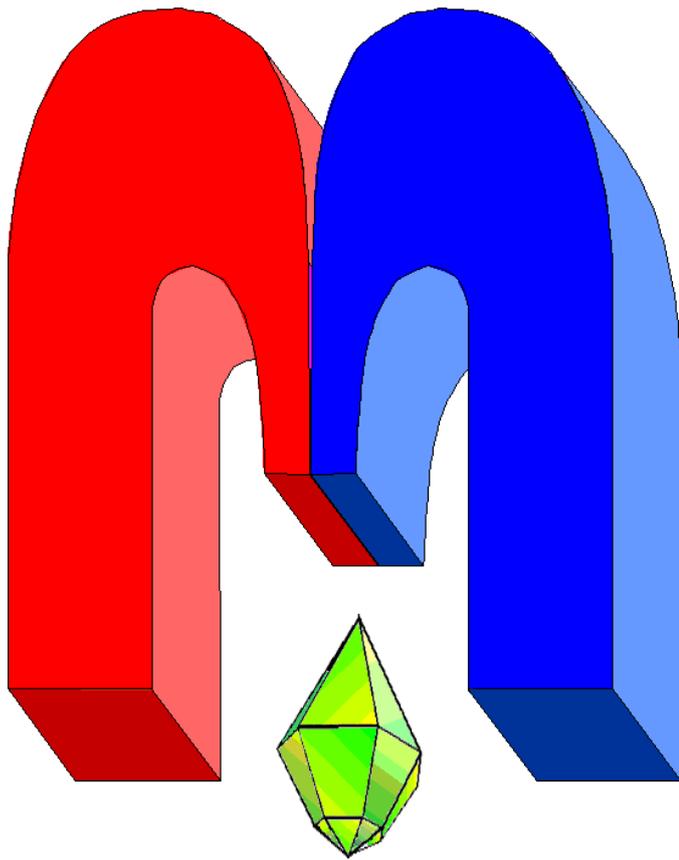


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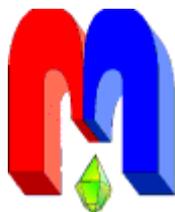
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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Paramagnetic centres in crystals YAlO_3 : Eu, Si

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In the spectra of the electron paramagnetic resonance of YAlO_3 :¹⁵¹Eu single crystals, the signals of the Eu^{2+} , Gd^{3+} , Cr^{3+} , and Mo^{3+} paramagnetic centers were observed. Using high-frequency EPR, it was shown that the signals of Mo^{3+} ions observed in the X-range belong to two intra-doublet transitions of the same center with $S = 3/2$.

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Keywords: yttrium aluminium perovskite, insulators, point defects, EPR.

*Dedicated to Boris Malkin
on the occasion of his 80th birthday*

1. Introduction

Interest in the study of YAlO_3 crystals doped with ions of the iron group and rare earths is associated with their applications in laser physics and optoelectronics. To optimize the characteristics of these materials, information about the nature, structure, and number of defects in real crystals is needed. The presence of uncontrolled impurities during the growth can lead to changes in the properties of single crystals, and therefore their concentration is sought to be minimized. For yttrium orthoaluminate crystals grown in molybdenum containers, molybdenum ions can be such an uncontrolled impurity. One of the direct and most informative methods for obtaining information about paramagnetic impurities is the electron paramagnetic resonance (EPR) method.

The EPR spectra of Mo^{3+} ions (electron configuration is $4d^3$, the electron and nuclear spins are $S = 3/2$, $I = 5/2$) in YAlO_3 doped with Er, Nd, Ce were first studied in [1]. The authors of [2] suggested that the Mo^{3+} spectra observed by them in YAlO_3 belong to two paramagnetic molybdenum centers with large zero-field splittings, one of which is caused by the Mo^{3+} ion in the aluminum position, and the second by the Mo^{3+} ion in the same position, but with a nearby defect. The orientational behavior of the signals of these Mo^{3+} centers was described in [2] in three crystallographic planes by rhombic spin Hamiltonian with an effective spin $S = 1/2$.

In [3, 4] monoclinic centers Eu^{2+} and Gd^{3+} ($S = 7/2$) were observed in YAlO_3 , and the parameters of the fine structure were determined. However, the crystal was doped with europium with a natural abundance of isotopes, and its EPR spectrum demonstrated a complex weakly resolved hyperfine structure.

In the present work, the YAlO_3 sample doped with europium enriched with the ¹⁵¹Eu isotope is studied at different frequencies by the EPR method.

2. Materials and methods

The crystals were grown by the method of vertical directional crystallization, using crystalline sapphire (99.95%), high-purity yttrium oxide (ITO-B brand) and oxide of the europium isotope $^{151}\text{Eu}_2\text{O}_3$ (97.5% ^{151}Eu and 2.5% ^{153}Eu). The SiO_2 oxide was additionally introduced into the melt to stabilize the Eu^{2+} centers in the lattice. The composition of the initial melts corresponded to $Y_{1-x}\text{Eu}_x\text{Al}_{1-y}\text{Si}_y\text{O}_3$ ($x = 0.02$; $y = 0.04$). The quality control was carried out on a polarization microscope MPS-2. The presence of europium ions in crystals (Eu^{2+} and Eu^{3+}) was observed in the absorption spectra recorded on a SPECORD200 PLUS spectrophotometer for the f-f transitions of Eu^{3+} ions and the charge-transfer band $\text{Eu}^{3+}-\text{O}^{2-}$.

The EPR spectra were measured at room temperature using an EMX Plus Bruker X-band spectrometer. The orientation of the sample in the magnetic field was carried out using a standard automatic goniometer and a device for rotating the sample in the plane perpendicular to the axis of rotation of the goniometer. For measurements in the high-frequency range at 4.2 K, a home-built wide-band EPR spectrometer based on microwave oscillators (backward-wave tubes) was used.

3. Results and discussion

Yttrium orthoaluminate crystals have a distorted perovskite structure with the space group Pbnm (D_{2h}^{16}) [5]. The unit cell parameters are $a = 5.176 \text{ \AA}$, $b = 5.332 \text{ \AA}$, $c = 7.356 \text{ \AA}$ [6]. In the EPR spectra of the samples under study at room temperature in the orientations: $\mathbf{B}||\mathbf{a}$, $\mathbf{B}||\mathbf{b}$, $\mathbf{B}||\mathbf{c}$ (Fig. 1, \mathbf{B} – magnetic field induction, \mathbf{a} , \mathbf{b} , \mathbf{c} – crystallographic axes), intense groups of signals are observed, which can be attributed to the centers Cr^{3+} , Eu^{2+} , Gd^{3+} and Mo^{3+} . Impurity ions of molybdenum and chromium replace aluminum Al^{3+} in the crystal lattice and have magnetic multiplicity of 4 (local symmetry group $\bar{1}(C_i)$). These positions are related to each other by the reflection operation in the planes normal to the axes \mathbf{a} , \mathbf{b} , \mathbf{c} as a result of

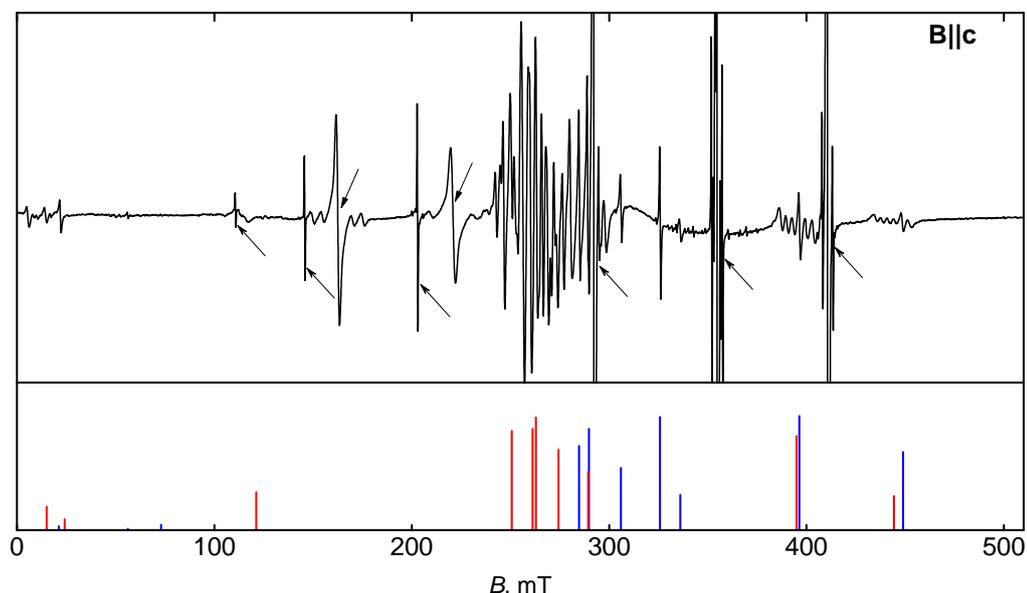


Figure 1. The EPR spectrum of $YAlO_3$ doped with $^{151}\text{Eu}^{2+}$ at $\mathbf{B}||\mathbf{c}$, $T = 300 \text{ K}$; the frequency is 9833 MHz, the lower arrows indicate the transitions of the Cr^{3+} centers, the upper ones are Mo^{3+} ; the bottom part of the figure shows the result of calculating the positions and integral intensities of the transitions: the blue bars are for Gd^{3+} , the red ones are for the centers of the hyperfine structure of the Eu^{2+} transitions.

which two pairs of Cr^{3+} and Mo^{3+} centers become equivalent in the indicated planes. This leads to the fact that in the orientations of the magnetic field parallel to the crystallographic axes $\mathbf{B} \parallel \mathbf{a}, \mathbf{b}, \mathbf{c}$ the signals of the four centers merge.

The rare-earth impurity ions Eu^{2+} and Gd^{3+} (electron spin $S = 7/2$) replace the Y^{3+} ions (the point symmetry group is m (C_S)) and have magnetic multiplicity of 2. If the charge compensation for Eu^{2+} by silicon ions is nonlocal, then there will be two magnetically nonequivalent centers that become equivalent in the \mathbf{ca} and \mathbf{cb} planes. The four positions of yttrium ions in the crystal structure are pairwise connected by inversion and reflection operations in these planes.

The signals of the listed paramagnetic centers were identified taking into account their hyperfine structure. For the orientation of the sample in a magnetic field, the angular dependences of the transition positions of the Cr^{3+} , Mo^{3+} and Gd^{3+} paramagnetic centers were used.

The Eu^{2+} transitions overlap with each other and with the signals of Gd^{3+} or Cr^{3+} , making it difficult to analyse the complex hyperfine structure of $^{151}\text{Eu}^{2+}$ center ($I = 5/2$). The reason for the intense chromium signals in the sample can most likely be considered to be low quality molybdenum tubes used in growing, containing chromium contaminants.

The positions of aluminum ions with point symmetry [7], which are replaced by molybdenum ions Mo^{3+} , are surrounded by six oxygen ions [8]. Since the charge states of the impurity and matrix ions are the same, the association of the molybdenum ion with any other defect in the aluminum position seems unlikely. At the same time, there are no valid arguments in favor of the existence of alternative localization of Mo^{3+} in the YAlO_3 crystal lattice. Thereby, in contrast to [2], it was suggested that two transitions of molybdenum centers with magnetic multiplicity 4, observed in the X-range, belong to two intra-doublet transitions of one Mo^{3+} center with spin $S = 3/2$. To describe such a center, we used the spin Hamiltonian in the following definition [9]

$$H_{sp} = \beta (\mathbf{BgS}) + 1/3 (b_{20}O_{20} + b_{21}O_{21} + b_{22}O_{22} + c_{21}\Omega_{21} + c_{22}\Omega_{22}), \quad (1)$$

where \mathbf{g} is the g -factor, β is the Bohr magneton, O_{nm} are the Stevens spin operators [9], and b_{nm} are the fine structure parameters. The parameters of the spin Hamiltonian in the $\mathbf{x} \parallel \mathbf{a}, \mathbf{y} \parallel \mathbf{b}, \mathbf{z} \parallel \mathbf{c}$ coordinate system, describing the experimental angular dependences, were obtained by the least-squares method on the set of experimental transition positions and are listed in the Table 1. To describe the positions and intensities of the Gd^{3+} and Eu^{2+} signals (Fig. 1), we used the monoclinic spin Hamiltonian in the definition [9], which includes terms of the fourth rank with the parameters from [3]. With the parameters given in the Table 1, the angular dependence of the transition positions of the Mo^{3+} centers in the \mathbf{cb} plane for the frequency of 9.8 GHz was built (Fig. 2). The splitting of the experimental angular dependences in Fig. 2 can be explained by a small deviation (≈ 3 deg) of the magnetic field from the \mathbf{cb} plane.

The high-field transition (between levels 3-4 in the indicated orientation) in magnetic fields of about 1500 mT (see Fig. 2) was predicted by the obtained parameters. Due to the large zero-field splitting for Mo^{3+} centers, it is impossible to observe inter-doublet resonant transitions

Table 1. The spin Hamiltonian parameters of Mo^{3+} triclinic centers in the $\mathbf{x} \parallel \mathbf{a}, \mathbf{y} \parallel \mathbf{b}, \mathbf{z} \parallel \mathbf{c}$ coordinate system, $T = 300$ K; b_{nm} , c_{nm} , and $F(N)$ are given in MHz, $F(N)$ – the standard deviation of the calculated frequencies from experimental, N – the number of experimental signal positions, the sign of b_{20} was not determined [4].

g_x	g_y	g_z	b_{20}	b_{21}	b_{22}	c_{21}	c_{22}	$F(N)$
1.970	1.975	1.970	-10350	-23030	-9940	113560	-20560	32(163)

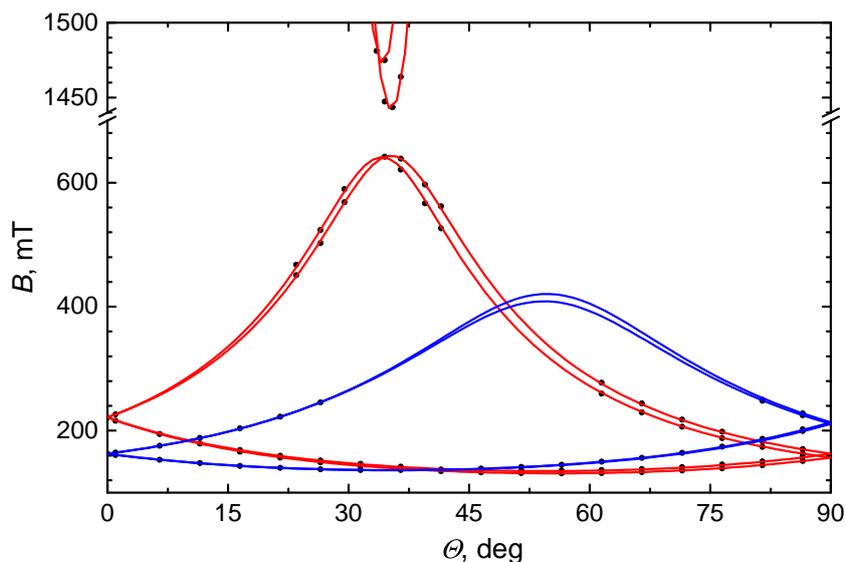


Figure 2. The orientational dependence of the positions of the resonant transitions of Mo^{3+} centers at a frequency of 9833 MHz when the magnetic field rotates near the **zy** (**cb**) plane, the points show the experimental data, the curves are the calculation (the red curves indicate the $3 \leftrightarrow 4$ transition, the blue ones are the $1 \leftrightarrow 2$ transition). The slight splitting of the observed signals is due to the deviation of the magnetic field from the **bc** plane.

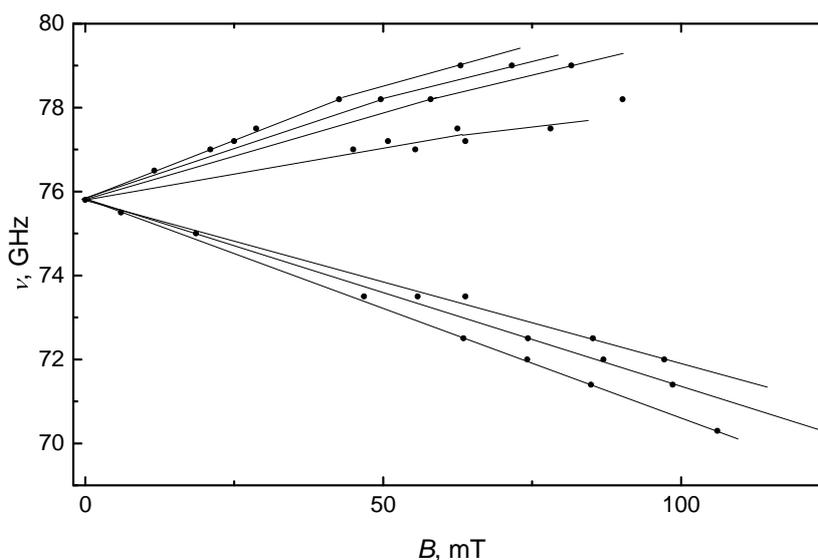


Figure 3. The frequency-field dependence of the inter-doublet resonant transitions of Mo^{3+} ions in a YAlO_3 crystal at 4.2 K; the signals' splitting with an increase in the magnetic field is due to the existence of four magnetically nonequivalent centers.

in the X-band, which can adversely affect the accuracy of the determined experimental spin Hamiltonian parameters. Therefore, in order to obtain additional experimental information and to observe inter-doublet transitions, measurements of high-frequency EPR were performed.

In Fig. 3, the experimental frequency-field dependence of the inter-doublet resonant transitions of Mo^{3+} ions, at a temperature of 4.2 K, is shown. From this, we can determine the magnitude of the zero-field splitting, which turns out to be about 75.8 GHz. In turn, the calculation of the zero-field splitting using the parameters of the spin Hamiltonian determined from measurements in the three-centimeter range (see Table 1) for paramagnetic molybdenum centers

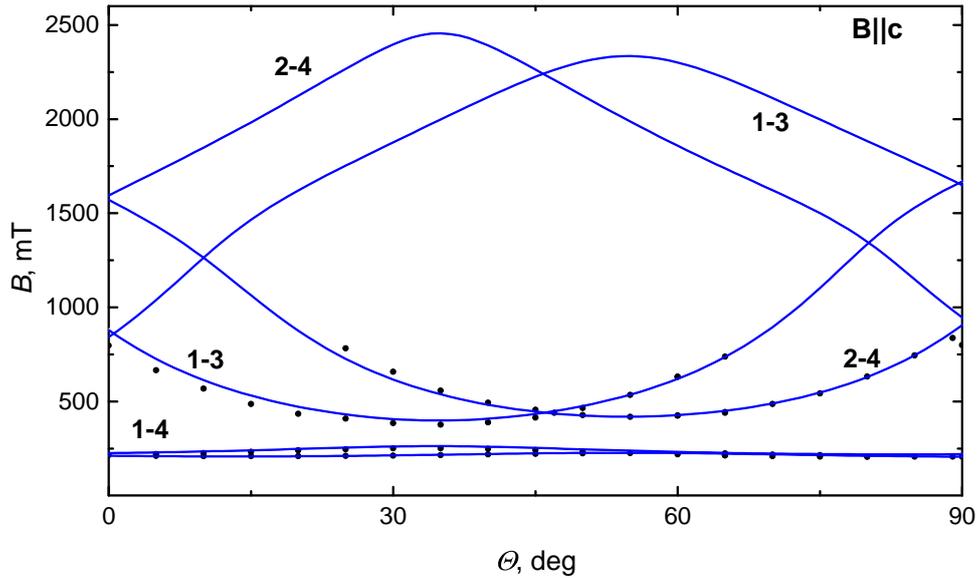


Figure 4. The angular dependence of the positions of the Mo^{3+} center transitions when the magnetic field rotates in the \mathbf{zy} (\mathbf{cb}) plane at 4.2 K at a frequency of 86250 MHz, the points are experimental values, the curves are calculation with parameters from the Table 1, the numbers indicate the energy level numbers.

showed the value of 75 GHz, which is close to the zero-field splitting obtained from the frequency-field dependence. Thus, despite the fact that high-frequency measurements and measurements in the X-range were performed at different temperatures (4.2 K and 300 K, respectively), it can be concluded that the parameters of the fine structure of the centers of Mo^{3+} ion predict well the splitting value in zero-field.

The angular dependences of the positions of the resonant transitions of molybdenum centers measured at a frequency of 86250 MHz at 4.2 K are shown in Fig. 4. The calculated curves demonstrate the quality of the description by the obtained parameters of the orientational behavior of the inter-doublet transitions of all four molybdenum centers. This, as well as experimental data from the X-range, confirm the adequacy of the chosen approach and allow us to conclude that only one Mo^{3+} triclinic center with spin $S = 3/2$, which is localized in the Al^{3+} position, exists in yttrium orthoaluminate.

4. Summary

In single crystals of yttrium aluminate YAlO_3 : ^{151}Eu , the EPR spectra of centers with a complex hyperfine structure Cr^{3+} , Eu^{2+} , Gd^{3+} , and Mo^{3+} were observed. Magnetic resonance measurements were performed at high frequencies and in the X-band. From the frequency-field dependence of the inter-doublet resonant transitions of the Mo^{3+} centers, the zero-field splitting for paramagnetic molybdenum centers was determined, the value of which is close to that calculated using the fine structure parameters. The angular dependence of the positions of the resonant inter-doublet transitions of Mo^{3+} centers at a frequency of 86.25 GHz, which are well described by the calculated curves, was measured.

All this, together with the results of the EPR of the three-centimeter range, confirms the conclusion that the observed signals of Mo^{3+} centers are due to two intra-doublet transitions of one center with electron spin $S = 3/2$.

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