисунка стрелками условно показана преимущественная

ориентация спинов электронных и дырочных центров в области сильных магнитных полей вследствие распределения Больцмана и схематически лвойной стрелкой с крестиком показано отсутствие рекомбинации для параллельных спинов. Характер тушения, как и в случае CsBr: CsPbBr<sub>3</sub>, соответствует рекомбинации двух центров с электронными д-факторами  $\sim 2.0$  и спинами  $S = \frac{1}{2}$ . Расчетная зависимость интенсивности послесвечения от магнитного рекомбинации для поля такой электронно-дырочной электронными пары с спинами для электрона и  $S_e = S_h = \frac{1}{2}$  и g дырки факторами  $g_e = 1.965$  и  $g_h =$ 2.003 показана пунктирной линией.

На Рис.3 представлен сигнал ОДМР на частоте 35.2 GHz при 2 K, зарегистрированный по





Рис.2 Зависимость интенсивности туннельного послесвечения от магнитного поля в квантовых точках ZnO в присутствии микроволнового поля на частоте 35.2 GHz при температуре 2 К . На вставке показана зависимость TП в области магнитных полей 1.2-1.3 Т при медленной развертке магнитного поля, чтобы исключить влияние релаксационных процессов на сигнал. Расчетная зависимость интенсивности TП от

магнитного поля показана пунктирной линией. Вертикальными стрелками условно показаны ориентации спинов электронных (*e*) и дырочных (*h*) центров в условиях Больцмановского равновесия (верхняя схема) и в условиях ЭПР для дырочных и электронных центров; двойной горизонтальной стрелкой схематически показан процесс рекомбинации, запрещенный для одинаковой ориентации спинов (крестик на схеме).

полному спектру ТП через два часа после прекращения УФ возбуждения. Внизу показаны симулированные спектры ОДМР мелких электронных центров (мелких доноров) и трех типов дырочных центров глубокими уровнями с (глубоких акцепторов), которые ранее обсуждались в [11]: работе центров, с связанных атомами Na, локализованными вблизи интерфейса, вакансий цинка V<sub>Zn</sub>, и атомов лития в позиции цинка Li<sub>Zn</sub>. В спектрах ОДМР проявляются мелкие доноры *g*-фактор имеющие 1.965, совпадающий с *g*-фактором, полученным методом высокочастотного ЭПР. Таким образом, показано, что ТП обусловлено рекомбинацией мелкие доноры и глубоких акцепторы двух типов: (i)



Рис.3 Сигнал ОДМР на частоте 35.2 GHz при 2 К, зарегистрированный по полному спектру ТП через два часа после прекращения УФ возбуждения. Внизу показаны симулированные спектры ОДМР мелких электронных центров и трех типов дырочных центров с глубокими уровнями.

глубокие акцепторы, традиционные для объемных кристаллов ZnO - атомоы лития, замещающие атомы цинка  $Li_{Zn}$  и вакансий цинка  $V_{Zn}$ ; (ii) глубокие акцепторы, связанные с натрием, расположенным вблизи интерфейса.

Перспективным представляется использование методов, развитых в настоящей работе, для исследования спин-зависимых процессов в квантовых точках ZnO, активированных магнитными ионами, являющихся перспективными системами при создании материалов для спинтроники.

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# Химическая поляризация ядер мицеллизованных радикальных пар в присутствии нитроксильных радикалов

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## Введение

Влияние нитроксильных радикалов на магнитные и спиновые эффекты в химических реакциях активно обсуждается в ряде работ в последние годы [1-4]. Для объяснения этого влияния предложены два механизма: 1) увеличение скорости парамагнитной релаксации радикалов пар вследствие обменного и дипольного спин-спинового взаимодействия с добавленными нитроксильными радикалами, 2) изменения спиновой динамики спин-коррелированных радикальных пар за счет образования трёх-спиновых столкновительных комплексов. В работе [4] были проведены расчеты полевых зависимостей ХПЯ в трех-спиновых комплексах и было предсказано появление экстремумов на полевых зависимостях ХПЯ в диамагнитных продуктах реакций рекомбинации и диспропорционирования в таких системах.

В настоящей работе с целью изучения трёх-спиновых систем мы исследовали эффекты ХПЯ на ядрах <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P в двух фотохимических реакциях фотодиссоциации: (1) дибензилкетона (ДБК), (2) 2,4,6-триметилбензоил-дифенилфосфиноксида (ДТФО) в мицеллярных растворах додецилсульфата натрия (ДДС) в присутствии нитроксильных радикалов в сильных и слабых магнитных полях. Уникальная особенность мицеллизированных радикальных пар состоит в больших временах жизни геминальной стадии. Если в мицелле, содержащей радикальную пару, присутствует нитроксильный радикал, то образуется относительно устойчивая, с временем жизни, лимитированной скоростью выхода радикалов из мицелл, трёх-спиновая система.

## Результаты

ДБК и ДТФО испытывают фотодиссоциацию α-Норриш типа I из электронновозбуждённого триплетного состояния. Время жизни образующихся геминальных пар лимитируется тремя процессами: спин-селективной реакционной гибелью (рекомбинацией и/или диспропорционироваием), спин-неселективной гибелью (выход из мицеллярной фазы и/или мономолекулярными превращениями радикалов) и парамагнитной релаксацией. Времена жизни рассматриваемых радикальных пар лежат в диапазоне от десятков наносекунд до микросекунд. Времена их парамагнитной релаксации не короче чем 50-100 нс. Типичная скорость парных столкновений радикалов в мицеллах додецил сульфата натрия лежит в диапазоне  $2*10^7 - 2*10^8$  с<sup>-1</sup> [5]. Т.к. константа СТВ в образующихся радикальных парах находится в диапазоне от 1 до 380 Гс, спиновый обмен в рассматриваемых радикальных пар может быть как быстрым, так и медленным.

## Фотолиз ДБК

При фотолизе ДБК образуются триплетные геминальные радикальные пары бензильного и фенацильного радикалов. ХПЯ наблюдается на геминальных продуктах (ДБК и толилбензилкетоне) и внеклеточном продукте (дибензиле). Добавление

ТЕМПО в концентрациях 1-1.5 мМ приводит к полному исчезновению ХПЯ на ядрах <sup>1</sup>Н и <sup>13</sup>С в слабых магнитных полях в экспериментах с переносом образца. Спектры <sup>1</sup>Н ХПЯ в сильном магнитном поле при задержке между импульсом лазера и детектирующим рч-импульсом (длительностью 8 мкс) равным 0, приведены на рис. 1. Как видно из рисунка главным отличием в спектре ЯМР, является существенно



Рис.1. <sup>1</sup>Н ХПЯ, наблюдаемая в реакции фотолиза 3 мМ дибензилкетона в растворе ДДС мицеллах в D<sub>2</sub>O. a) [ТЕМПО] = 0, б) [ТЕМПО] = 2 мМ, в) [ТЕМПО] = 6 мМ, 1-СН<sub>2</sub> группа ДБК, 2- СН<sub>2</sub> группа дибензила, 3- паратолилбензоил, 4- СН<sub>2</sub> –группа алкоксимина –ТЕМПО-СН<sub>2</sub>-Ph.

[TEMIIO]	3.82 м	.д. (СН2	2.86 м.д. (CH <sub>2</sub>		
мМ	Д	БК)	ДБ)		
	шир.	интенс.	шир.	интенс.	
	ЛИН.	интегр.	ЛИН.	интегр.	
	Γц		Γц		
0	1.22	1	1.22	0.44	
2	5.1	1	3.5	0.19	
6	15.8	1	не		
			наблюдается		

Таблица 1. Зависимость ширин и интенсивностей поляризованных линий ЯМР дибензилкетона и дибензила от концентрации ТЕМПО.

большая ширины линий. Зависимость ширины линий ЯМР CH<sub>2</sub>-группы ДБК СН<sub>2</sub>-группы ДБ приведены в И таблице 1. Оценка времени ядерной релаксации лля ДБК В случае лобавления 6 мМ ТЕМПО лает величину 0.13 секунды. Отметим, что интенсивность ХПЯ на ДБК при добавлении ТЕМПО не меняется, т.е. ТЕМПО не уменьшает квантовый выход разложения ДБК. Меньшая ширина линий ДБ, с нашей точки зрения. связана с тем, что ОН образуется как внутри мицелл, так и снаружи.

# Фотолиз ДТФО.

Нами также было исследовано влияние добавок ТЕМПО на другую модельную реакцию – фотолиз ДТФО. тем, Эта пара интересна что образующийся 2.4.6триметилбензоильный раликал содержит большую константу СТВ на фосфоре равную 38.5 мТ. Большая величина константы СТВ определяет особенности магнитного эффекта [6], СПЯ ХПЭ [7], ХПЯ [8], И наблюдаемые ранее при фотолизе ДТФО в алкилсульфатных мицеллах.

Фотолиз ДТФО в водном растворе [8] додецилсульфата натрия ведет к образованию триплетной геминальной радикальной пары, состоящей из фосфиноильного и 2,4,6-триметилбензоильного радикалов. Радикальные реакции этой пары ведут к образованию следующих основных продуктов, на которых наблюдается ХПЯ <sup>1</sup>Н и <sup>31</sup>Р: регенерация исходного 1) соединения. 2) образование дифенилфосфиноксида (Ph<sub>2</sub>P(O)H) и дифенилфосфиновой кислоты.





3) образование 2,4,6-триметилбензойной кислоты.

кислоты. ХПЯ, наблюдаемая по линиям ЯМР <sup>31</sup>Р при фотолизе 6 мМ ДТФО в мицеллярном растворе ДДС в H<sub>2</sub>O в слабом магнитном поле (B<sub>0</sub> = 26 мТ), представлена на рис. 2а. Как видно из рисунка, ХПЯ на ядрах фосфора продуктов и исходного соединения имеет эмиссионный характер, что можно объяснить

доминированием S-T\_ механизма [8]. Спектр на рис. 26 представляет ХПЯ при фотолизе в той же системе, но в присутствии 1.5 мМ ТЕМПО. Добавление ТЕМПО приводит к полному разрушению <sup>31</sup>Р ХПЯ, за исключением сигнала на атоме фосфора дифенилфосфиноксида.

Качественное объяснение наблюдаемым особенностям может быть сформулировано следующим образом, время переноса образца ИЗ внешнего магнита в магнит ЯМР спектрометра составляет около 1 секунды. Т.к. ТЕМПО локализовано преимущественно в мицеллярной фазе, гидрофильные соединения, такие как дифенилфофиноксид будут иметь ЯMР, невозмущённый спектр а время

релаксации гидрофобных соединений (ДТФО) укорачивается, что и приводит к сильному уменьшению на них сигнала ХПЯ. Действительно, молекулы, локализованные в мицеллах, занятых ТЕМПО, имеют сильно уширенные линии вследствие столкновения с ТЕМПО, что полностью объясняет экспериментальные наблюдения. Зависимость <sup>31</sup>Р ХПЯ от магнитного поля в присутствии 1.5 мМ ТЕМПО (рис. 3) сдвинута в слабые магнитные поля по сравнению с полевой зависимостью в



**Рис. 3.** Полевая зависимость <sup>31</sup>Р ХПЯ при фотолизе ДТФО в ДДС мицеллах в H<sub>2</sub>O при различных концентрациях ТЕМПО, [ДФТО] = 6 мМ.

отсутствии ТЕМПО. Сдвиг полевой зависимости хорошо объясняется увеличением электронной спиновой релаксации за счет взаимодействия ТЕМПО с радикалами пары [9]. Другим фактором, определяющим сдвиг полевой зависимости ХПЯ, могла бы быть реакция рекомбинации ТЕМПО с ацильными фосфонильными радикалами. И Однако, нам не удалось наблюдать ни ХПЯ продуктах на рекомбинации, сигналов ΗИ В спектрах ЯМР после прохождения фотолиза до полного разложения ДТФО. Для идентификации линии ЯМР продукта рекомбинации ТЕМПО и фосфонильного радикала,
нами были исследованы эффекты ХПЯ при фотолизе ДТФО в присутствии ТЕМПО в бензоле. Было обнаружено, что добавление ТЕМПО приводит к появлению нового сигнала ХПЯ, наблюдаемого на 33.9 м.д. и соответствующего продукту рекомбинации ТЕМПО и фосфонильного радикала.

## Обсуждение результатов

Таким образом, нам не удалось зарегистрировать ХПЯ в слабых магнитных полях на продуктах реакции, у которых ожидаемая (или известная) скорость выхода из мицеллярной фазы достаточно мала, за исключением продукта (Ph)<sub>2</sub>P(O)OH. Отметим, что (Ph)<sub>2</sub>P(O)OH локализован в воде и, таким образом, контакты с локализованным в мицеллах ТЕМПО, минимальны. С нашей точки зрения наиболее вероятной причиной отсутствия ХПЯ в слабых магнитных полях при добавлении ТЕМПО является влияние ТЕМПО на ядерную спиновую релаксацию диамагнитных продуктов. В отличие от ситуации с проведением фотолиза в гомогенных растворах, частота бимолекулярных встреч между диамагнитными продуктами реакции и быстро релаксирующим ТЕМПО (который тоже находится в мицелле) намного выше. Короткое время ядерной релаксации диамагнитных продуктов в присутствии ТЕМПО и является причиной, не позволяющей получить ХПЯ в слабых магнитных полях. Это объяснение также подтверждает тот факт, что в случае проведения ХПЯ в сильных магнитных полях в магнитном поле ЯМР спектрометра, где нет необходимости в переносе облучённого образца, удается зарегистрировать ХПЯ как на продуктах мицеллизованных РП, так и на продуктах рекомбинации ТЕМПО и радикалов партнеров.

В тех случаях, когда диамагнитный продукт реакции локализован в водной среде, ХПЯ может быть успешно зарегистрирована. Таким примером является случай на продукте (Ph)<sub>2</sub>P(O)OH, который находится в водной среде, а не в мицелле. Время ядерной релаксации <sup>31</sup>P (Ph)<sub>2</sub>P(O)OH в присутствии ТЕМПО (1.5 мМ) составляет 6 секунд и существенно превышает время ядерной релаксации ДТФО, которое в этих же условиях не превосходит 0.5 секунды, хотя в случае без ТЕМПО, оно равняется 1.6 секунды. ХПЯ, наблюдаемая на (Ph)<sub>2</sub>P(O)OH, может быть сформирована либо в геминальной РП в присутствии ТЕМПО, либо в диффузионных РП двух фосфонильных радикалов. Отметим, что нам не удалось наблюдать дополнительных экстремумов в полевых зависимостях ХПЯ, а сдвиг полевой зависимости в слабые магнитные поля хорошо согласуется с укорочением электронной релаксации в РП.

## Выводы

Экспериментально исследовано влияние нитроксильных радикалов на <sup>1</sup>Н и <sup>31</sup>Р ХПЯ, формирующуюся в радикальных парах в мицеллах в сильных и слабых магнитных полях. Показано, что добавление нитроксильных радикалов, приводящее к увеличению скорости ядерной релаксации в диамагнитных молекулах, существенно уменьшает ХПЯ в слабых магнитных полях. В случаях, когда влияние нитроксильного радикала на ядерную поляризацию продуктов мало ((i) реакция происходит в гомогенных растворах, (ii) реакция происходит в мицеллах, но нитроксил и продукт локализованы в мицеллярном ядре и водной среде, соответственно) эффект третьего спина проявляется в ускорении электронной спиновой релаксации, индуцированной столкновениями со стабильными радикалами.

Эта работа выполнена при поддержке грантов РФФИ № 04-03-32604 и № 06-03-91362-ЯФ.

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