

# Electron paramagnetic resonance studies of manganese and cobalt ions in $\text{YAlO}_3$ crystals

IRENEUSZ STEFANIUK<sup>1</sup>, IWONA ROGALSKA<sup>1\*</sup>, ANDRZEJ SUCHOCKI<sup>2,3</sup>,  
MAREK BERKOWSKI<sup>2</sup>, BOGUMIŁ CIENIEK<sup>4</sup>, PIOTR POTERA<sup>4</sup>

<sup>1</sup>Centre for Microelectronics and Nanotechnology, University of Rzeszów,  
Pigonia 1, 35-959 Rzeszów, Poland

<sup>2</sup>Institute of Physics, Polish Academy of Sciences,  
Aleja Lotników 32, 02-668 Warszawa, Poland

<sup>3</sup>Institute of Physics, University of Bydgoszcz,  
Weysenhoffa 11, 85-072 Bydgoszcz, Poland

<sup>4</sup>Institute of Physics, University of Rzeszów,  
Rejtana 16a, 35-310 Rzeszów, Poland

\*Corresponding author: i.rogalska@if.univ.rzeszow.pl

The results of X-band electron paramagnetic resonance measurements of  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  ions in  $\text{YAlO}_3$  (YAP) crystals in the temperature range 100–300 K are presented. Additionally, we observe electron paramagnetic resonance spectra of unintentional impurities  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  in YAP crystals. The angular dependence for Mn ions in YAP crystals can be presented. We aim at obtaining a better insight into the spectroscopic properties of paramagnetic Mn centers and structural information about their nearest environment in YAP host and at determining the valence of manganese ion. In this paper we compare electron paramagnetic resonance spectra for Co and Mn ions in YAP crystals.

Keywords: electron paramagnetic resonance (EPR), spin Hamiltonian,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  ions,  $\text{YAlO}_3$  (YAP) crystals.

## 1. Introduction

Yttrium orthoaluminate crystals ( $\text{YAlO}_3$  or YAP) are one of the most widely used host materials for solid-state lasers. Recently, some new interesting properties of Mn-doped  $\text{YAlO}_3$  have been reported, among them a strong photochromic effect [1] and intensive thermally stimulated luminescence (TL) after  $\gamma$ -irradiation [2].

Manganese ions in  $\text{YAlO}_3:\text{Mn}$  crystals as a rule are present in the form of  $\text{Mn}^{4+}$  ions in octahedral coordination ( $\text{Al}^{3+}$  positions) and  $\text{Mn}^{2+}$  ions in strongly distorted dodeca-

hedral coordination ( $Y^{3+}$  positions) [1, 3–6]. The crystals being exposed to blue-green laser light show an intensive bluish-gray coloration caused by  $Mn^{5+}$  ions created as a result of the  $Mn^{4+} \rightarrow Mn^{5+} + e^{-}$  photoionization process [1, 3]. In such a way, the  $Mn^{4+}$  ions demonstrate sensitivity to the visible light exposure. The  $Mn^{2+}$  ions are sensitive to the ionizing radiation such as X- or  $\gamma$ -rays as well as UV radiation [7].

The coexistence of  $Mn^{2+}$  and  $Mn^{4+}$  ions can provide charge compensation for each other. Besides, additional charge compensation for  $Mn^{4+}$  ions may be due to intrinsic crystal defects such as  $Y^{3+}$  vacancies [1, 5].

Co-doped oxide crystals are attractive materials for “eye safe” lasers operation near 1.5  $\mu m$  as well as nonlinear absorbers for passive Q-switching [8, 9]. The electron paramagnetic resonance (EPR) spectra of various ions in  $YAlO_3$  crystals, *e.g.*,  $3d^N$  ions ( $Cr^{3+}$ ,  $Ti^{3+}$ ,  $Mn^{4+}$ ,  $Mn^{5+}$ ,  $Fe^{3+}$ ) [10, 11], and  $4f^N$  ions ( $Er^{3+}$ ,  $Nd^{3+}$ ,  $Ce^{3+}$ ) [12, 13], were also previously studied.

In our previous work we described the EPR spectra of  $Co^{2+}$  ions in  $YAlO_3$  and  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Er^{3+}$  and  $Nd^{3+}$  undesirable impurities which occupied the aluminum and yttrium site [14, 15].

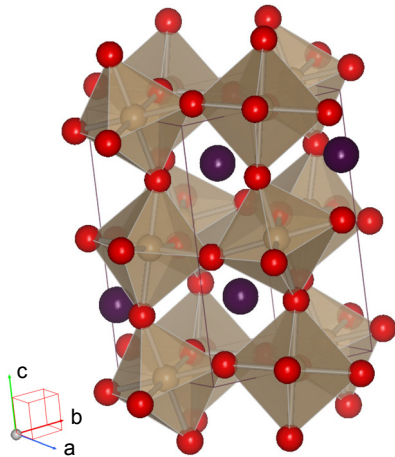
In this work we investigate the X-band EPR spectra of Mn ions in  $YAlO_3$  (YAP) crystals in the temperature range 100–300 K. We aim at obtaining a better insight into the spectroscopic properties of paramagnetic Mn centers and structural information about their nearest environment in YAP host and at determining the valence of manganese ion.

## 2. Experimental details

### 2.1. Crystal structure

The structural data indicate that YAP crystallizes in an orthorhombically distorted perovskite structure with the lattice parameters:  $a = 0.518$  nm,  $b = 0.533$  nm,  $c = 0.737$  nm [4, 16, 17]. The space group  $D_{2h}^{16}$  was chosen to describe the symmetry of the unit cell in YAP crystals using the  $Pbnm$  group coordinate system [16, 17]. The structure of  $YAlO_3$  can be represented (see Fig. 1) as a grid of tilted  $AlO_6$  octahedra with the yttrium ions occupying the empty space between the octahedra. The ionic radii of the cations  $R$  are:  $R(Y^{3+}) = 0.097$  nm,  $R(Al^{3+}) = 0.057$  nm,  $R(Co^{3+}) = 0.064$  nm,  $R(Co^{2+}) = 0.078$  nm,  $R(Mn^{2+}) = 0.096$  nm,  $R(Mn^{4+}) = 0.067$  nm,  $R(Nd^{3+}) = 0.099$  nm,  $R(Er^{3+}) = 0.085$  nm [18]. It is then expected that cobalt ions substitute Al cations rather than Y cations in the YAP host.

Four structurally equivalent  $Al^{3+}$  sites exist in YAP unit cell with Al cations located at the centers of nearly perfect  $AlO_6$  octahedra [10]. The O–Al–O angles in the respective octahedra vary in the range from  $89.6^\circ$  to  $90.6^\circ$ . Since the deviations of the respective angles from  $90^\circ$  and the bond-length distortion are small, the  $AlO_6$  octahedra may be considered as distorted only slightly. The nearest surrounding of the yttrium cations is formed by eight oxygen anions, whereas the Y–O bond-lengths in the  $YO_8$



◀ Fig. 1. The unit cell of  $\text{YAlO}_3$  (YAP) crystal and orientations of the sample for measurement.

dodecahedra differ one from another, *e.g.*, in the range from 0.2284 to 0.2597 nm for YAP-1% Nd. Hence, the  $\text{YO}_8$  dodecahedra are considerably distorted with the bond-length distortion equal to 3.15 [4].

## 2.2. Crystal growth and experimental techniques

Single crystals of  $\text{YAlO}_3$  doped with manganese were grown by the Czochralski method in the Institute of Physics, Polish Academy of Sciences. The crystals were grown in a pure nitrogen atmosphere from a melt containing 4 mol% more yttrium than aluminium oxide in comparison with the stoichiometric composition. The manganese concentration in the  $\text{YAlO}_3\text{:Mn}$  crystal studied corresponds to 0.2 mol% in the melt with respect to aluminium content. Single crystals of  $\text{YAlO}_3$  doped with cobalt also were grown by the Czochralski method. Yttrium alumina compound  $\text{YAlO}_3$  (YAP) melts congruently at 1870 °C and the growth process is carried out from stoichiometric composition. As raw materials  $\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and dopant ions (Co, rare-earth elements) in the form of oxides of purity 4N (99.99%) were used.

EPR measurements were performed on the  $\text{YAlO}_3\text{:Mn}$  samples cut out from the as-grown single crystals in the directions parallel to the crystallographic axes (*a*, *b* and *c*) with the dimensions of 3×4×4.5 mm, respectively. The EPR spectra were investigated in a wide range of temperatures from 100 K to 300 K using an EPR X-band spectrometer (Bruker multifrequency and multiresonance FT-EPR ELEXSYS E580). Measurements at low temperatures were carried out using a helium cryostat (3.8 K to 400 K with the Helium Temperature Control System ER4112HV). The samples were rotated in the resonance cavity using a one-degree goniometer. Changes of the rotation plane were realized by changing the sample position on the sample holder. The accuracy of the sample setting in each new plane was verified by a series of preliminary control measurements, which enabled comparing and matching the EPR spectrum

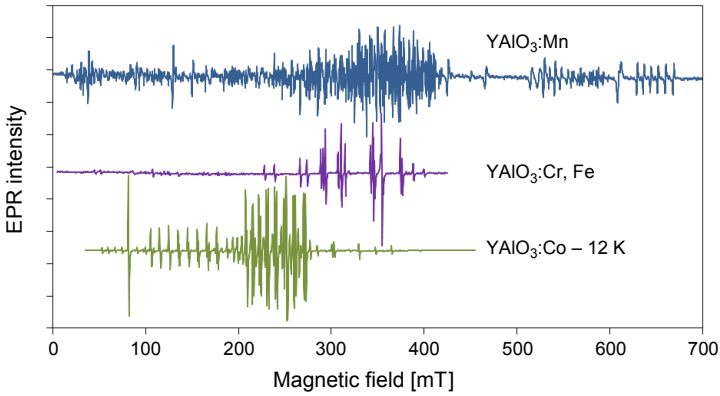


Fig. 2. EPR spectra of Co<sup>2+</sup> ions in YAP crystals at 12 K and Mn ions at room temperature in YAP crystals in different orientations. EPR spectra of Cr<sup>3+</sup> and Fe<sup>3+</sup> in YAP crystals doped Co<sup>2+</sup> ions at room temperature.

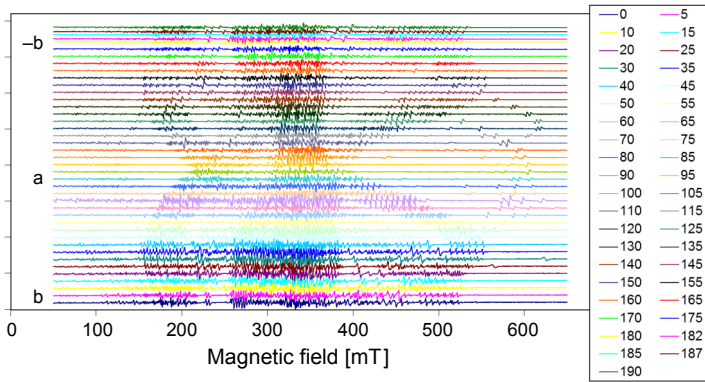


Fig. 3. Angular dependence of the EPR spectra for YAlO<sub>3</sub>:Mn with the magnetic field in the *ba* plane.

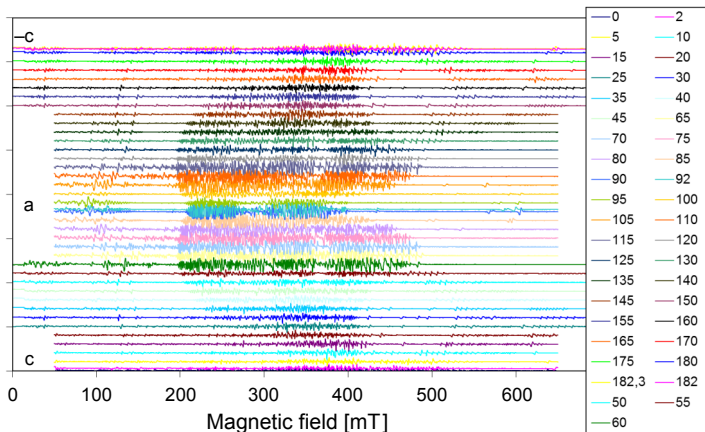


Fig. 4. Angular dependence of the EPR spectra for YAlO<sub>3</sub>:Mn with the magnetic field in the *ca* plane.

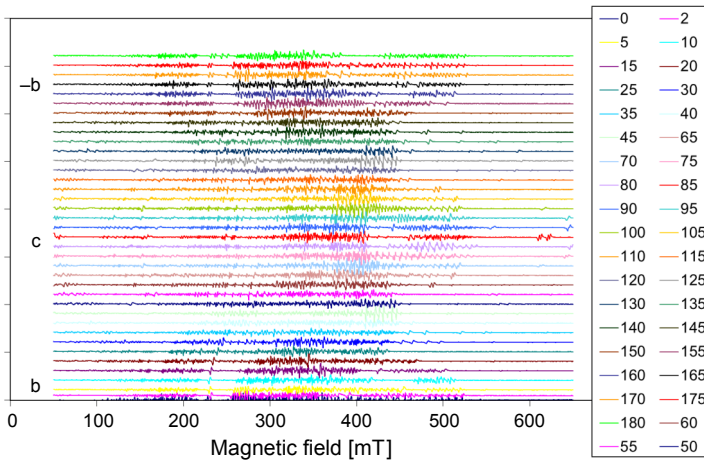


Fig. 5. Angular dependence of the EPR spectra for  $\text{YAlO}_3\text{:Mn}$  with the magnetic field in the  $bc$  plane.

along one common axis in the new plane with that in the previous plane. Subsequent corrections of the sample setting were made by adjusting the gluing of the sample to the holder.

Representative EPR spectra for  $\text{YAlO}_3\text{:Co}$ ,  $\text{Mn}$  samples are presented in Fig. 2. At room temperature for the crystals doped cobalt, we do not observe the spectrum derived from  $\text{Co}^{2+}$  ions. However, visible are spectra of unintentional dopants  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  ions. For the  $\text{YAlO}_3\text{:Mn}$  samples, the angular dependence of EPR spectra and their anisotropy were studied in the three crystallographic planes:  $ab$ ,  $bc$ , and  $ca$ . The angular variations of EPR spectra are presented in Figs. 3–5.

### 2.3. Analysis of EPR spectra

Analysis of EPR spectra enables assignment of specific lines to various paramagnetic centers as follows. The two distinct groups of EPR lines observed (see Figs. 3–5) were identified as due to  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  ions. Thus the angular variations of EPR spectra for  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  ions are similar to those presented in our earlier paper [15]. Four sets of lines were observed for each type of ions, which occupy four crystallographically equivalent but magnetically inequivalent positions in the YAP unit cell, which consists of four aluminium-oxygen pseudo-cells each with a different orientation with respect to the crystallographic axes. The next group of EPR spectra is assigned to a manganese ion. Four sets of lines of 150–600 mT were observed for  $\text{Mn}^{4+}$  ions, which occupy four crystallographically equivalent but magnetically inequivalent positions in the YAP unit cell. The next group of EPR lines of 250–400 mT is assigned to the  $\text{Mn}^{2+}$  ion and takes two crystallographically equivalent but magnetically inequivalent positions in the YAP unit cell. EPR spectra of  $\text{Co}^{2+}$  ions in YAP are observed only at temperatures below 30 K.

The electron configuration of  $\text{Mn}^{2+}$  ion is  $3d^5$  (state  $S$ ). In the case of  $d^5$  metal ions, it is known that the axial distortion of octahedral symmetry gives rise to three Kramers

doublets  $|\pm 5/2\rangle$ ,  $|\pm 3/2\rangle$ , and  $|\pm 1/2\rangle$  [19]. For the  $\text{Mn}^{4+}$  ions we have two Kramers doublets  $|\pm 3/2\rangle$  and  $|\pm 1/2\rangle$ . An application of Zeeman field eliminates the spin degeneracy of the Kramers doublets. For sufficiently high  $|D|$  ( $|D| > |A|$ ), the EPR spectrum of  $\text{Mn}^{2+}$  features five separate “allowed” fine structure components:  $M = \pm 5/2 \leftrightarrow \pm 3/2$ ,  $M = \pm 3/2 \leftrightarrow \pm 1/2$  and  $M = 1/2 \leftrightarrow -1/2$ , where  $M$  is the magnetic quantum number of the electron spin  $S$ . Each fine structure multiplet splits into six “allowed” hyperfine components with  $\Delta m = 0$  ( $m = -I, \dots, I$ ). The hyperfine structure originates from the interaction between the manganese electron cloud and the  $^{55}\text{Mn}$  nucleus (100% natural abundance) with spin  $I = 5/2$ .

A full analysis of the spectrum of Mn ions in the crystal  $\text{YAAlO}_3$  will be presented in a separate work.

The identification of EPR spectra of Mn ions was conducted with the use of the computer program EPR-NMR (version 6.5 [20]), similarly as the calculation of the angular dependence of  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$  ions in YAP crystals. The temperature dependence of the EPR spectra of Mn ions in YAP crystal is presented in Fig. 6.

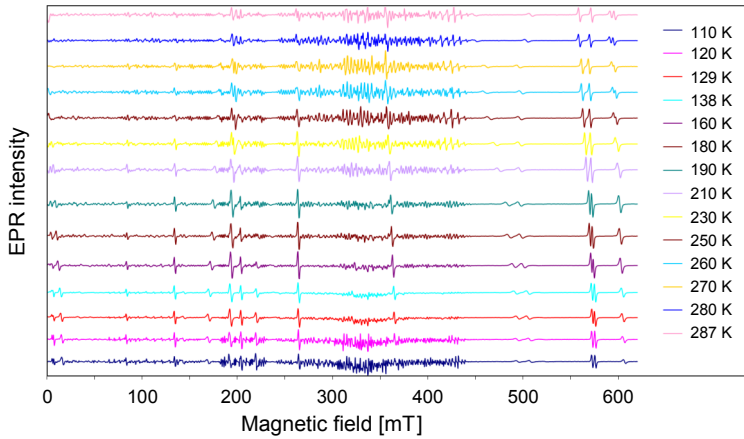


Fig. 6. Temperature dependence of the EPR spectra for Mn ions in YAP crystals.

The temperature dependence of the EPR line intensities and that of the peak-to-peak line widths were also measured. From these measurements, the values of the broadening ( $\Delta B$ ) of the EPR lines, *i.e.*, the spin-phonon part of the EPR line width [21], can be determined.

The observed line intensity for the  $\text{Mn}^{4+}$  complex (Fig. 6) shows the behavior typical for the paramagnetic saturation process. The observed increase in the line widths with increasing temperature can be attributed to the  $\text{Mn}^{4+}$  relaxation time. The estimation of the spin-lattice relaxation time  $T_1$  can be made using the conventional method of line broadening [19] using the following expression [21]:

$$T_1^{-1} = 2.8 \times 10^{10} \pi g \Delta B \quad (1)$$

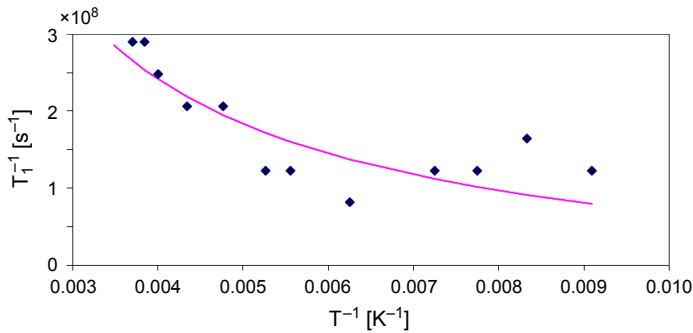


Fig. 7. Temperature dependence of the spin-lattice relaxation time  $T_1$  for  $\text{Mn}^{4+}$  ions in YAP crystal; the solid line represents an exponential fit using Eq. (2) with  $A = 12 \times 10^{10} \text{ s}^{-1}$ , and  $\delta = 70 \text{ cm}^{-1}$ .

In the temperature range 110–290 K the relaxation time  $T_1$  is governed by the Orbach process [19, 21]:

$$T_1^{-1} = A \left[ \exp\left(\frac{\delta}{k_B T}\right) - 1 \right]^{-1} \quad (2)$$

where  $\delta$  represents the energy splitting between the ground  $\text{Mn}^{4+}$  state and the first excited state (in  $\text{cm}^{-1}$ ), whereas  $A$  is the constant characteristic for the Orbach process (in  $\text{s}^{-1}$ ). Figure 7 presents the experimental temperature dependence of  $T_1$  for the  $\text{Mn}^{4+}$  ion in YAP and a theoretical curve fitted using Eq. (2) with  $A = 12 \times 10^{10} \text{ s}^{-1}$  and  $\delta = 70 \text{ cm}^{-1}$ . The different temperature dependences indicate the different spin-lattice relaxation times, thus confirming the existence of the two distinct  $\text{Co}^{2+}$  complexes with structurally different environment in the unit cell [14]. It appears that the changes in the EPR line intensity with temperature observed for the  $\text{Co}^{2+}(\alpha)$  and  $\text{Co}^{2+}(\beta)$  complex are close to those for the  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  ions, respectively [14].

### 3. Conclusions

The results of X-band EPR measurements of  $\text{YAlO}_3$  (YAP) crystals doped with manganese ions are presented. The analysis of various characteristic features of the EPR spectra indicates that the impurity Mn ions are located at two crystallographically distinct sites, denoted here as the  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  complex.

The results of X-band EPR measurements of  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  ions in  $\text{YAlO}_3$  (YAP) crystals in the temperature range 100–300 K ( $\text{Mn}^{2+}$ ), and 1.8–40 K ( $\text{Co}^{2+}$ ) [15] are presented. The temperature and angular dependences of EPR spectra have been analysed using a triclinic spin Hamiltonian (SH) consisting of the electronic Zeeman and fine and hyperfine terms. Two distinct positions  $\alpha$  and  $\beta$  are identified for  $\text{Co}^{2+}$  complexes and ascribed to the substitutional  $\text{Co}^{2+}$  ions at the  $\text{Al}^{3+}$  and  $\text{Y}^{3+}$  sites, respectively.

The EPR spectra of YAP crystals doped with  $Mn^{4+}$  ions, as well as their analysis confirm the existence of paramagnetic  $Mn^{4+}$  centers, which occupy four magnetically inequivalent aluminum positions in the unit cell with the octahedral coordination exhibiting triclinic site symmetry and  $Mn^{2+}$  centers, which occupy two magnetically inequivalent yttrium positions in the unit cell.

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