

ESR has been used to study crystals of yttrium aluminum borate $\text{YAl}_3[\text{BO}_3]_4$, grown from solution in a $\text{PbF}_2\text{--B}_2\text{O}_3$ melt. $\text{YAl}_3[\text{BO}_3]_4$ is isostructural with $\text{NdAl}_3[\text{BO}_3]_4$ [1] and belongs to the symmetry group $D_3^7\text{--}R32$. The rhombohedral unit cell has the parameters $a = 9.288$, $b = 7.226$ Å [2]. The coordination polyhedra of Y^{3+} , Al^{3+} , and B^{3+} are respectively trigonal prisms, octahedra, and triangles, formed by oxygen ions; the Al octahedra form spirals along the [001] axis, joined to isolated B triangles and Y prisms [1].

The ESR spectra were recorded on a Varian IES-3B radiospectrometer at a frequency of 9.1 GHz with high-frequency modulation of the magnetic field, 100 kG. At 295 and 77°K the observed spectrum consisted of three lines, assigned to the axially symmetric center with an axis of symmetry parallel to the [001] axis, with width from the points of inflection 8–10 G and relative integral intensities 100:9:6. The orientation $H \parallel [001]$ corresponds to the resonance values $H_1 = 3.246$, $H_2 = 5465.5$ and $H_3 = 9276$ G ($T=77^\circ\text{K}$, $\nu = 9122$ MHz). Change in the orientation from $H \parallel [001]$ to $H \perp [001]$ corresponds to a change in the resonance values of the lines by -2.5 , $+7.5$, and 40 G respectively.

The resonance values of the magnetic field given here for the three lines are characteristic of the ESR spectrum of Pb^{3+} ions observed in calcite [3], ThO [4], CaF_2 [5], NaCl [6], and CaWO_4 [7]. The ratio of the integral intensities of lines 2 and 3 and line 1 corresponds to the abundance of the odd isotope ^{207}Pb (22.6%) and the even isotope (77.4%).

The Pb^{3+} ion with electronic configurations $6S^1$ is characterized by an electron spin $S = 1/2$ (state $^2S_{1/2}$) and the nuclear spin of the ^{207}Pb isotope is $I = 1/2$. Assuming that line 1 is due to the even isotopes of Pb^{3+} and is described by a spin Hamiltonian of the form

$$\hat{\mathcal{H}} = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y),$$

it is possible to determine the principal values of the g tensor, which were found to be

$$g_{\parallel} = 2.0079 \pm 0.0005; g_{\perp} = 2.0095 \pm 0.0005 (T = 77\text{K}).$$

Since for ^{207}Pb the hyperfine splitting has a value of the order of 10,000 G, the description of the HFS from the odd isotope requires the use of the Breit-Rabi equation for the weak field case [8]. The calculation of the resonance values of the magnetic field for the case of an axially symmetric spectrum was carried out in [7]:

$$H_1 = \frac{2h\nu}{g_{\parallel} \beta} \left[\frac{1 + (A_{\parallel}/h\nu)}{2 + (A_{\parallel}/h\nu)} \right] + \frac{h\nu}{2g_{\parallel} \beta} \left[\frac{(A_{\parallel}/h\nu)^2 - (A_{\perp}/h\nu)^2}{2 + (A_{\parallel}/h\nu)} \right], \quad H \parallel C; \quad (1)$$

$$H_1 = \frac{2h\nu}{g_{\perp} \beta} \left[\frac{1 + (A_{\perp}/h\nu)}{2 + (A_{\perp}/h\nu)} \right] - \frac{h\nu}{2g_{\perp} \beta} \left[\frac{(A_{\parallel}/h\nu)^2 - (A_{\perp}/h\nu)^2}{2 + (A_{\perp}/h\nu)} \right], \quad H \perp C. \quad (2)$$

Equations (1) and (2), and the above values of g_{\parallel} and g_{\perp} , found for the even isotopes, were used to carry out the computer calculation, with an accuracy of $1 \cdot 10^{-4} \text{ cm}^{-1}$. The following were obtained for the principal values of the HFS tensor:

$$A_{\parallel} = 1.3219; A_{\perp} = 1.3224 \text{ cm}^{-1}.$$

Using these values, it is possible to find the isotropic and anisotropic parts of the hyperfine interaction using the equations: $A_{\parallel} = a - 2b$, $A_{\perp} = a + b$. By substituting the values found for A_{\parallel} and A_{\perp} , we obtain: $a = 1.3222$; $b = 0.2 \cdot 10^{-3} \text{ cm}^{-1}$.

Table 1 gives the characteristics of the structural positions for the symmetry group $R32\text{--}D_3^7$ [9]. The symbol α denotes the type of structural position, G_{α} its symmetry point

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TABLE 1. Types of Structural Positions in the Structure R32-D₃⁷

α	2(a,b)	1(c)	2(d,e)	1(f)
G_α	$D_3(32)$	$C_3(3)$	$C_2(2)$	$C_1(1)$
K_α/K_α^M	1/1	2/2	3/3	6/6
Orientation of the axes	+++	---+	+---	----
Ion	Y ³⁺	B ³⁺	Al ³⁺	O ²⁻

group, and K_α and K_α^M the number of structurally equivalent and magnetically equivalent differently oriented positions. The signs + and - correspond to the presence or absence of magnetic axes coinciding with the crystallographic axes of type [100].

The observed center corresponds to only one Pb³⁺ center in the unit cell, and the magnetic axis z coincides with the crystallographic axis [001]. Thus the Pb³⁺ ions in the YAl₃[BO₃]₄ structure occupy the Y³⁺ positions.

YAl₃[BO₃]₄ crystals containing a small quantity of Pb³⁺ have an orange color, the density of which increases in the same sense as the intensity of the ESR spectrum of Pb³⁺.

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