

== ORDER, DISORDER, AND PHASE TRANSITION IN CONDENSED MEDIA ==

MAGNETOELECTRIC EXCITATION OF RESONANCE TRANSITIONS IN THE ELECTRON SPIN SYSTEM OF IMPURITY ^{167}Er IONS IN YTTRIUM ORTHOSILICATE (Y_2SiO_5)

© 2024 V.F. Tarasov^{a*}, N.K. Solovarov^a, A. A. Sukhanov^a, Yu.D. Zavartsev^b

^aZavoisky Physical-Technical Institute, FRC Kazan Scientific Center of the RAS, 420029 Kazan, Russia

^bProkhorov General Physics Institute of the RAS, 119991 Moscow, Russia

*e-mail: tarasov@kfti.knc.ru

Received June 15, 2023

Revised October 20, 2023

Accepted October 21, 2023

Abstract. Study of continuous wave electron paramagnetic resonance spectra of impurity erbium ions in yttrium orthosilicate Y_2SiO_5 on an ELEXSYS spectrometer with a dielectric resonator reveals unusual dependence of the shape of the resonance lines on the intensity of microwave excitation. At a relatively high intensity and partial saturation of the resonance transition, the shape of the line is a superposition of a usual line corresponding to the derivative of the resonant absorption and an anomalous line corresponding to the resonance absorption itself. It is proposed that the appearance of the anomalous component of the line is associated with the simultaneous excitation of magnetic dipole and electric quadrupole transitions in the coupled system of magnetic dipole and electric quadrupole oscillators of the electron spin system of erbium ions.

Keywords: *electron spin resonance; Y_2SiO_5 ; Er^{3+} ; quadrupole resonance*

DOI: 10.31857/S00444510240210e9

1. INTRODUCTION

Currently, impurity rare-earth (RE) elements in dielectric crystals are considered as a promising material basis for the creation of solid-state quantum memory devices [1, 2]. Odd RE isotopes with non-zero nuclear spin allow to realize reversible coherence transfer from the optical band to electron-nuclear spin states possessing long coherence lifetime [3–6]. To increase the coherence lifetime of such states, special techniques of dynamical decoupling are used, in which the spin system is affected by special pulse sequences that excite resonance transitions between electron-nuclear spin levels [7, 8]. Therefore, of great interest is study the peculiarities of spin dynamics of impurity RE ions in their interaction with external and internal magnetic and electric fields. The dynamics of spin systems with spin $S = 1/2$ in an external magnetic field is described by the phenomenological Bloch equations [9, 10]. These equations are linear in the components of the magnetic dipole moment (or spin). However, it is known that for an adequate description of the spin dynamics of high-spin systems ($S > 1/2$) it is necessary

to consider higher spin multipole moments [11–14]. Therefore, the experimental study of the peculiarities of the dynamics of such systems seems to be a very important task. It should be kept in mind that there is a rule stating that multipoles are alternately forbidden for quantum systems in lower (ground) states. For example, electric monopole (charge), magnetic dipole and electric quadrupole are allowed [15].

Electron paramagnetic resonance (EPR) presents unique opportunities for determining the structure of impurity paramagnetic centers in crystals and studying the peculiarities of spin dynamics of their electron-nuclear levels [16–26]. In particular, ^{167}Er ions in yttrium orthosilicate (Y_2SiO_5) attract great attention [27–31].

In this work we investigate the features of the line shape of continuous wave (CW) EPR spectra of impurity ion ^{167}Er in single crystal Y_2SiO_5 (YSO) recorded by the conventional technique with magnetic field modulation on ELEXSYS E680 EPR spectrometer with dielectric resonator. An anomalous dependence of the resonance signal line shape on the microwave power value in the

resonator is found. We discuss the possible nature of the resonance lines of anomalous shape associated with resonant excitation of electric quadrupole transitions between the electron-nuclear levels of ^{167}Er ions.

2. SAMPLE PROPERTIES AND EXPERIMENTAL CONDITIONS

The YSO crystal structure is characterized by monoclinic symmetry $I2/a$, it has one axis of second-order symmetry b and a sliding reflection plane perpendicular to it. In this setup, the unit cell parameters $a = 1.04$ nm, $b = 0.67$ nm, $c = 1.25$ nm [32]. Impurity erbium ions can substitute for yttrium in two structurally non-equivalent positions with point group symmetry C_1 , denoted Y1 and Y2 [32], or Site 1 and Site 2 [33], respectively. Each of these positions has two magnetically nonequivalent positions, which become equivalent if the external magnetic field is directed parallel or perpendicular to the axis b . We investigated samples YSO, monoisotopically doped with trivalent ^{167}Er ions, which were grown in a weakly oxidizing atmosphere by the Czochralski method on an industrial unit “Crystall-3M” from melt with a relative concentration of erbium 0.005 at. %. The degree of isotope enrichment ^{167}Er was 96.3 at. %. At the same time isotopically pure ^{28}Si , without its own nuclear momentum, was used. The investigated samples had the form of parallelepipeds with dimensions $2.5 \times 2.5 \times 2.5$ mm³ and $3 \times 3 \times 10$ mm³ for measurements with dielectric and metal resonators, respectively. The facets of the parallelepipeds were perpendicular to the crystallographic axes D_1 , D_2 , b [34] with an accuracy of $\pm 1^\circ$.

The EPR spectra were measured in the X -band in the CW mode with magnetic field modulation at 100 kHz. Two spectrometers manufactured by Bruker were used: ELEXSYS E680 with cylindrical dielectric resonator ER4118MD5-W1 and EMXplus with cylindrical metallic resonator ER4122SHQ. Both resonators were operated in TE_{011} -mode, where the magnetic component of the microwave field B_1 is centered along the cylinder's central axis and the electric field lines follow circular paths perpendicular to the cylinder axis. Metal and dielectric resonators have fundamentally different distributions of the electric and magnetic components of the microwave field inside the resonator. The dimensions of the inner cavity of the metal resonator are comparable to the wavelength of the X -band (3 cm). Therefore, the magnetic and electric fields inside the resonator are spatially separated [35]. The investigated sample has small dimensions and is located on the

longitudinal axis of the resonator. Therefore, only the magnetic component of the microwave field acts on it. The dielectric resonator is a sapphire cylinder with inner and outer diameters of 5 and 10 mm, respectively, and a height of 13 mm, which is much smaller than the wavelength. In such a resonator, the vortex electric field is zero at the resonator axis but has a significant intensity near the walls of the dielectric cylinder [36]. The investigated sample occupies a significant part of the inner cavity of the resonator, so it is under the influence of both magnetic and electric components of the microwave field.

3. EXPERIMENTAL RESULTS

The Er^{3+} ion has an electronic configuration $4f^{11}$ with a ground multiplet $^4I_{15/2}$. It is a Kramers doublet. The energy of the first excited doublet is $W_{ex} = 39$ cm⁻¹ [37]. The nuclear spin of the ^{167}Er isotope $I = 7/2$. Therefore, the EPR spectra of this isotope contain $(2I + 1) = 8$ “allowed” resonance transitions between nuclear sublevels with the same projection of the nuclear spin I_z on the quantization axis ($\Delta m = 0$). In addition, the “forbidden” transitions with $\Delta m = 1$ and $\Delta m = 2$ are registered on the spectra. The orientation dependences of the spectra are well described by the effective spin Hamiltonian used in [26], which takes into account the Zeeman energy of the electron and nuclear spins in the external magnetic field and the energy of the hyperfine interaction of the electron spin with the nuclear spin and with the nuclear electric quadrupole moment. Figure 1 shows the EPR spectra of the $^{167}\text{Er}^{3+}$ ion in the crystallographic position Site 1 of the YSO single crystal, recorded on the ELEXSYS spectrometer at the orientation of the external magnetic field B along the crystallographic b -axis. The magnetic component of the microwave field was directed along the D_1 -axis.

There are 8 intensive single lines on the spectra, corresponding to “allowed” transitions. Between them there are weaker lines corresponding to “forbidden” transitions with $\Delta m = 1$. The doublet structure of the “forbidden” transitions is due to the contribution of electric quadrupole interactions [26]. It can be seen that the shape of the lines on the spectra depends significantly on the value of power P . At $P < 100$ μW the line shape corresponds to the usual for CW EPR spectra derivative of the absorption line contour. At $P = 300$ μW the line shape of “allowed” transitions becomes asymmetric, and at $P > 1$ mW there appears a noticeable contribution of the line of anomalous shape characteristic for the resonance absorption

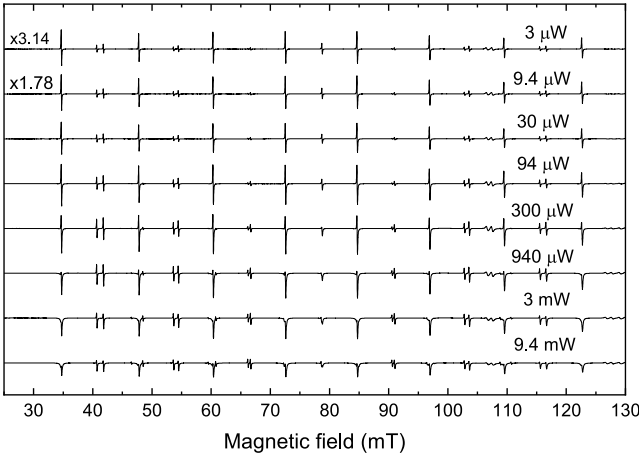


Fig. 1. Experimental spectra of $^{167}\text{Er}^{3+}$ in YSO, recorded on an ELEXSYS spectrometer with dielectric resonator at different microwave power P , indicated in the right part of the spectra. The numbers in the left part show the relative increase in the scale of the spectrum.

itself. For “forbidden” transitions, the line shape also changes its shape at slightly higher power. The analysis of the line shape has shown that the experimentally observed line shape can be approximated by the sum of two lines: the normal for CW EPR derivative of the absorption line and the anomalous line representing the inverted absorption line. Examples of such a decomposition of the resonance line into two components, performed using the EasySpin software package [38], for one “resolved” transition are shown in Fig. 2. The spectra were normalized by the amplitude of the normal component of the resonant lines. It turned out that the normal and anomalous components of the lines have a shape close to the Lorentzian one. At high microwave power, the amplitude of the “allowed” resonance transition line decreases due to saturation, and the “forbidden” transitions with $\Delta m = 2$ become visible on the spectra next to the “allowed” transitions. The probability of these “forbidden” transitions is small, so for them the line shape does not depend on the microwave power.

When the EPR spectra of this sample were measured under the same conditions on an EMXplus spectrometer with a metal resonator, the shape of the resonance lines did not depend on the microwave power. Fig. 3 shows the microwave power dependence of the amplitudes of the normal and anomalous components of the resonance lines for one “allowed” transition in the magnetic field of 47.8 mT when measured on the ELEXSYS spectrometer and the amplitude of the normal signal when measured on the EMXplus spectrometer.

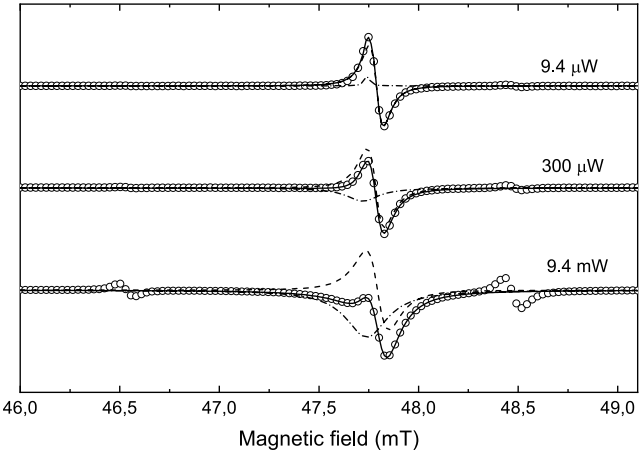


Fig. 2. Line shape of the “allowed” resonance transition of the $^{167}\text{Er}^{3+}$ ion when measured on the ELEXSYS spectrometer with different microwave powers, shown in the right part of the spectra. The circles are experiment, the dashed and dot-dashed lines are the contributions of the normal and anomalous components, respectively. The solid line is the sum of two components.

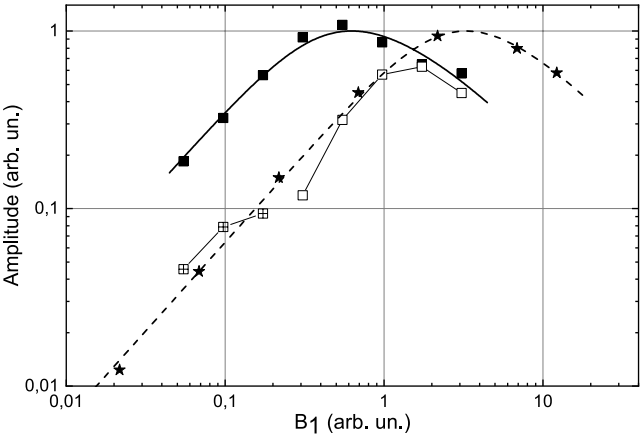


Fig. 3. Dependence of the amplitude of the resonance lines on the microwave field amplitude. Filled squares correspond to the normal component of the “allowed” transition measured on the ELEXSYS spectrometer. Empty squares correspond to the anomalous component of this transition. Crossed out empty squares correspond to the anomalous line of positive sign. Asterisks correspond to the intensity of the resonance transition measured on the EMXplus spectrometer. Thick lines are the calculation taking into account the partial saturation of the resonance transition. Thin lines connect experimental points with each other.

The results of measurements on the two spectrometers are normalized by the maximum of theoretical dependences. It can be seen that at low power P one observes a linear dependence of the amplitude of lines of the usual shape on the power on a logarithmic scale. This is typical for resonant absorption in the absence of saturation. As P increases, the resonance transition becomes saturated, the population difference between

the two Zeeman levels decreases, and the dependence of the line amplitude on the value of P becomes non-linear. Such dependences are characteristic for saturation of the inhomogeneously broadened resonance transition taking into account the processes of spectral diffusion [39]. To calculate these dependences, we modified expression (2.12) in [39] to emphasize the dependence of the signal amplitude on the microwave field magnitude expressed in relative units $B_1 = \sqrt{P}$:

$$A = K_1 \frac{K_2 B_1}{\sqrt{1 + (K_2 B_1)^2 + \beta (K_2 B_1)^2}} \quad (1)$$

The value of K_1 is determined by the parameters of the spin system. The dependence of the amplitude of the resonance line on the value of B_1 at constant temperature is determined only by the parameter

$$K_2 = \alpha \frac{(g\mu_B S_x) / \hbar}{\omega_1 + \omega_D}, \quad (2)$$

where α defines the ratio between the microwave power and the value of B_1 , g is the spectroscopic splitting factor, μ_B is the Bohr magneton, S_x is the matrix element of the resonance transition between two levels of a spin system with arbitrary spin [40, 41], ω_1 is the spin-lattice relaxation rate, ω_D is the spectral diffusion rate. The value β reflects the role of spectral diffusion in spin dynamics processes. In the absence of spectral diffusion $\beta = 0$. The optimal values of the coefficients for the best description of the experimental data are summarized in the table. The thick lines in Fig. 3 represent the theoretical calculation of the dependence of the amplitude of the normal line components on the microwave power at these coefficients.

Table

Spectrometer	K_1	K_2	β
ELEXSYS	1.6124	2.0559	0.3712
EMXplus	2.2929	0.3005	0.7348

Within the framework of this paper, we do not discuss the magnitude and physical nature of the parameters in (1) and (2). We only note that the influence of spectral diffusion processes on the saturation processes of resonance transitions is much stronger when measured on the EMXplus spectrometer. The small

value of the parameter K_2 at measurements on the EMXplus spectrometer is a consequence of a much smaller value of the magnetic component of the microwave field in the metal resonator at the same microwave power compared to the dielectric resonator.

4. DISCUSSION

Fig. 2 shows that the shape of the resonance lines is the sum of two components. These are the usual for CW EPR line, representing the derivative of the resonance absorption by the magnetic field, and the anomalous component, representing the resonance absorption line. At low microwave power, a small anomalous component of positive sign is present in the decomposition of the experimental line shape. We believe that the appearance of this component is caused by a small asymmetry of the resonance transition line shape. The amplitude of this line is approximately proportional to the amplitude of the normal component of the resonance line. We attribute the appearance of intense resonance lines of anomalous shape at high microwave power to the excitation of electric quadrupole transitions in the spin system. These transitions are excited by the oscillating gradient of the electric component of the microwave field, which is always present in the dielectric resonator of the EPR spectrometer [36].

This phenomenon was first detected by us when studying the EPR spectra of impurity Ho^{3+} paramagnetic centers in synthetic forsterite [42, 43]. Later, resonance lines were detected in the EPR spectra of impurity Yb^{3+} ions in Mg_2SiO_4 [44] during measurements on an EPR spectrometer with a dielectric resonator. We believe that the observed changes in the shape of the resonance lines are a spectroscopic manifestation of the interaction between the magnetic dipole and electric quadrupole subsystems of the high-spin system. Evidence that the observed changes in the line shape of the EPR spectra are indeed due to the resonant excitation of electric quadrupole transitions is given in [43]. This paper is mainly devoted to a new interpretation of the nature of physical interactions leading to the observed effect.

The following was found in [42, 43].

1. Electric quadrupole transitions are excited by the gradient of the electric component of the microwave field in a dielectric resonator.

2. There is a strong dependence of the amplitude of the anomalous component of the EPR spectrum on the power of microwave field the resonator, which has a threshold character.

3. The power threshold at which the anomalous component appears decreases with decreasing temperature.

4. The phase of the anomalous component is shifted with respect to the phase of the normal component, coinciding with the phase of the magnetic field modulation.

5. The anomalous signal has a different phase for resonance transitions with different sign of the derivative of the dependence of the resonance frequency on the magnetic field.

In order to explain the appearance of anomalous lines in the EPR spectra, we must consider the algorithm of operation of the receiving path of the EPR spectrometer in the mode with magnetic field modulation. It consists in the fact that in each half-period of modulation the signal coming from the microwave detector of the spectrometer is integrated, and the output signal is the difference of the integrals of two half-periods. If the amplitude of the magnetic field modulation is much smaller than the width of the resonance transition line, the line shape on the EPR spectra represents the derivative of the resonance absorption line by the magnetic field.

Formally, to obtain an anomalous form of the EPR signal, it is necessary to replace the difference of the integrals of the absorption signal for two modulation half-periods by their sum in the algorithm of the receiving tact of the EPR spectrometer. The equivalent operation consists in inverting the sign of the integral in one of the two modulation half-periods of the magnetic field. For resonance transitions in EPR spectroscopy, this can be at oscillations of resonance absorption and resonance emission of the electromagnetic field synchronous with the magnetic field modulation. In physical systems such a situation is realized for an oscillator oscillating at its own frequency ω_0 and under the action of an external periodic force modulated in frequency $\omega = \omega_0 \sin(\omega_m \cdot t)$, where ω_m is the modulation frequency. In the modulation half-period, when $\omega > \omega_0$, the phase of the external force will be ahead of the oscillator phase, and the energy of the external force will be absorbed by the oscillator. In the other half-period, the phase of the external force will lag behind the phase of the oscillator, and the energy of the oscillator will be radiated [15]. Thus, synchronously with the frequency of the magnetic field modulation there will be an oscillation of the sign of the S_y component of the spins in the rotating coordinate system. In [42, 43], we assumed that these two coupled oscillators are the magnetic dipole moment and the existing electric quadrupole moment of the electron shell

of the impurity ion, which are simultaneously excited by the magnetic and electric components of the microwave field in the resonator of the EPR spectrometer.

At the same time, no convincing explanation was given for the threshold character of the appearance of resonance lines of anomalous shape and the dependence of the magnitude of this threshold on temperature. This can be done on the basis of the results of [41], where it was shown on the example of the electron spin $S = 1$ that selective excitation of one resonance transition in a three-level spin system leads to a reversible transformation of the components of the magnetic dipole moment into the components of the electric quadrupole moment. This leads to a change in the absolute value of the dipole moment of the spin system and the associated transformation of the dipole polarization of the spin system into a quadrupole alignment.

In this case, the gradient of the electric component of the microwave field interacts with the resulting dynamic quadrupole moment. In this case, the magnetic dipole moment and the electric quadrupole moment are related by the master-slave relation. When the magnetic field is increased during the magnetic field modulation, the precession phase of the transverse components of the magnetic dipole moment is ahead of the precession phase of the transverse components of the electric quadrupole moment, and when the magnetic field is decreased, the phase of the transverse components of the magnetic dipole moment lags behind the phase of the electric quadrupole moment. As a result, there appears an oscillating alternating phase shift between the transverse components of the magnetic dipole moment and the electric quadrupole moment. The sign of this shift changes twice during the modulation period, and the energy exchange between these two oscillators oscillates with the frequency of the magnetic field modulation. As a result, the signal at the output of the receiving path of the EPR spectrometer takes the form of the resonance absorption line rather than its derivative.

The rate of conversion of the dipole moment into a quadrupole moment is determined by the frequency of “nutation” of the S_z -component of the dipole moment in the rotating reference frame at resonant excitation. This rate is proportional to the amplitude of the magnetic component of the microwave field B_1 . The magnitude of the generated quadrupole moment depends on the ratio of two competing processes: the nutation of spins at resonance excitation and the relaxation processes tending to return the spin system to an equilibrium state. The degree of conversion of the dipole moment into a quadrupole moment can

be judged by the deviation of the value of the S_z -component of the dipole moment from the equilibrium value at a given temperature in the absence of resonance excitation. Here there is a complete analogy with the well-known phenomenon of saturation of the resonance transition, where there is also a threshold value of the microwave power, at which the intensity of the resonance line ceases to depend linearly on the microwave power due to a decrease in the value of the S_z . The threshold value of the microwave radiation intensity in both cases is determined by the equality of the rate of change of the S_z -component of the dipole moment at resonance excitation and the rate of relaxation of the spin system to the unperturbed state. According to (2), the threshold value B_1 depends on the spin-lattice relaxation rate, which for the Er^{3+} ions in YSO rapidly increases with increasing temperature [45]. Therefore, the magnitude of the microwave power threshold at which the anomalous line shape appears, as noted in [42, 43], also increases with increasing temperature. Fig. 3 shows that the anomalous line in the EPR spectra and the saturation effect appear at approximately the same microwave power.

Note that electric quadrupole transitions caused by the resonant interaction of the oscillating gradient of the electric field with the quadrupole moment of the electron and nuclear spins have been previously observed. In [46], electric quadrupole transitions were excited by a traveling electromagnetic wave in a magnetically ordered spin system $\text{Sr}_2\text{CoGe}_2\text{O}_7$. Electric quadrupole transitions with a change in the projection of the nuclear spin on the quantization axis $\Delta I_z = \pm 2$, forbidden by the selection rules for dipole transitions, were observed in an oscillating capacitor electric field for nuclear spins ^{75}As , ^{69}Ga , and ^{71}Ga in a GaAs single crystal [47]. When magnetic dipole and electric quadrupole transitions were co-excited on the nuclei ^{75}As , ^{69}Ga , and ^{71}Ga , the effect of electric quadrupole transitions on the intensity of resonance lines of magnetic dipole transitions was observed [48]. In [49], intense acoustic oscillations were excited in NaCl to create an oscillating electric field gradient on the nuclear ^{23}Na spins. In [50, 51], nuclear spin echo signals excited by a combination of resonant electromagnetic and acoustic pulses were recorded on nuclear spins ^{127}I in CsI. In this case, electromagnetic pulses excited magnetic dipole transitions and acoustic pulses excited electric quadrupole transitions.

5. CONCLUSIONS

In the conventional technique of studying the CW-state EPR spectra of impurity $^{167}\text{Er}^{3+}$ ions in Y_2SiO_5 single crystal on the ELEXYS E680 EPR spectrometer with dielectric resonator, an anomalous dependence of the shape of resonance lines on microwave power was found. At low microwave power, the resonance lines in the spectra have the usual shape of the derivative of the resonance absorption line. At increasing microwave power and partial saturation of the resonance transition, the shape of the lines changes and represents a superposition of the usual derivative of the resonance absorption line and an anomalous line having the form of the resonance absorption line itself. The appearance of the anomalous line shape under intense resonance influence on the high-spin system is explained by the transformation of the magnetic dipole moment of the electron spin system into the electric quadrupole moment and the formation of a system of coupled magnetic dipole and electric quadrupole oscillators. We assume that in the dielectric resonator of an EPR spectrometer, the microwave electromagnetic field simultaneously excites two types of resonance transitions. The magnetic component excites magnetic dipole transitions, and the gradient of the electric component excites electric quadrupole transitions in the dynamic quadrupole subsystem created by the intense resonance excitation. The anomalous component of the resonant line is a consequence of the oscillatory phase shift between the coherences of the dipole and quadrupole subsystems arising in this case with the frequency of the magnetic field modulation. The possibility of excitation of electric quadrupole transitions in high-spin systems should be taken into account when studying and interpreting the EPR spectra of such systems using spectrometers equipped with dielectric resonator.

ACKNOWLEDGEMENTS

The authors are grateful to V. A. Shustov for the X-ray structural studies of the specimen. The measurements were carried out at equipment of Distributed Spectral-Analytical Center of Shared Facilities for Study of Structure, Composition and Properties of Substances and Materials of FRC Kazan Scientific Center of RAS

FUNDING

The work was performed with the financial support from the government assignment for FRC Kazan Scientific Center of RAS with the use of scientific

equipment of Distributed Spectral-Analytical Center of Shared Facilities for Study of Structure, Composition and Properties of Substances and Materials of FRC Kazan Scientific Center of RAS.

REFERENCES

1. C.W. Thiel, T. Böttger, R. L. Cone, *J. Lumin.* **131**, 353 (2011).
2. J.J.L. Morton, P. Bertet, *J. Magn. Reson.* **287**, 128 (2018).
3. M. Rančić, M.P. Hedges, R.L. Ahlefeldt et al., *Nature Physics* **14**, 50 (2018).
4. M. Businger, A. Tiranov, K. T. Kaczmarek et al., *Phys. Rev. Lett.* **124**, 053606 (2020).
5. A. Ortu, A. Tiranov, S. Welinski et al., *Nature Materials* **17**, 671 (2018).
6. J.J. Longdell, E. Fraval, M. J. Sellars et al., *Phys. Rev. Lett.* **95**, 063601 (2005).
7. E. Fraval, M. J. Sellars, and J. J. Longdell, *Phys. Rev. Lett.* **92**, 077601 (2004).
8. G.A. Álvarez, A. Ajoy, X. Peng and D. Suter, *Phys. Rev. A* **82**, 042306 (2010).
9. M.A.A. Ahmed, G. A. Álvarez, and D. Sute, *Phys. Rev. A* **87**, 042309 (2013).
10. F. Bloch, Nuclear Induction, *Phys. Rev.* **70**, 460-474 (1946).
11. A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition ions*, Clarendon Press, Oxford, (1970).
12. U. Fano, *Phys. Rev.* **133**, B828 (1964).
13. R.C. Hilborn, L. R. Hunter, K. Johnson et al., *Phys. Rev. A* **50**, 2467 (1994).
14. R. Wieser, *Phys. Rev. B* **84**, 054411 (2011).
15. H.-J. Stöckmann, D. Dubbers, *New J. Phys.* **16**, 053050 (2014).
16. J. D. Macomber, *The Dynamics of Spectroscopic Transitions*, Wiley, New York, London, Sydney, Toronto, 1976, ch. 3.
17. G. Wolfowicz, H. Maier-Flaig, R. Marino et al., *Phys. Rev. Lett.* **114**, 170503 (2015).
18. S. Welinski, A. Ferrier, M. Afzelius et al., *Phys. Rev. B* **94**, 155116 (2016).
19. H.-J. Lim, S. Welinski, A. Ferrier et al., *Phys. Rev. B* **97**, 064409 (2018).
20. G. Dold, C. W. Zollitsch, J. O'Sullivan et al., *Phys. Rev. Applied* **11**, 054082 (2019).
21. M.N. Popova, S. A. Klimin, S. A. Moiseev et al., *Phys. Rev. B* **99**, 235151 (2019).
22. A.A. Sukhanov, V. F. Tarasov, R. M. Eremina et al., *Appl. Magn. Reson.* **48**, 589 (2017).
23. A.A. Sukhanov, V. F. Tarasov, Yu.D. Zavartsev et al., *JETP Letters* **108**, 210 (2018).
24. R.M. Eremina, V.F. Tarasov, K. B. Konov et al., *Appl. Magn. Reson.*, **49**, 53 (2018).
25. R.F. Likеров, V. F. Tarasov, A. A. Sukhanov et al., *Optical Materials* **85**, 414 (2018).
26. R.F. Likеров, V. F. Tarasov, A. A. Sukhanov et al., *Magn. Reson. Solids* **22**, 20201(2020).
27. O. Guillot-Noël, Ph. Goldner, and Y. Le Du, *Phys. Rev. B* **74**, 214409 (2006).
28. O. Guillot-Noël, H. Vezin et al., *Phys. Rev. B* **76**, 180408(2007).
29. S. Welinski, C. W. Thiel, J. Dajczgewand et al., *Optical Materials* **63**, 69 (2017).
30. S. Welinski, Ph.J.T. Woodburn, N. Lauk et al., *Phys. Rev. Lett.* **122**, 247401 (2019).
31. Y-H. Chen, X. Frnandez-Gonzalvo, S. P. Horvath et al., *Phys. Rev. B* **97**, 024419 (2018).
32. J.-Y. Huang, P. Y. Li, Z-Q. Zhou, at al., *Phys. Rev. B* **105**, 245134 (2022).
33. B.A. Maksimov, Yu.A. Kharitonov, V. V. Ilyukhin et al., *Proceedings of the Academy of Sciences* **183**, 1072 (1968).
34. S. Campos, A. Denoyer, S. Jandl et al., *J. Phys.: Condens. Matter* **16**, 4579 (2004).
35. Y. Sun, T. Böttger, C. W. Thiel et al., *Phys. Rev. B* **77**, 085124 (2008).
36. N.L. Jobbitt, J.-P.R. Wells, M. F. Reid et al., *Phys. Rev. B* **104**, 155121 (2021).
37. S. Stoll, A. Schweiger, *J. Magn. Reson.* **178**, 42 (2006).
38. E.L. Wolf, *Phys. Rev.* **142**, 555 (1966).
39. A.V. Astashkin and A. Schweiger, *Chem. Phys. Letters* **174**, 595 (1990).
40. K.M. Salihov, *JETP* **162**, 630 (2022).
41. J.L. Harthoorn, J. Smidt, *Appl. Sci. Res.* **20**, 148 (1969).
42. V.F. Tarasov, R. B. Zaripov, N. K. Solovarov, A. A. Sukhanov, E. V. Zharikov, *JETP Letters*, **93**, 282 (2011).
43. V.F. Tarasov, R. B. Zaripov, N. K. Solovarov et al., *Appl. Magn. Reson.* **45**, 239 (2014).
44. V.F. Tarasov, A. A. Sukhanov, V. B. Dudnikova at al., *JETP Letters*, **106**, 78 (2017).
45. I.N. Kurkin, K. P. Chernov, *Physica B+C* **101**, 233 (1980).
46. M. Akaki, D. Yoshizawa, A. Okutani, T. Kida, J. Romhányi, K. Penc, M. Hagiwara, *Phys. Rev. B* **96**, 214406 (2017).
47. I.I.Sadykov, E. P. Khaimovich, *JETP Letters*, **34** 441 (1981).
48. N. E. Brun, R. J. Mahler, H. Mahon, W. L. Pierce, *Phys. Rev.* **129**, 1965-1970, (1963).
49. W.G. Proctor, W. A. Robinson, *Phys. Rev.* **104**, 1344 (1956).
50. V.A. Golenischev-Kutusov, N. K. Solovarov, V. F. Tarasov, *JETP Letters*, **22**, 266 (1975).
51. V.A. Golenischev-Kutusov, A. I. Sirasiev, N. K. Solovarov, V. F. Tarasov, *JETP*, **71**, 1074 (1976) [in Russian].