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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.
High-resolution optical and EPR spectroscopy in solid-state research

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(Received May 20, 2019; accepted May 28, 2019; published June 6, 2019)

A brief review is presented of high-resolution optical Fourier spectroscopy and EPR research on crystals containing 4f or/and 3d transition-metal ions, performed in the Institute of Spectroscopy RAS, in collaboration with the Kazan Federal University, the E.K. Zavoisky Kazan Physical-Technical Institute RAS, and many other institutions in Russia and abroad. The theoretical basis of these studies was developed by Boris Malkin.

PACS: 78.30.-j, 78.40.-q, 76.30.Kg, 78.20.Bh, 71.70.-d.

Keywords: dielectric crystals, rare earth ions, hyperfine structure, isotopes, crystal field, electron-phonon interaction, multiferroics, low-dimensional magnetics, phase transitions, high-resolution Fourier spectroscopy, EPR.

This review is inspired by my long-lasting collaboration with Boris Malkin

1. Introduction

First, a bit of history. Back in 1985, a unique high-resolution (0.005 cm$^{-1}$) infrared Fourier spectrometer UFS-02 was installed in the Institute of Spectroscopy. This instrument was a result of a hard work on the development of high-resolution Fourier spectroscopy in the USSR, initiated by Professor S.L. Mandelshtam in 1950-ies in the P.N. Lebedev Physical Institute. When the Institute of Spectroscopy was founded in 1968 and S.L. Mandelshtam became its director, UFS-01 and, then, UFS-02 high-resolution Fourier spectrometers were built in collaboration with the Central Construction Bureau for Unique Instrumentation of the Academy of Sciences. At that time, there were only few instruments of this class in the world and all of them were used for high-resolution atomic and molecular spectroscopy research. It was implicitly assumed that such high resolution is useless for solids because of a relatively large inhomogeneous spectral line broadening in the optical spectral range. Head of our Department of Solid State Spectroscopy in the Institute of Spectroscopy Professor G.N. Zhizhin entrusted me to find a solid-state problem for high spectral resolution. Our search ended with success: hyperfine [1–3] and, then, isotope [4] structures were found and studied in optical spectra of the LiYF$_4$:Ho$^{3+}$ single crystals.

In autumn 1990, I presented a poster at the IX Feofilov symposium, which took place in Repino near Leningrad, concerning our results on the isotope structure in the spectra of the monoisotopic Ho$^{3+}$ ion doped into the LiYF$_4$ matrix. We put forward a hypothesis that the spectral structure, which experimentally depended on the composition of the $^7$Li and $^6$Li isotopes in the crystal, was caused by small crystal-field changes connected with subtle differences in the equilibrium positions of the fluorine atoms nearest to the $^7$Li or $^6$Li isotopes, due to anharmonicity of zero-field vibrations. The opinion of scientific community at the symposium was almost unanimous that this cannot be true. Only one participant, after a brief reflection, said that he could calculate what changes in the crystal field would be. It was Professor B.Z. Malkin. At the beginning of 1991, our paper on the subject appeared in Physical Review Letters [4] but in 1993
a joint article containing a microscopic theory of the isotope structure connected with an isotopic disorder in a matrix was published in the Journal of Experimental and Theoretical Physics [5]. A detailed analysis [5,6] of the formation mechanisms of the isotopic structure of optical spectra allowed B.Z. Malkin to make a conclusion about the dominant role of static lattice deformation induced by the impurity isotope of lithium in comparison with the dynamic effect caused by the electron-phonon interaction. This was a beginning of our collaboration that continues up to the present time. Several topics of our joint research, some of them involved also EPR studies, are mentioned below. This is, by no means, a complete report on our collaboration.

2. Effects due to the isotopic disorder in the crystal lattice

Our paper [4] on the fine structure of hyperfine components in the spectra of the monoisotopic ion Ho$^{3+}$, due to isotopic disorder in the LiYF$_4$ matrix had a pronounced impact on the future research. In Ref. [7], which was released soon after [4], Macfarlane et al., based on their results on monoisotopic in lithium $^7$LiYF$_4$-Er$^{3+}$ single crystals showing the Er linewidth as small as 40 MHz, discussed inhomogeneous broadening by nuclear spin fields as a new limit for optical transitions in solids. Later, the linewidth of 16 MHz was registered for a 0.005% $^{170}$Er:$^7$LiYF$_4$ crystal [8]. In the monoisotopic $^7$LiYF$_4$ matrix with an uncontrolled Nd$^{3+}$ impurity concentration at a level of several ppm, the authors of Ref. [9] managed to resolve the isotope, hyperfine, and superhyperfine structures of Nd$^{3+}$ lines and to detect a record-narrow (10 MHz) inhomogeneously broadened line. These results as well as the infrared reflection spectra of the $^6$Li$_x$,$^7$Li$_{1-x}$YF$_4$ single crystals with different content of the lithium isotopes [10] were successfully modeled by B.Z. Malkin on the basis of his theory [9, 10]. A fine structure of EPR lines observed in the LiYF$_4$:Ho$^{3+}$ crystal with natural abundance of the Li isotopes was also interpreted as a result of the isotopic disorder in the Li-sublattice [11].

It was realized by the scientific community that the narrowest inhomogeneously broadened lines can be obtained in monoisotopic crystals. At present, we observe a revival of the interest to the research on the nature of inhomogeneous broadening of spectral lines and on their hyperfine structure in rare-earths-doped crystals, in connection with modern quantum information technologies [12]. Long coherence times are inherent in the hyperfine levels of the ground states of rare-earth ions in crystals (times up to 6 hours were observed [13]) and this can be used for information storage. Ref. [14] reported on a realization of 9 qubits on the hyperfine levels of $^{167}$Er$^{3+}$:CaWO$_4$ in a magnetic field. Qubits were manipulated by a microwave field in the EPR configuration. More convenient is to use optical laser radiation for this purpose by adding the third (metastable) level in the optical region (the so-called three-level Λ system) [12]. For all kinds of quantum memory, knowledge of the levels’ hyperfine structure is necessary to choose a suitable material. The resolved hyperfine structure is also favorable for the implementation of the gradient-echo [15] and off-resonant Raman-echo [16] protocols of optical quantum memory. Monoisotopic materials are now considered as the most promising for applications in quantum memory devices [8,12,17,18].

3. Studies of hyperfine and electron-phonon interactions in rare-earths-doped crystals

Construction of quantum informatics devices based on rare-earths-doped crystals requires knowledge of the energy levels’ hyperfine structure (HFS) and of relaxation processes. In a majority of cases HFS is masked by inhomogeneous broadening and is taken from calculations. So, the development of methods for accurate calculation of HFS is relevant. In not numerous cases
of the resolved HFS these methods can be directly tested and the information on relaxation processes can be obtained from the analysis of line widths. Our papers [19–22] are in line with these tasks. B.Z. Malkin has developed an algorithm for calculating the hyperfine structure in the spectra of rare-earth ions, based on the numerical diagonalization of the Hamiltonian (which included the Hamiltonian of a free ion and the interaction energy of $4f$ electrons with a crystal field) in the full basis of $4f$ shell states and subsequent projection of the hyperfine interaction operator on the subspace of electronic states of the selected LS-term. A high accuracy of the used calculation procedure made it possible to reproduce the subtle spectral effects found in the high-resolution spectra and to obtain quantitative estimates of the parameters of various interactions [19,21,22].

4. Fine structure of spectral lines due to random lattice deformations

A series of our joint works [23–26] was devoted to another type of a fine structure observed in the optical and EPR spectra of RE ions in crystals, namely, to the splitting of spectral lines corresponding to transitions with orbitally degenerate states involved. Lines with a specific dip in the center were observed in high-resolution optical spectra of tetragonal [23, 25, 26] and cubic [24] RE centers in crystals. To account correctly for such line shapes, a microscopic theory of deformation broadening and splitting of spectral lines was developed by B.Z. Malkin and his coworkers, including the derivation of the generalized distribution function of the components of the random strain tensor induced by point defects in an elastically anisotropic continuum [26]. The creation of this theory marked a new step in understanding the inhomogeneous broadening of spectral lines in crystals. Until now, the theory of inhomogeneous broadening of spectral lines used one-dimensional distribution functions of random deformations, which led, in particular, to erroneous interpretations of experimental results. Measurements of the evolution of the line shape (dip widths) with a change in the concentration of rare-earth ions made it possible to estimate the strengths of defects induced by impurity ions in activated crystals [25,26].

Random lattice deformations induce anticrossing gaps at the $\Delta m = 0$ crossing points of hyperfine levels of Ho$^{3+}$ characterized by the value $m$ of nuclear moment projection in the EPR [11] and optical [27] spectra of $^{7}$LiYF$_4$:Ho$^{3+}$ single crystals. These gaps can be used as a sensitive tool for the characterization of random lattice deformations. The results of the works [23–27] demonstrated the possibility of using high-resolution spectroscopy to quantify the quality of optical materials and optimize methods of their synthesis.

5. Rare-earth probe in studies of magnetic multiferroics: rare-earth iron borates

A significant part of our joint work concerns studies of crystals that undergo structural and magnetic phase transitions, using impurity ions as probes of the local structure, local electric and magnetic fields. Here, I’ll focus on only one class of such compounds, namely, on the extremely interesting RE iron borates that belong to a new class of multiferroics. These compounds, described by the general formula $R$Fe$_3$(BO$_3$)$_4$, $R =$ La, Pr – Er, Y, crystallize in the trigonal structure of the natural mineral huntite. There are isolated chains of iron ions in the structure interconnected by $RO_6$ and BO$_3$ isolated units. Iron borates exhibit diverse magnetic and magnetoelectric properties, which depend on a particular $R^{3+}$ ion. They are intensively studied, since L.N. Bezmaternykh and his coworkers in the Kirenskii Institute of Physics in Krasnoyarsk managed to grow large single crystals of good optical quality. We have performed high-resolution broad-band temperature-dependent optical spectroscopy studies of single crys-
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tals of $RFe_3(BO_3)_4$, $R = Pr, Nd, Sm, Eu, Tb, Dy$, and determined the energies and symmetries of the crystal-field levels of the $R^{3+}$ ions and the levels’ splittings at magnetic ordering [28–33]. On the basis of this information, B.Z. Malkin has found reliable physically grounded crystal-field parameters, using his earlier developed exchange-charge model [34]. Also the parameters of exchange interactions were found, herewith, to account for the quasi-one-dimensionality of the magnetic subsystem of iron, a model of a dimer containing two neighboring iron ions in a chain was developed. The crystal-field and exchange-interaction parameters were used to simulate the magnetic properties of rare-earth iron borates [28–32], the chiral structure of electric quadrupole moments [33], and to calculate the electric polarization [32]. The efficiency of various mechanisms of the magnetoelectric response of iron borates was estimated [32]. The measured characteristics of the high-resolution spectra, supplemented by calculations, enabled us to determine the type of magnetic structure in the magnetically ordered phase of the compounds studied, even when it was impossible or difficult to do that by magnetic neutron scattering [31, 32]. We have predicted the chirality effect of field-induced magnetic moments in the paramagnetic phase of dysprosium iron borate [33]. A new effect was discovered – the appearance of forbidden spectral lines at a magnetic ordering of a crystal [35]. Coupled electron-phonon excitations were detected and investigated [36, 37]. A new effect was discovered and explained, caused by a resonant electron-phonon interaction in an antiferromagnetic dielectric placed in an external magnetic field, namely, the formation of a gap in the spectrum of electronic excitations [37].

6. Spectroscopy of quasi-one-dimensional magnets

One-dimensional (1D) magnets exhibit unusual and interesting properties of quantum nature, they behave differently in the cases of integer and half-integer spins. In particular, there is a gap (Haldane gap) in the spectrum of magnetic excitations of chains of integer spins. This is not the case for chains of half-integer spins but, in real crystals, the spin-phonon interaction results in dimerization of atoms in the chain and formation of a singlet ground state separated by a gap from the first excited triplet state (the so-called spin-Pierls magneto-structural phase transition).

Several our papers were devoted to the study of a crossover from 1D to 3D magnetism in the family of $Y_{2-x}R_xBaNiO_5$ chain nickelates ($R$ is a rare earth) – quasi-1D Haldane magnets ($Ni^{2+}$ ion has the spin $S = 1$) [38–43]. While yttrium nickelate is an ideal 1D Haldane magnet (there is no magnetic ordering in it, at least down to 0.1 K, a Haldane gap is observed in the spectrum of magnetic excitations), replacing yttrium with rare earth leads to an increase of interchain interaction and 3D magnetic order. Magnetic phase transitions were detected by the erbium-probe method and the types of magnetic structures in $R_2BaNiO_5$ compounds were defined [38–40]. Comparison of the measurement data with the results of calculations performed by B.Z. Malkin led to the conclusion that the type of magnetic structure is determined by the single-ion magnetic anisotropy of the rare-earth ion [41, 42].

In the infrared spectra of chain gadolinium nickelate, a new type of optical excitations of a 1D chain of spins $S = 1$ was found, namely, a spinon-phonon bound mode [43]. Using the results of the lattice-dynamics calculations, we considered a possible mechanism for the formation of spinon-phonon excitations [43].

For another quasi-1D magnet, $NaV_2O_5$, containing chains of spins $S = \frac{1}{2}$, which undergoes a complex spin-Pierls-like transition accompanied by orbital ordering, we have performed a thorough experimental and theoretical study of the lattice dynamics in both high- and low-temperature phases [44–47]. Numerous folded modes signifying a lattice dimerization were found and interpreted.
Acknowledgments


This work was supported in part by the Presidium of RAS under the Program No. 5 “Photonic technologies in probing inhomogeneous media and biological objects”. The latest optical spectroscopy research was performed on the Unique Scientific Installation of the Institute of Spectroscopy “Multifunctional wide-range high-resolution spectroscopy” (http://www.ckp-rf.ru/usn/508571).

References

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