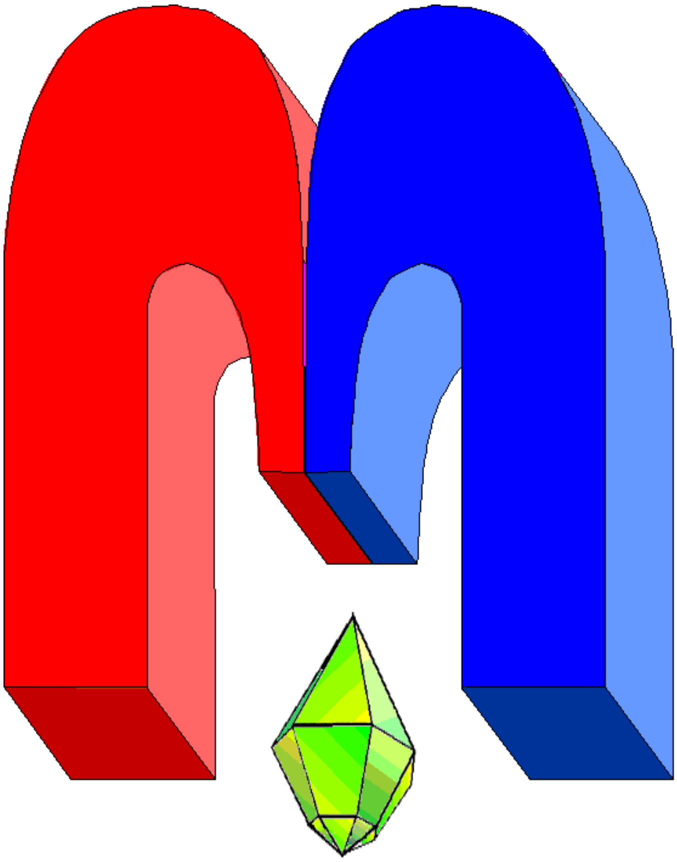
ISSN 2072-5981
doi: 10.26907/mrsej



Magnetic Resonance in Solids

Electronic Journal

Volume ***21***
Special Issue ***4***
Paper No ***19404***
1-6 pages
2019
doi: **10.26907/mrsej-19404**

http://mrsej.kpfu.ru
http://mrsej.ksu.ru

Established and published by Kazan University
Endorsed by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press (#015140),
August 2, 1996
First Issue appeared on July 25, 1997

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"*Magnetic Resonance in Solids. Electronic Journal*" (**MRSej**) is a peer-reviewed, all electronic journal, publishing articles which meet the highest standards of scientific quality in the field of basic research of a magnetic resonance in solids and related phenomena.

Indexed and abstracted by
Web of Science (*ESCI*, Clarivate Analytics, from 2015),
Scopus (Elsevier, from 2012), *RusIndexSC* (*eLibrary*, from 2006), *Google Scholar*,
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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Quantum magnetism of single molecules and diluted rare-earth alloys[†]

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(Received May 24, 2019; accepted May 28, 2019; published June 6, 2019)

This paper is a short overview of the works performed with Boris Malkin in a friendly and fruitful collaboration which started fifteen years ago and will, hopefully, be continuing for as many years as possible. Dealing with quantum tunnelling and coherence in non-cooperative magnetic systems such as $3d$-based single-molecules or $4f$-based diluted alloys, those works also involved our respective students, post-docs and colleagues of the time who all appear in the reference list. If most of those papers were published in usual physics journals, some of them were also published in the proceedings of conferences organized or co-organized by Boris or myself in Kazan, St. Petersburg or Les Houches.

PACS: 62.25.Fg ,76.60.Lz, 03.65.Yz.

Keywords: rare-earths ions, single molecules, quantum coherence, decoherence, electronic paramagnetic resonance.

Boris Malkin and I published our first common paper in 2005. It appeared in the proceedings of the CMDMR conference in Kazan [1]. Entitled "Direct measurements of anti-crossings of the electron-nuclear energy levels in $\mathrm{LiY}_{1-x}\mathrm{Ho}_x\mathrm{F}_4$ with sub-millimetre EPR spectroscopy", it showed a series of EPR measurements on Ho^{3+} ions, with controlled abundance of ^{6}Li and ^{7}Li isotopes. Here, the Ho^{3+} ground multiplet is split by a crystal field of S_4 symmetry, giving a non-Kramers ground doublet and a first excited singlet. The transitions between the two (in a double well picture: transitions between the ground levels in each well and the top of the barrier) were accurately detected, enabling first to refine the set of crystal-field parameters and the effective magnetic hyperfine constant. The fine structure of the $\mathrm{LiY}_{1-x}\mathrm{Ho}_x\mathrm{F}_4$ EPR lines were interpreted as a result of the isotopic disorder in the Li sublattices. The energy gaps at the anti-crossing points of the electron-nuclear sublevels of the ground doublet, induced by hyperfine interaction and, also, by weak random crystal-fields, were measured for the first time. Weak EPR signals from distorted single ion and Ho^{3+} pair were also observed.

One year later, we published the work "Cross-relaxation and phonon bottleneck effects on magnetization dynamics in $\mathrm{LiY}_{1-x}\mathrm{Ho}_x\mathrm{F}_4$" [2] dealing with the dc- and ac-susceptibility of the same system. The data were analyzed in the comprehensive framework of the microscopic theory of relaxation rates in the manifold of 24 electron-nuclear sublevels of the lowest doublet and the first excited singlet. The one-phonon transition probabilities were obtained using the electron-phonon coupling constants calculated in the framework of the exchange charge model and were checked by optical piezo-spectroscopic measurements. Interestingly, the specific features observed in the field dependences of the in- and out-of-phase susceptibilities (humps and dips, respectively) at the crossings (anti-crossings) of the electron-nuclear sublevels were well reproduced by simulations, only when the phonon bottleneck effect and the cross-spin relaxation were both taken into account. This effect, which had rarely been mentioned before, and probably never in the case of coherent dynamics, comes from the too slow heat transfer at the EPR frequencies.

[†] This paper is dedicated to Professor B.Z. Malkin on the occasion of his 80th jubilee.

The same year we published another paper entitled “Rare-earth solid state qubits” [3] which had and still has a significant impact: the first evidence of Rabi oscillations with a rare-earth ion opening the possibilities of quantum computation with what we called later “spin-orbit qubits” (see [9], a term which is now used by many authors). After having shown and studied in detail (different temperatures, field directions, microwave powers. . .) the electron-nuclear Rabi oscillations in the $J = 15/2$ system $\mathrm{Ca}_{1-x}\mathrm{Er}_x\mathrm{WO}_4$, we demonstrated that the rare-earth qubits, showing long decoherence times and large figures of merit – with expectations going up to 50 μs and 10^3 to 10^4 respectively, at ^{4}He temperatures – are suitable for scalable quantum information processing.

In 2007, we published an invited paper for the 2006 ICM conference held in Kyoto [4]. Entitled “Environmental effects on quantum relaxation and coherent dynamics in rare-earth ions”, it showed how the environment affects the fast coherent dynamics – of Rabi oscillations – and the slow quantum relaxation – after tunnelling – of the above mentioned rare-earth systems (Ho and Er highly diluted in YLiF_4) and the single-molecules Mn_{12}-ac and V_{15}, showing two different facets of the Stamp and Prokof’ev spin-bath model. In particular, a discussion of the ac susceptibility measurements performed on those systems allowed us to clarify the roles played by the phonon bath and the spin bath on the single-ion and two-ion electron-nuclear tunnelling of the rare-earth effective ground-state spins.

Until this point, except for the samples that had been elaborated in Saint Petersburg by Alexandra Tkachuk, the experiments were made in Kazan or/and in Grenoble. This was not the case for the following paper, entitled “Laser-polarimetric measurements of magnetic ac-susceptibility in $\mathrm{LiY}_{1-x}\mathrm{Ho}_x\mathrm{F}_4$ crystals” [5], the experiments of which have all been made in St. Petersburg. This technique, with shot-noise-limited polarimetric sensitivity was developed by Valerii Zapasskii and his group. It gives access to the magnetic ac-susceptibility in the range of Zeeman energies comparable with that of the hyperfine interaction in Ho^{3+} ions, with a signal/noise ratio exceeding 10^2. The obtained field and frequency dependences of the ac-susceptibility strikingly confirmed that the observed susceptibility resonant peaks mainly resulted from cross-relaxation transitions between the electron-nuclear sublevels of Ho^{3+} ions.

The same year we published the paper “Relaxation rates of magnetization in $\mathrm{LiY}_{1-x}\mathrm{Ho}_x\mathrm{F}_4$: crystals” [6], in which we developed a theory of magnetization relaxation of diluted alloys, based on the relaxation rates calculations of electron-phonon couplings and magnetic dipole-dipole interactions. Assuming a fast establishment of equilibrium in the spin system and a Gaussian spectral density of the dipole-dipole reservoir, we derived the master equation for a paramagnetic ion. This approach was then used to interpret the dynamical magnetic measurements of $\mathrm{LiY}_{1-x}\mathrm{Ho}_x\mathrm{F}_4$ single crystals. We showed specific variations of the low-temperature magnetization dynamics at magnetic field corresponding to the electron-nuclear anti-crossings of the Ho^{3+} ground-state. The measured dependences of the ac-susceptibility on frequency, Ho^{3+} concentration and applied magnetic field were described in detail when taking into account the phonon bottleneck and the cross-relaxation effects, as we did before [2].

The next paper entitled “^{19}F nuclear spin relaxation and spin-diffusion effects in the single-ion magnet $\mathrm{LiY}_{1-x}\mathrm{Ho}_x\mathrm{F}_4$” [7] came out in 2008. The temperature and magnetic field dependences of the ^{19}F nuclear spin-lattice relaxation were described, thanks to a detailed description of the magnetic dipole-dipole interactions between nuclei and paramagnetic impurities in the nuclear spin-diffusion processes. The observed non-exponential long time recovery of the nuclear magnetization after saturation at intermediate temperatures was found in agreement with predictions of the spin-diffusion theory for diffusion limited relaxation. In particular, the rates of nuclear spin-lattice relaxation increase at the Ho^{3+} electron-nuclear avoided level crossings due to quasi-resonant energy exchange between nuclei and paramagnetic ions spins, in contrast to the predominant role played by electronic cross-relaxation of the low-frequency ac-susceptibility.

The year after we switched to another rare-earth ion: Yb^{3+}. In a paper [8] entitled "Coherent spin manipulations in Yb^{3+}:$CaWO_4$ at X- and W-band EPR frequencies", the coherent spin dynamics of Yb^{3+} ions in X- and W-band EPR was demonstrated showing, in particular, Rabi oscillations with important single-qubit figures of merit in the high-field $^{171}Yb^{3+}$ X-band EPR spectrum (connected with the number of oscillations before full damping, often related to the phase memory time). This figure of merit, reaching values as large as 10^4 confirmed our predictions extrapolated from previous results in ref [3]. We also showed that the spin-lattice relaxation time of Yb^{3+} ions shortens when the resonance frequency increases, while the phase memory time, in contrast, grows noticeably. The variations of phase memory times were interpreted in terms of spectral and instantaneous diffusions. Clearly enough, the large coherence time in the W band could be used for the first applications of this rare-earth ion as qubit in quantum computing.

In the next paper "Spin-orbit qubits of rare-earth-metal ions in axially symmetric crystal-fields" [9], we studied the strong influence of the crystal field on the rare-earth spin-orbit qubits, in opposition to the usual $3d$-based spin qubits. At low temperature and in the presence of resonance microwaves, it is the magnetic moment associated with the crystal-field ground angular momentum which nutates, and the Rabi frequency Ω_R is anisotropic. We measured and interpreted the variations of the Rabi frequency with the magnitude and direction of the applied static magnetic field for the odd $^{167}Er^{3+}$ isotope diluted in a single-crystal $CaWO_4$. The hyperfine interactions split the curve representing the field dependence of the Rabi frequency, into eight different curves, which were fitted numerically and described analytically. Those "spin-orbit qubits" should enable detailed studies of decoherence mechanisms relevant at relatively high temperature (1.5-4.2 K) and open new ways for qubit addressing by using properly oriented magnetic fields.

In 2011, we published a study of the spin dynamics in our $LiY_{1-x}Ho_xF_4$ system, by measuring muon spin relaxation (μ-SR): "μ-SR study of spin dynamics in $LiY_{1-x}Ho_xF_4$" [10]. Zero-field positive muon spin relaxation (μ-SR) was measured for samples with $x = 0.0017$, 0.0085, 0.0406, and 0.0855. We characterized the dynamics associated with the formation of the (F-μ-F) complexes by comparing our data with Monte Carlo simulations to determine the concentration range over which the spin dynamics are determined primarily by the Ho^{3+}-μ interaction rather than by the F-μ interaction. The simulations showed that F-μ-F oscillations should evolve into a Lorentzian Kubo-Toyabe decay for an increasing static magnetic field distribution Gamma (i.e., increasing x), but the data did not show this behaviour, consistent with the recently reported existence of strong magnetic fluctuations in this system at low temperatures. Anisotropy in the field distributions causes small deviations – of the order of 10% – from the behaviour predicted for an isotropic distribution.

The year after, this study was extended into a comparison between muon spin relaxation and ac-susceptibility experiments: "Evolution of spin relaxation processes in $LiY_{1-x}Ho_xF_4$ studied via ac-susceptibility and muon spin relaxation" [11]. Measurements of the magnetic field and frequency dependences of the low-temperature ac-susceptibility and of the temperature and field dependence of the longitudinal-field positive muon spin relaxation were performed for $x = 0.0017$, 0.0085, 0.0408, and 0.0855. Numerical simulations enabling to fits the susceptibility data for the three first concentrations showed that Ho-Ho cross-relaxation becomes more important at higher concentrations, pointing out a crossover from single-ion to correlated multi-ions behaviour. Numerical simulations of the muon spin depolarization using the parameters extracted from the simulated susceptibility agree well with the data for $x = 0.0017$ and 0.0085. The μSR data for samples with higher concentrations and at $T < 10\,\mathrm{K}$ could not be described within a single-ion picture of magnetic field fluctuations giving evidence for additional mechanisms of depolarization associated with Ho^{3+} correlations. We also observed an unusual peak in the magnetic field dependence of the muon relaxation rate between 10 and 20 K that we ascribed to a modification of the Ho^{3+} fluctuation rate due to a field induced shift of the energy difference between the ground and the first excited crystal-field doublets, resulting from a peak in the phonon density of states centred near $63\,\mathrm{cm}^{-1}$.

The next paper "Decoherence window and electron-nuclear cross relaxation in the molecular magnet V_{15}" [12] was published the same year. It was dealing with the low-spin single-molecule system V_{15} embedded in the surfactant $[\mathrm{CH}_3(\mathrm{CH}_2)_{16}\mathrm{CH}_2]_2\mathrm{N}^+$ in order to dilute the V centers. Rabi oscillations have been studied at different microwave powers. An intense damping peak was observed when the Rabi frequency Ω_R falls in the vicinity of the Larmor frequency of protons Ω_N. The experiments were interpreted by a model showing that the damping time τ_R is directly associated with decoherence caused by electron-nuclear cross relaxation in the rotating reference frame. This decoherence induces energy dissipation in the range $\omega_\mathrm{N} - \sigma_e < \omega_\mathrm{R} < \omega_\mathrm{N}$, where σ_e is the mean super-hyperfine field induced by protons at V_{15}. Weaker decoherence without dissipation takes place outside this window. Specific estimations suggest that this rapid cross-relaxation in a resonant microwave field, observed here for the first time, may also take place in other single molecule systems such as the so-called Fe_8 and Mn_{12} systems.

The next paper appeared two years later when Boris'es former student, Eduard Baibekov, got involved in those subjects. With the title "Broadening of paramagnetic resonance lines by charged point defects in neodymium-doped scheelites" [13], it consisted in the study of the paramagnetic resonance line-width in a series of CaWO_4 and CaMoO_4 crystals with different concentrations of neodymium ions going from 0.0031 to 0.81 at %. The experimental data were interpreted in the framework of the statistical theory of line-broadening by charged point defects. Three different contributions were singled out, arising from the local electric fields, electric field gradients and magnetic fields of the nearby point defects. The interaction parameters were determined from the spectroscopic data available for the Nd:CaWO_4 crystals. Direct calculations of the line-width were performed for different crystal orientations with respect to the applied magnetic field. It was concluded that the major contribution to the broadening comes from the interactions with the random electric fields produced by neodymium and charge compensator ions.

The two last papers, in the same vein, appeared in 2014 and 2017 respectively. The first one "Coherent manipulation of dipolar coupled spins in an anisotropic environment" [14] consisted in a theoretical study of the coherent dynamics of a system of dipolar-coupled spin-qubits diluted in a solid and subjected to a driving microwave field. As it was shown before, the crystal-field effect of earth ions results in anisotropic g-tensors and thus modifies the dipolar coupling. A microscopic theory of spin relaxation in a transient regime for the frequently encountered case of axially symmetric crystal field was developed. The calculated decoherence rate was found to be nonlinear in the Rabi frequency. Interestingly, it was shown that the direction of a static magnetic field that corresponds to the highest spin g-factor is preferable in order to obtain a higher number of coherent qubit operations. The results of the calculations were in excellent agreement with the experimental data on Rabi oscillations recorded for the series of CaWO_4 crystals with different concentrations of Nd^{3+} ions.

The last paper was dealing with Gd, the single S-state rare-earth ion. Entitled "Coherent spin dynamics in a Gadolinium-doped $CaWO_4$ crystal" [15], it gave the first observation of Rabi oscillations of this rare-earth ion. Its main interest is the relatively large spin 7/2 associated with the large g-factor $\sim$2 – resulting from the S character of the lowest electronic multiplet – giving a magnetic moment as large as $\sim 7\,\mu$B. This system is therefore comparable to the previously studied 3d-based spins of the literature, but with a significantly larger size, implying a larger number of transitions. Also, this 8-state ground manifold of Gd^{3+} ion can represent an effective three-qubit quantum system. Those transitions were studied using the usual combination of continuous-wave and pulsed electron paramagnetic resonance spectroscopy (spin-echo technique). The corresponding Rabi damping curves and the spin coherence times were detected for various strengths of the microwave field. Those data were well reproduced in a theoretical model accounting for the intrinsic non-homogeneity of the microwave field within the microwave resonator and the magnetic dipole interactions in the diluted spin ensemble.

As a result of our collaboration, the quantum dynamics of diluted rare-earth alloys ($LiY_{1-x}Ho_xF_4$, $LiY_{1-x}Er_xF_4$, $Ca_{1-x}Gd_xWO_4$, $Ca_{1-x}Yb_xWO_4$, $Ca_{1-x}Nd_xWO_4$) and of low-spin (V_{15}) or large-spin (Mn_{12}-ac) single-molecules were studied in detail theoretically and experimentally for the first time. The experimental approach was based on different techniques such as ac-susceptibility, millimetre and sub-millimetre electron paramagnetic resonance, nuclear and muons spins relaxation, laser-polarimetric measurements.

To conclude this short review, I would like to thank Boris for his very effective and friendly collaboration during all those years. With his high expertise in theoretical physic and his availability in all circumstances, he has been the main pillar of this collaboration. Interestingly, this year is also the 80th anniversary of the collaboration between the Russian ministry of science and education and the French national centre for scientific research. We hope that our modest collaboration will contribute to the continuation of this agreement between our two countries.

I thank warmly Eduard Baibekov for his proofreading and his comments.

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