Abstract—EPR spectra of the Er$^{3+}$, Nd$^{3+}$, and Ce$^{3+}$ ions substituting for the Y$^{3+}$ ion in the YAIo$_3$ yttrium orthoaluminate lattice are studied. The EPR spectra of these rare-earth ions are described by a spin Hamiltonian of rhombic symmetry with an effective spin $S = 1/2$. The principal values of the $g$ tensors were determined from an analysis of the angular dependences of the EPR spectra. The orientation of the local magnetic axes of paramagnetic centers relative to the YAIo$_3$ crystallographic directions are shown to depend on the actual rare-earth species. The EPR spectra exhibit a hyperfine structure due to the $^{167}$Er, $^{143}$Nd, and $^{145}$Nd odd isotopes, which permitted unambiguous identification of these spectra. The hyperfine coupling constants for the odd erbium and neodymium isotopes are determined. © 2002 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Rare-earth-doped single crystals of yttrium orthoaluminate (YAIo$_3$), also called yttrium aluminum perovskite (YAP), enjoy wide application in quantum electronics [1, 2]. Interest in these materials has been increasing in recent years in connection with the possibility of the use of cerium-doped YAP as fast high-efficiency scintillators [3–7]. For instance, lutecium orthoaluminate LuAIo$_3$ doped with cerium has demonstrated the highest scintillator efficiency, to date, for the detection of positron annihilation, which makes it a potentially promising material for use in positron emission tomography in medicine [8]. Although EPR is widely employed in studies of laser crystals, it has thus far been only scarcely applied to YAP materials. Only a few ions (Cr$^{3+}$, Fe$^{3+}$, Gd$^{3+}$, Ti$^{3+}$) have been investigated in YAIo$_3$ single crystals by EPR to date [9–16].

We report here on a comprehensive study of EPR spectra of three rare-earth ions (Er$^{3+}$, Nd$^{3+}$, Ce$^{3+}$) in yttrium orthoaluminate. These ions were detected and studied by EPR in YAIo$_3$ for the first time, and the results were published by us in [17].

2. EXPERIMENTAL TECHNIQUES

We studied YAIo$_3$ single crystals doped by cerium, erbium, and neodymium ions to concentrations of up to ~0.3 at. %. The crystals were grown by the Czochralski method and by directed horizontal crystallization at Preciosa Crytur, Ltd (Turnov, Czech Republic), and at the Institute for Raw Materials Synthesis (Aleksandrov, Russia). The EPR spectra were obtained in the 3-cm wavelength range at temperatures from 4 to 50 K on commercial JEOL-JES-PE-3X and ERS-230 radiospectrometers. The samples were oriented by x-ray diffraction to within ±0.5° and cut in the $ab$, $ac$, and $bc$ crystallographic planes to form rectangular parallelepipeds measuring 1.5 × 2 × 5 mm. More precise alignment of the principal magnetic axes relative to the external magnetic field was achieved radiospectroscopically, directly in the microwave cavity, by matching the EPR signals due to inequivalent positions. Our samples exhibited, in addition to the EPR response of the Er$^{3+}$, Nd$^{3+}$, and Ce$^{3+}$ ions, signals from residual impurities, which made comprehensive investigation of the orientational dependences of the spectra and, in particular, of the hyperfine structure (HFS) due to the odd $^{167}$Er, $^{143}$Nd, and $^{145}$Nd isotopes difficult. It should be pointed out that the EPR spectra of Mo$^{3+}$ ions in yttrium orthoaluminate crystals grown in molybdenum containers were observed for the first time and the results of their detailed investigation will be published separately.

3. EXPERIMENTAL RESULTS

The crystal structure of yttrium orthoaluminate belongs to the $D_{2h}^{16}$–$P_{hmm}$ orthorhombic space group and has been described in detail in a number of publications (see, e.g., [18–20]). The orthorhombic unit cell of YAIo$_3$ contains four distorted perovskite pseudocells. Therefore, the Y$^{3+}$ and Al$^{3+}$ ions reside in four structurally inequivalent positions. The aluminum ions are surrounded by six oxygen ions, forming a weakly distorted octahedron (local symmetry $C_3$). The nearest neighbor environment of the Y$^{3+}$ ions is more complex and is more strongly distorted (local symmetry $C_3$). Figure 1...
presents the structure of yttrium orthoaluminate with identification of the positions of the Y$^{3+}$ ions (large hatched circles) substituted by Er$^{3+}$, Nd$^{3+}$, and Ce$^{3+}$. In contrast to the aluminum positions, all ions of oxygen and yttrium are displaced by a few tenths of an angstrom with respect to the ideal perovskite positions. The aluminum sites have only inversion symmetry, and the yttrium sites possess a mirror symmetry plane perpendicular to the c axis of the crystal.

One of the principal g-tensor axes for the paramagnetic ions localized at the Y$^{3+}$ sites must coincide with the crystal c axis, and the two others must lie in the ab plane. Moreover, the Y$^{3+}$ ions are related pairwise by inversion site symmetry through the aluminum positions, such that there are only two magnetically inequivalent positions for an arbitrary orientation of an external magnetic field B, as well as for B rotating in the ab plane. If the external magnetic field rotates in the bc or ac planes, the pattern becomes simplified, because in this case, all four positions are magnetically equivalent and the EPR spectrum has one line only (neglecting the HFS). Thus, one EPR line is also observed when the external magnetic field is parallel to the principal crystal axes.

Figure 2 presents EPR spectra recorded in three principal magnetic-field orientations (B || a, B || b, and B || c) at 12 K for a frequency of 9.24 GHz. One can separate spectra of four types out of the EPR response, which, as will be shown later, belong to the rare-earth ions Er$^{3+}$, Nd$^{3+}$, and Ce$^{3+}$, as well as to the transition element Mo$^{3+}$. Erbium, neodymium, and molybdenum have odd-number isotopes that possess a nuclear magnetic moment, and their EPR spectra allow unambiguous identification based on the HFS.

### 3.1. Erbium Ions

The erbium ion Er$^{3+}$ has an electronic configuration $4f^{11}$ with the ground state $4I_{15/2}$. The energy level diagram of the Er$^{3+}$ ion in YAlO$_3$ single crystals was studied in [1, 2]. The ground-state multiplet $4I_{15/2}$ is crystal-field split into a number of Stark components, with the lowest of them involved in an EPR transition in the 3-cm range. Because of the large splitting between the ground and the next Stark level (51 cm$^{-1}$), detection of the excited state in EPR spectra has not been successful. Natural erbium contains, in addition to even isotopes with a zero nuclear spin moment, an odd isotope $^{167}$Er with a nuclear spin $I = 7/2$. Its natural abundance is 22.94%. The EPR spectrum of YAlO$_3$ (Fig. 2) agrees fully with the one expected for Er$^{3+}$. We observed eight nonequidistant lines in it representing the magnetic HFS components due to the odd isotope, whereas the strong central line should be assigned to the even isotopes. The line intensity ratio is in accord with the natural abundance of the erbium isotopes. The EPR spectrum of the Er$^{3+}$ ions in YAlO$_3$ is anisotropic; as the orientation of the external magnetic field relative to the crystal crystallographic axes changes, the EPR lines shift with the magnetic field and the distance between the HFS components also changes; however, their separation remains nonequidistant. The circles in Figs. 3 and 4 refer to the experimental positions of the strong Er$^{3+}$ line of the even erbium isotope obtained with the crystal rotated in a magnetic field in the ab and bc planes, respectively.

These experimental orientational relations can be described by a rhombic-symmetry spin Hamiltonian,

$$
\mathcal{H} = \beta B g S + S A I,
$$

where the effective spin $S = 1/2$; $g$ and $A$ are the tensors of the $g$ factor and HFS interaction, respectively; and $\beta$ is the Bohr magneton. The solid lines in Figs. 3 and 4 show the theoretical plots obtained by direct diagonalization of the spin Hamiltonian (1) using the R-Spectr code [21]. The g-tensor parameters used are as follows: $g_x = 8.98 \pm 0.01$, $g_y = 8.13 \pm 0.01$, and $g_z = 2.73 \pm 0.01$. Note that the principal directions of the Er$^{3+}$ local magnetic axes in yttrium orthoaluminate are oriented so that the x axes are along the c axis of the crystal and the y and z axes lie in the ab plane. Experimental measurements showed that the local magnetic axis $z$ makes an angle of 41.4° with the a axis of the crystal in the ab plane. The orientational relations of the HFS components yielded the following HFS constants for $^{167}$Er: $A_x = 329 \times 10^{-4}$, $A_y = 315 \times 10^{-4}$, and $A_z = 250 \times 10^{-4}$ cm$^{-1}$. 

Fig. 1. Projection of the YAlO$_3$ lattice structure on the ab plane.