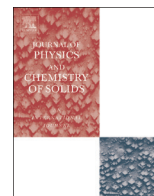




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journal homepage: [www.elsevier.com/locate/jpcs](http://www.elsevier.com/locate/jpcs)EPR, ENDOR and optical spectroscopy of Yb<sup>3+</sup> ion in KZnF<sub>3</sub> single crystalsM.L. Falin<sup>a,\*</sup>, K.I. Gerasimov<sup>a,b</sup>, V.A. Latypov<sup>a</sup>, A.M. Leushin<sup>b</sup>, S. Schweizer<sup>c</sup>, J.-M. Spaeth<sup>d</sup><sup>a</sup> Kazan Zavoisky Physical-Technical Institute, 420029 Kazan, Russian Federation<sup>b</sup> Kazan (Volga Region) Federal University, 420008 Kazan, Russian Federation<sup>c</sup> South Westphalia University of Applied Sciences, Department of Electrical Engineering, 59494 Soest, Germany<sup>d</sup> University of Paderborn, Department of Physics, 33098 Paderborn, Germany

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## ABSTRACT

The paramagnetic center of tetragonal symmetry formed by the Yb<sup>3+</sup> ion in the KZnF<sub>3</sub> crystal has been studied using methods of EPR, ENDOR and optical spectroscopy. The location of the impurity ion and the structural model of the complex differing from the model of the Yb<sup>3+</sup> center in KMgF<sub>3</sub> have been established. The empirical scheme of the energy levels of the Yb<sup>3+</sup> ion has been found. The parameters of its interaction with the crystal electrostatic field and the hyperfine interaction with ligands of the nearest environment have been determined. The parameters of the crystal field were used for the analysis of the distortions of the crystal lattice in the vicinity of Yb<sup>3+</sup>. The parameters of the transferred hyperfine interaction have been calculated for the distances between Yb<sup>3+</sup> and F<sup>-</sup> ions of the nearest environment obtained taking into account the found distortions. They are in good agreement with the experimental values.

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## 1. Introduction

The composition of crystals of double fluorides (Me<sup>+</sup>Me<sup>2+</sup>F<sub>3</sub><sup>-</sup>) with the perovskite-type structure is more complicated than that of, e.g., widely used matrices of the homologous series of fluorite (Me<sup>2+</sup>F<sub>2</sub><sup>-</sup>). The high cubic symmetry and a wide variety of physicochemical properties make the study of impurity crystals of double fluorides interesting both from the theoretical and practical point of view.

Using rare-earth (RE) elements as probes makes perovskites useful subjects for studying the behavior of RE ions located in two different positions in the crystal: either in the a-type sites in the environment of the octahedron of six fluorine ions or in b-type sites in the coordination of the same 12 ligands.

However, the introduction of trivalent RE ions in perovskite structures is hampered, on the one hand, by the considerable difference of sizes of RE ions and lattice cations, and on the other hand, by the ion valence of the substitution.

In [1] we presented the results of the detailed study of the tetragonal paramagnetic center of the Yb<sup>3+</sup> ion in the KMgF<sub>3</sub> crystal using electron paramagnetic resonance (EPR), electron-nuclear double resonance (ENDOR) and optical spectroscopy. These results showed conclusively that the tetragonal center is

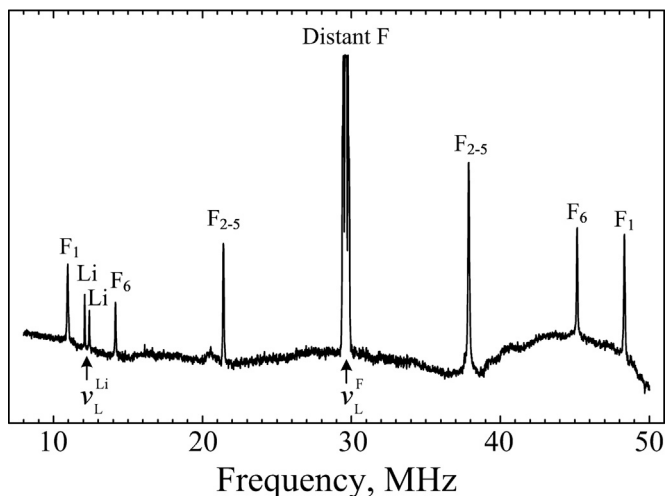
formed during the incorporation of Yb<sup>3+</sup> in the octahedral positions of Mg<sup>2+</sup> ions, and not as a result of substituting univalent K<sup>+</sup> ions surrounded by 12 fluorine ions, as it was supposed earlier in [2,3]. The excessive positive charge is compensated by the non-magnetic oxygen ion O<sup>2-</sup>, which substitutes one of fluorine ions in the octahedron of the nearest environment of the Yb<sup>3+</sup> ion. One could expect that a similar center would exist in the KZnF<sub>3</sub> crystal, the structural parameters of which ( $a_0^{\text{KZnF}_3} = 0.4040$  nm) almost coincide with those of the KMgF<sub>3</sub> crystal ( $a_0^{\text{KMgF}_3} = 0.3987$  nm). However, this is not the case in reality. It was found that the tetragonal symmetry center of the Yb<sup>3+</sup> ion in KZnF<sub>3</sub> is formed only upon doping with YbF<sub>3</sub> fluoride and metal lithium. In this work we present the results of the experimental and theoretical study of such Yb<sup>3+</sup> ion centers in the KZnF<sub>3</sub> crystal using methods of EPR, ENDOR and optical spectroscopy.

## 2. Experimental results

Samples KZnF<sub>3</sub>:Yb were grown using the Bridgman–Stockbarger method in graphite crucibles in fluorine atmosphere. Crystals were activated by introducing 0.5–1.5 wt% YbF<sub>3</sub> in the charge with the addition of metallic lithium in specific cases. EPR and ENDOR experiments were carried out on modified X-band (9.5 GHz) ERS-231 (Germany) [4] and custom-built EPR/ENDOR X-band spectrometers (see, e.g., [5]) at the temperatures of 4.2 and

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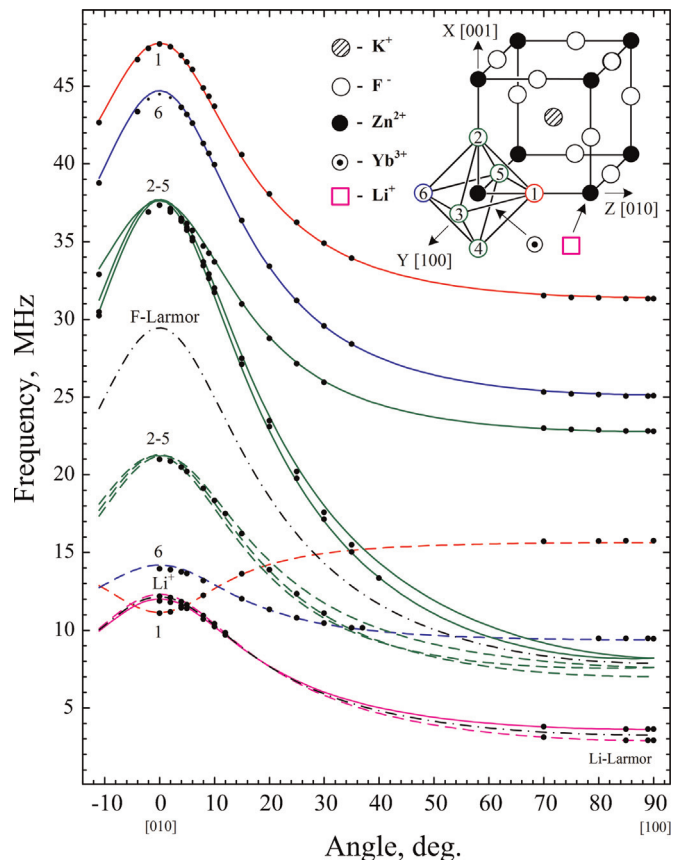
**Fig. 1.** ENDOR spectrum of  $\text{Yb}^{3+}$  ( $T_{\text{tet}}$ ) in  $\text{KZnF}_3$  at  $H \parallel C_4$ . The positions of the Larmor frequency of lithium and fluorine are denoted by arrows.  $H=725$  mT ( $g_{\text{H}}=0.922$ ),  $T=4.2$  K.

6–8 K, and optical spectra were measured on a home-built multifunctional optical spectrometer [6] at 2, 77 and 300 K. Three types of the paramagnetic center  $\text{Yb}^{3+}$  located in the structurally non-equivalent positions were singled out in  $\text{KZnF}_3:\text{Yb}^{3+}$  ( $T_{\text{cub}}$ ) of the cubic symmetry,  $\text{Yb}^{3+}$  ( $T_{\text{trig}}$ ) consisting of four magnetically non-equivalent complexes of the trigonal symmetry, and  $\text{Yb}^{3+}$  ( $T_{\text{tet}}$ ) consisting of three magnetically non-equivalent complexes of the tetragonal symmetry. As it was noted above,  $\text{Yb}^{3+}$  ( $T_{\text{tet}}$ ) in  $\text{KZnF}_3$ , in contrast to  $\text{KMgF}_3$  [1], is formed only, when metallic lithium is introduced into the charge. The ENDOR spectrum of  $\text{Yb}^{3+}$  ( $T_{\text{tet}}$ ) showed lines, which were identified as lines of fluorine and lithium ions (Fig. 1). The intensity of the ENDOR lines has the maximum value, when the constant magnetic field  $H$  is directed along the main crystallographic directions of the crystal, and decreases considerably at the deviation from them. The angular dependence of the ENDOR spectra in the (001) plane was studied in order to exactly identify the ENDOR lines according to their belonging to certain  $\text{F}^-$  and  $\text{Li}^+$ . Fig. 2 shows the plot of the angular dependence of these lines. It was established from the angular dependence of the ENDOR lines that  $\text{Yb}^{3+}$  is in the center of a regular octahedron, i.e., substitutes  $\text{Zn}^{2+}$ , and the local compensation of the additional positive charge is performed by the replacement of one of the  $\text{Zn}^{2+}$  ions of the nearest environment by a lithium ion. The inset in Fig. 2 shows a fragment of the crystal lattice  $\text{KZnF}_3$  with positions of the interstitial ion and ion-compensator. The complex  $[\text{YbF}_6]^{3-}$  is characterized by the symmetry  $C_{4v}$  and the absence of an inversion center. The local symmetry of  $\text{F}_{1,6}$  and  $\text{Li}^+$  ions is  $C_{4v}$ , and that of each of  $\text{F}_{2,3,4,5}$  ions is  $C_s$ . The spin Hamiltonian of the described system has the form:

$$\mathcal{H} = g\beta\mathbf{H}\mathbf{S} + \sum_i (\mathbf{S}\mathbf{A}_m^{(i)}\mathbf{I}^{(i)} - g_n^{(i)}\beta_n\mathbf{H}\mathbf{I}^{(i)}), \quad (1)$$

where  $S=1^{\text{F}}=1/2$ ,  $1^{7\text{Li}}=3/2$ ,  $g_n=5.525454$  (2.1707) for  $^{19}\text{F}^-$  ( $^7\text{Li}$ ),  $\mathbf{A}_m^{(i)}$  is the five-component tensor of the transferred hyperfine interaction (THFI) for  $\text{F}_{2,3,4,5}$  and two-component tensor for  $\text{F}_{1,6}$  and  $\text{Li}$ ,  $i$  labels the ligands,  $m$  labels the tensor components (1–5). Since the quadrupole moment of  $\text{Li}$  is small ( $Q \sim 0$ ) and the coupling between  $\text{Li}^+$  and  $\text{Yb}^{3+}$  is mainly due to the dipole–dipole interaction, instead of six ENDOR lines (sum and difference ENDOR lithium lines) only two are observed. Expressions for the frequencies of the ENDOR transitions are similar to those, which were used in ENDOR experiments of the tetragonal  $\text{Yb}^{3+}$  center in  $\text{KMgF}_3$  [1].

Experimental values of the THFI parameters are given in Table 1. The obtained THFI parameters are compared with the



**Fig. 2.** Angular dependence of ENDOR lines of fluorine and lithium ions for  $\text{Yb}^{3+}$  ( $T_{\text{tet}}$ ) in  $\text{KZnF}_3$  during the rotation of the magnetic field  $H$  in the (001) plane.  $\nu=9.355$  GHz,  $T=4.2$  K. • – experimental points; 1–6 – numbering of  $\text{F}^-$  ions corresponding to the notations in the inset; calculated lines: solid and dashed (summary and difference ENDOR frequencies, respectively) on the basis of data in Table 1, dash-dotted – Larmor frequencies of  $^{19}\text{F}$  and  $^7\text{Li}$  nuclei. Inset – structural model of  $\text{Yb}^{3+}$  ( $T_{\text{tet}}$ ).

parameters of cubic centers [7] in the following manner. It is known that  $\hat{B} = (h/g\beta)\hat{A}$  is a true tensor unlike  $\hat{A}$ , and that any asymmetric second-rank tensor can be decomposed into a symmetric and asymmetric parts. Using corresponding transformations, from the symmetric part one can single out a part called in the following  $B_s = (1/3)(hA_1/g\beta + hA_2/g\beta + hA_3/g\beta)$  which represents the isotropic (purely covalent regardless of the dipole–dipole interaction) contribution to the THFI. When comparing the  $B_s$  values from the three sets of  $\text{F}_1$ ,  $\text{F}_6$  and  $\text{F}_{2-5}$  with the corresponding  $B_s$  from the cubic center  $\text{Yb}^{3+}$  (Table 1), it is seen that the parameters of  $\text{F}_{2-5}$  ions almost coincide with the purely covalent contribution (with distances due to the deformation) of

**Table 1**

Experimental values of the THFI parameters  $A_m^{(i)}$  (in MHz) and  $B_s$  (in  $10^{-4}$  T) of the  $\text{Yb}^{3+}$  ion with the first fluorine shell and the  $\text{Li}$  ion in  $\text{KZnF}_3$ . 1–6 –  $\text{F}^-$  labels corresponding to the notations in the structural model of  $\text{KZnF}_3$  (Fig. 1). The results for the cubic  $\text{Yb}^{3+}$  center in  $\text{KZnF}_3$  [7] are given for comparison.

	Tetragonal				Cubic
	$\text{F}_{2-5}$	$\text{F}^1$	$\text{F}^6$	$\text{Li}^+$	
$A_1$	29.80 (3)	47.05 (2)	34.53 (2)	0.730 (10)	29.030
$A_2$	3.63 (3)				
$A_3$	16.42 (3)	36.64 (2)	30.52 (2)	−0.305 (10)	11.136
$A_4$	0.9 (1)				
$A_5$	0.9 (1)				
$B_s$	6.53	15.90	12.61	0.02	6.38

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