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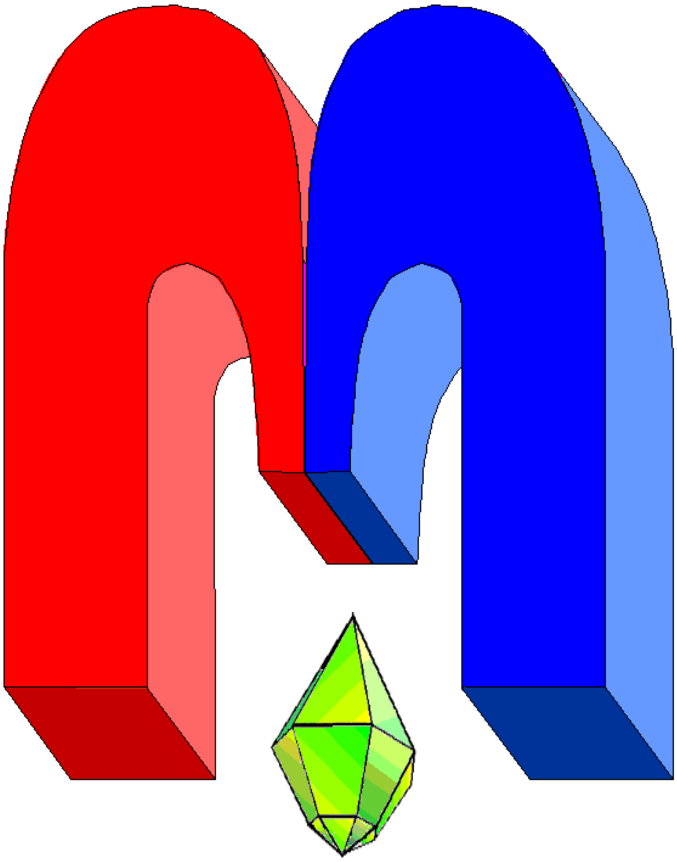

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To the structure of the trigonal center of Yb^{3+} ion in hexagonal perovskite crystal RbMgF_3

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EPR and optical spectra are used for the analysis of distortions of a crystal lattice in the vicinity of an impurity ion Yb^{3+} of trigonal symmetry in RbMgF_3 crystal. Within the framework of the superposition model, it is established that three F^- ions of the nearest-neighboring octahedron, located symmetrically along the threefold axis of the trigonal center, move away from the impurity ion and have considerable angular deviations from the symmetry axis of the center. The next three F^- ions, which enter the other octahedra, shift towards the paramagnetic ion and, on the contrary, come a bit closer to the axis.

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Keywords: perovskite RbMgF_3, crystal field, syperposition model, rare earth.

Preface

Author expresses deep gratitude to B.Z. Malkin, who often advised him during their collaboration on the projects related to the analysis of the structure of impurity centers, and who performed such researches at the highest level, taking into account both static and dynamic effects.

1. Introduction

Resently, EPR and optical spectroscopy data of the trigonal paramagnetic centers ($\mathrm{T}_{\mathrm{trig}}$) of Yb^{3+} ion in RbMgF_3 crystal have been published [1]. The results of these experiments make it possible to conclude that Yb^{3+} ions replace two different host cation sites of Mg^{2+} forming three different types of paramagnetic centers (PC). In RbMgF_3 [2,3] there are two nonequivalent sites (Mg_{I} and $\mathrm{Mg}_{\mathrm{II}}$), both with C_{3v} symmetry (Fig. 1), and Yb^{3+} resides in both sites, forming three kinds of centers. Two kinds of trigonal Yb^{3+} centers (Yb^{3+} (I) $\mathrm{T}_{\mathrm{trig}}$ and Yb^{3+} (II) $\mathrm{T}_{\mathrm{trig}}$) with Yb^{3+} ions in a single MgF_6 unit (Mg_{I} site) were identified. One of them Yb^{3+} (I) $\mathrm{T}_{\mathrm{trig}}$ may be ascribed to the Yb^{3+} ion simply substituting at the Mg_{I} site without any charge compensators in its immediate neighborhood, while the other Yb^{3+} (II) $\mathrm{T}_{\mathrm{trig}}$ was identified as the substitution with the Yb^{3+} ion at the Mg_{I} site with the nearest Rb^+ vacancy. The center of the third type Yb^{3+} (III) $\mathrm{T}_{\mathrm{trig}}$ is formed by the Yb^{3+} ion when it substitutes another Mg^{2+} site in the $\mathrm{Mg}_2\mathrm{F}_9$ unit composed of two face-sharing fluorine octahedra ($\mathrm{Mg}_{\mathrm{II}}$ site). In [1] the crystal field parameters B_k^q of a Hamiltonian of interaction of the Yb^{3+} ions with the crystal field (CF) of all centers were determined from the schemes of energy levels and g-factors of the ground Kramers doublets. The value and sign of the parameter B_2^0 was used to qualitatively describe the nearest surrounding of the Yb^{3+} ion.

In this work, the found parameters B_k^q (except B_2^0) of CF trigonal symmetry were used in order to obtain more detailed information on the structure of the basic Yb^{3+} (I) center $\mathrm{T}_{\mathrm{trig}}$ ((I) $\mathrm{T}_{\mathrm{trig}}$). The quantitative assessment of distortions of a crystal lattice near Yb^{3+} was carried out on the basis of superposition model (SM) taking into account only the nearest F^- ions forming a deformed octahedron.

2. Structure of the (I) $\mathrm{T_{trig}}$

Interaction of an ion of Yb^{3+} with CF $\mathrm{T_{trig}}$ is described by a Hamiltonian

$$H_{\mathrm{cr}}(C_{3v}) = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + B_6^0 O_6^0 + B_6^3 O_6^3 + B_6^6 O_6^6. \qquad (1)$$

Parameters found in work [1] $B_k^q = A_k^q \langle r^k \rangle$ incorporating the relevant radial integrals $\langle r^k \rangle$ are presented in Table 1 (the line "(I) $\mathrm{T_{trig}}$ (exp.)"). Operators $O_k^q = \sum_i O_k^q(\theta_i, \phi_i)$ are extended Steven's operators [4] depending on polar coordinates θ_i, ϕ_i of i-th electron of the paramagnetic ion (PI) defined in relation to trigonal axes of the PC. An arrangement of these axes (X, Y, Z) in relation to hexagonal axes of a crystal (a, a, c) is shown in Fig. 1.

Table 1. CF parameters B_k^q (in cm^{-1}) of (I) $\mathrm{T_{trig}}$ in RbMgF$_3$ crystal.

Parameters	B_2^0	B_4^0	B_4^3	B_6^0	B_6^3	B_6^6
(I) $\mathrm{T_{trig}}$ (exp.)	413	−175	−4763	19	433	−844
(I) $\mathrm{T_{trig}}$ (theory)		−99	−4827	14	377	−157

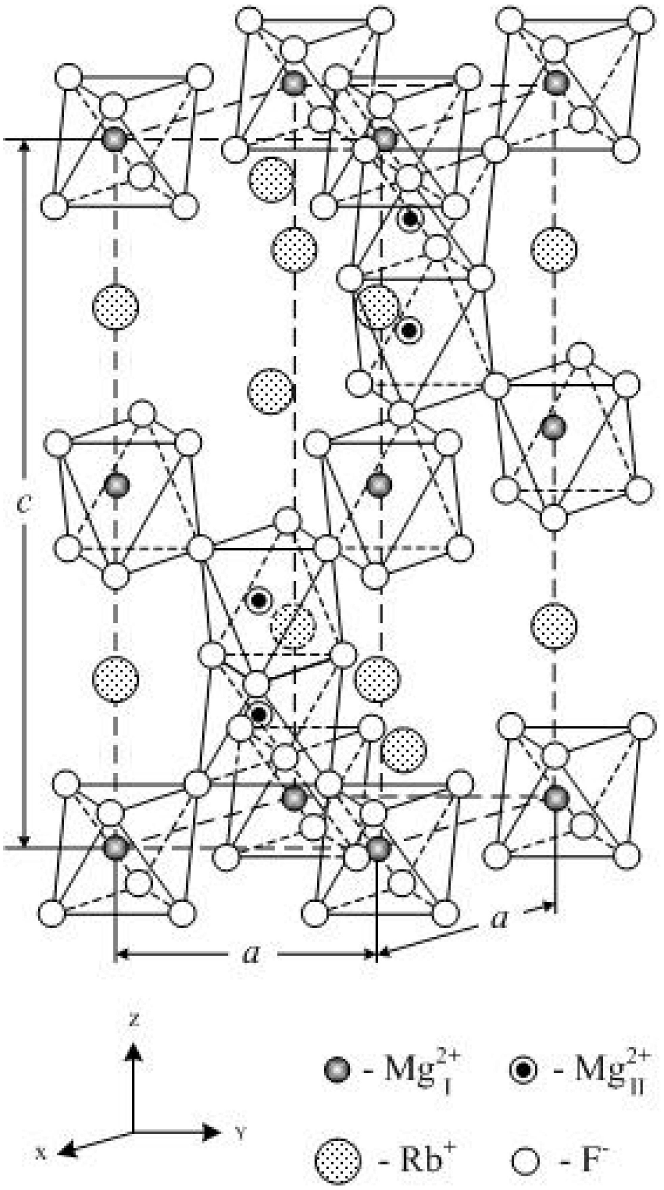

Figure 1. Unit cell of RbMgF$_3$ [5], where the Z axis is parallel to the hexagonal crystal axis.

For the analysis of quantitative distortions of a crystal lattice near Yb^{3+} we will use SM [6–10]. In this model, it is postulated that full CF is a linear superposition of the fields created by each ion of a crystal. The resulting CF parameters are then presented in the form

$$B_k^q = \sum_L \sum_i K_k^q(\Theta_i, \Phi_i)\overline{B}_k(R_L), \tag{2}$$

where $K_k^q(\Theta_i, \Phi_i)$ are the structural factors depending on angular coordinates (determined by spherical angles Θ_i and Φ_i) of all ions located at the distance R_L from PI, and $\overline{B}_k(R_L)$ are the "intrinsic" parameters depending on ligand type. Summation in (2) is performed over the coordination spheres of ligands (sum over L) and over all the ligands of each area (sum on i). After performance of summation over i, expression (2) can be written as

$$B_k^q = \sum_L K_k^q(L)\overline{B}_k(R_L), \tag{3}$$

where $K_k^q(L)$ is the structural factor of the coordination sphere L. The dependence of parameters $\overline{B}_k(R_L)$ on R_L in limited ranges of distances obeys a power law of the form

$$\overline{B}_k(R_L) = \overline{B}_k(R_0^L)(R_0^L/R_L)^{t_k}, \tag{4}$$

where t_k is the exponent, and $\overline{B}_k(R_L)$is the intrinsic model parameter relating to some average distance R_0^L which is often accepted equal to the sum of ionic radii of the magnetic ion and ligand.

In our modeling using the expression (4), in accordance to the majority of works which use SM, we will be accounting the contributions from only the first coordination sphere of fluorine ions F^-.

Fluorine ions 1, 2, 3 of the nearest octahedron of the $\mathrm{Mg}_\mathrm{I}^{2+}$ ion in the system of coordinates of the trigonal center shown on Fig. 2 occupy positions with coordinates: $R_1 = R_2 = R_3 = R_a^0 = 2.034$ Å [3], $\Theta_1 = \Theta_2 = \Theta_3 = \Theta_a^0 = 56.16°$ [3], $\Phi_1 = 60°$, $\Phi_1 = 180°$, $\Phi_3 = 300°$, while coordinates of the last three ions (4, 5, 6) are as follows: $R_4 = R_5 = R_6 = R_b^0 = 2.034$ Å [3], $\Theta_3 = \Theta_5 = \Theta_6 = \Theta_b^0 = 123.84°$ [3], $\Phi_4 = 0°$, $\Phi_5 = 120°$, $\Phi_6 = 240°$. Comparing the angles Θ_1 and Θ_4 with the corresponding angles $\Theta_1 = 54.74°$ and $\Theta_4 = 125.36°$ in regular octahedron, one can see that the $\mathrm{Mg_IF_6}$ octahedron of $\mathrm{RbMgF_3}$ crystal is slightly compressed along the c-axis.

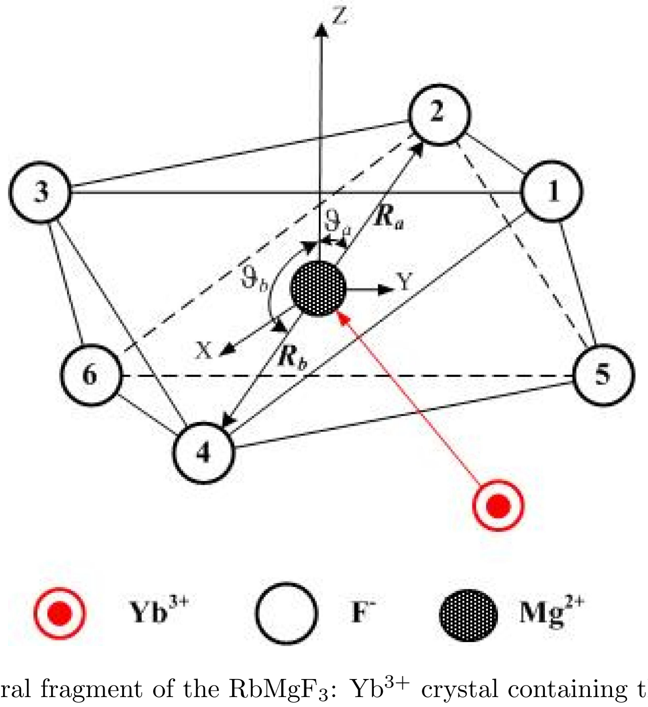

Figure 2. A structural fragment of the $\mathrm{RbMgF_3}$: Yb^{3+} crystal containing the trigonal center (I) $\mathrm{T_{trig}}$.

During formation of (I) $\mathrm{T_{trig}}$ in the $\mathrm{RbMgF_3}$ crystal, radial R^0 and angular Θ^0 coordinates of all six ions of fluorine change. However, owing to the symmetry of the center, R_1, R_2 and R_3 distances and the corresponding angles remain equal among themselves. We will designate them further through R_a and Θ_a, respectively. The same belongs to R_4, R_5 and R_6 distances and the corresponding angles of the last three ions of fluorine, which become equal to R_b and Θ_b, respectively. The experimental CF B_k^q $\mathrm{Yb^{3+}}$ (I) $\mathrm{T_{trig}}$ parameters found from (3) and (4) and with the use of an explicit form of the structural factors $K_k^q(\Theta_i, \Phi_i)$ [4] are described by the following system of the equations:

$$\begin{aligned}
B_4^0 &= \frac{3}{8}\overline{B}_4(R_a)K'^0_4(\Theta_a) + \frac{3}{8}\overline{B}_4(R_b)K'^0_4(\Theta_b),\\
B_4^3 &= -105\overline{B}_4(R_a)K'^3_4(\Theta_a) + 105\overline{B}_4(R_b)K'^3_4(\Theta_b),\\
B_6^0 &= \frac{3}{16}\overline{B}_6(R_a)K'^0_6(\Theta_a) + \frac{3}{16}\overline{B}_6(R_b)K'^0_6(\Theta_b),\\
B_6^3 &= -\frac{315}{8}\overline{B}_6(R_a)K'^3_6(\Theta_a) + \frac{315}{8}\overline{B}_6(R_b)K'^3_6(\Theta_b),\\
B_6^6 &= \frac{693}{32}\overline{B}_6(R_a)K'^6_6(\Theta_a) + \frac{693}{32}\overline{B}_6(R_b)K'^6_6(\Theta_b),
\end{aligned} \tag{5}$$

in which the factors $K'^q_k(\Theta)$ are defined by expressions:

$$\begin{gathered}
K'^0_4(\Theta) = 35\cos^4\Theta - 30\cos^2\Theta + 3, \quad K'^3_4(\Theta) = \sin^3\Theta\cos\Theta,\\
K'^0_6(\Theta) = 231\cos^6\Theta - 315\cos^4\Theta + 105\cos^2\Theta - 5,\\
K'^3_6(\Theta) = \sin^3\Theta\cos\Theta(11\cos\Theta - 3), \quad K'^6_6(\Theta) = \sin^6\Theta.
\end{gathered} \tag{6}$$

The values t_k and $\overline{B}_k(R_0^{\mathrm{F}})$ can be taken the same as values of elpasolite $\mathrm{Rb_2NaYF_6}$ [11] ($\overline{B}_4 = 105.57\,\mathrm{cm^{-1}}$, $t_4 = 5.49$, $\overline{B}_6 = -13.49\,\mathrm{cm^{-1}}$, $t_6 = 13.10$) besause $\mathrm{Yb^{3+}}$ ion substituting at the $\mathrm{Y^{3+}}$ site in $\mathrm{Rb_2NaYF_6}$ as well as at the $\mathrm{Mg_I}$ site in $\mathrm{RbMgF_3}$ is surrounded by an octahedron of $\mathrm{F^-}$ ions and by a cube of $\mathrm{Rb^+}$ ions.

From system (5) it is possible to find the parameters R_a, Θ_a, R_b, Θ_b characterizing structure of (I) $\mathrm{T_{trig}}$. Despite that the number of variables does not exceed the number of equations, the system (5) has many solutions, the majority of which are not satisfactory from the physical point of view. These are such solutions which lead either to very large, or to very small distances between ligands and PI, either to very big, or to very small changes of angular ligand coordinates. To select the satisfactory solutions, we were guided by requirements that the structure of the $\mathrm{T_{trig}}$ should be similar to that in which the first three fluorine ions can move from a PI or approach it, and free to deviate from the symmetry axis of the center, as it is not connected with the nearby ions of the lattice. The last three ions, on the contrary, will be restrained in their displacements because they are structurally (see Fig. 1) included in other octahedra that are surrounding the ions $\mathrm{Mg^{2+}}$ at $\mathrm{Mg_{II}}$ sites.

The self-consistent solution which follows these requirements leads to the values R_a, Θ_a, R_b, Θ_b presented in Table 2 (line "(I) $\mathrm{T_{trig}}$ (theory)". This solution is not the best one from the mathematical point of view, i.e. not giving the smallest value of the merit function of the system of equations. Comparing the values R_a, Θ_a, R_b, Θ_b to coordinates in an undistorted crystal lattice (2.034 Å, 56.16°, 2.034 Å, 123.84°, respectively, line 2 in Table 2), we see that three $\mathrm{F^-}$ ions of the nearest octahedron which are situated symmetrically along the threefold axis of the trigonal center (I) $\mathrm{T_{trig}}$ in $\mathrm{RbMgF_3}$ crystal move away from PI by 0.231 Å and deviate from the axis by 18.52°. Another three $\mathrm{F^-}$ ions move away too from PI by 0.061 Å and deviate by

Table 2. Structural parameters of undoped $RbMgF_3$ crystal and of (I) T_{trig} in $RbMgF_3$ crystal. Distances are in Å, and angles in degrees.

Parameter	R_a^0	Θ_a^0	R_b^0	Θ_b^0
Undoped crystal	2.034	56.16	2.034	123.84
Parameter	R_a	Θ_a	R_b	Θ_b
(I) T_{trig} (theory)	2.265	74.68	2.095	138.22

14.38° from the axis. The theoretical values of the parameters B_k^q of the CF (I) T_{trig} which are obtained with these values R_a, Θ_a, R_b, Θ_b are given in Table 1 (line "T_{trig} (theory)"). Comparing them to experimental values of the Table 1 (line "T_{trig} (exp.)"), we see that the structure of PC satisfactory corresponds to the CF experimental parameters. All parameters have the correct signs, but parameters B_4^0 and B_6^6 strongly differ by their absolute value. It is also not surprising, as the parameters of SM which are used in our calculations vere found for interpretation of interactions of ions Yb^{3+} and F^- in interval of distances near to $r_{Yb^{3+}-F^-} = 2.206$ Å of elpasolite Rb_2NaYbF_6 [12], while in $RbMgF_3$ crystal $r_{Yb^{3+}-F^-} = 2.034$ Å [2,3]. Note that the solution of the system of equations (5) gives the parameter B_6^6 almost equal to its experimental value ($845\,\mathrm{cm}^{-1}$), but the value of axial parameter B_4^0 diminishes almost by an order of magnitude. This implies large deviation of the first three F^- ions from the symmetry axis of the center ($\sim 34°$), as well as shift of all the fluorine ions towards PI by approximately 0.016 Å.

The structure of (I) T_{trig} established as a result of the carried-out analysis is given in Fig. 3 where the section of the center is represented by the plane passing through its axes Z and X and F_2, F_4 fluorine ions which are in this plane. The other two corresponding ions are located in the planes passing through each of these two fluorine ions perpendicular to axis Z of the center at the vertices of the corresponding triangles. At formation of (I) T_{trig} from the Mg_IF_6 octahedron the triangles of ions F^- are displaced in the opposite direction to the three F^- ions not bounding with the other ions. Shifts of the corresponding planes of the triangles are defined by values: $\delta_a = R_a^0 \cos\Theta_a^0 - R_a \cos\Theta_a = 0.534$ Å, $\delta_b = R_b^0 \cos\Theta_b^0 - R_b \cos\Theta_b = 0.429$ Å.

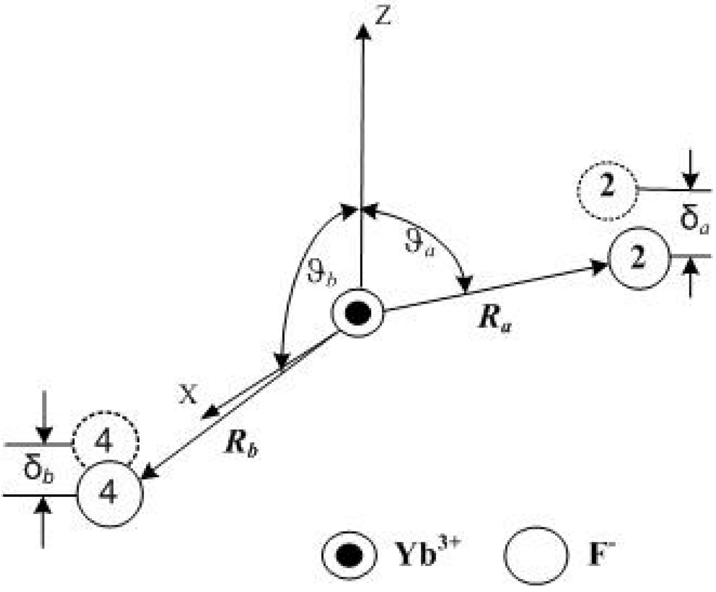

Figure 3. Structure of the trigonal center (I) T_{trig} of the Yb^{3+} ion in $RbMgF_3$ crystal. The section of the center is represented by the plane passing through its axes Z and X and F_2, F_4 fluorine ions which are in this plane. Dotted circles are the positions of ions in the undoped $RbMgF_3$ crystal.

3. Conclution

Analysis of an environment of the Yb^{3+} ion substituting at the Mg$_\mathrm{I}$ site of RbMgF$_3$ crystal without any charge compensators in its immediate neighborhood demonstrated that the nearest surrounding octahedron is considerably deformed from its form in undoped crystal. The CF theoretical parameters calculated for the found structure of the center on the basis of SM satisfactorily correspond to experimental values. Structures of two other centers of ions of Yb^{3+}, found in the RbMgF$_3$ crystal, will be more difficult for an analysis, as in a center (II) Yb^{3+} the already distorted octahedron of (I) Yb^{3+} is additionally exposed to the action of a nearest Rb$^+$ vacancy, and in (III) Yb^{3+} to the field of the distorted octahedron the effects of three ions of F$^-$ symmetrically located in relation to the axis of center and of nearby axial ion of Mg^{2+} are added.

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