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Analysis of low symmetry aspects revealed by the zero-field splitting parameters and the crystal field parameters for Cr^{3+} ions doped into yttrium aluminum borate $YAl_3(BO_3)_4$ crystal

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ABSTRACT

Structural modeling has been carried out for Cr^{3+} centers in $YAl_3(BO_3)$, YAB, single crystal, which is a potential laser host material. Superposition model (SPM) analysis is applied to predict the zero-field splitting parameters (ZFSPs) the as well as the crystal field parameters (CFPs) for Cr^{3+} ions located at possible cation sites in YAB. Our analysis of the crystal structure data and the available EPR spectra has revealed considerable low symmetry features. These findings indicate an approximated nature of the previous interpretation of EPR spectra and necessitate their reconsideration taking into account low symmetry aspects. The theoretically predicted ZFSPs and CFPs corroborate the significance of low symmetry aspects. Comparison of the theoretical and experimental ZFSP values obtained from EPR measurements enables analysis of the structural distortions at the Y^{3+} and Al^{3+} sites. It is shown that the ZFSPs of the six-coordinated Cr^{3+} centers are well described by a structural model for the Y^{3+} and Al^{3+} sites based on the angular distortions of the surrounding oxygens. The results obtained from our SPM analysis support the earlier finding that Cr^{3+} ions substitute for Al^{3+} ions in $YAl_3(BO_3)$. The predicted ZFSPs and CFPs may be useful in future studies aimed at technological applications of the Huntite-type borates with the formula $RM_3(BO_3)_4$.

1. Introduction

Yttrium aluminum borate, $YAl_3(BO_3)_4$ (hereafter YAB), has been attracting a growing attention since it was discovered in the 1960s [1]. YAB crystals doped with rare-earth (RE) ions have great potential for applications in laser engineering [2,3] and nonlinear optics [4]. Among many interesting chemical and physical properties of YAB crystals, incommensurate phase [5], wide optical transparency [6], and defect-induced phase transitions [7] are of particular interest. Several investigations were devoted to YAB doped with RE ions, e.g. Nd^{3+} [8,9], Er^{3+} [10,11], Ce^{3+} [10], and Yb^{3+} [10]. The ground state of Gd^{3+} ions in YAB was also studied by EPR [12]. The crystal-field (CF) energy levels of Yb^{3+} [13] and Er^{3+} [14] ions in YAB were calculated using CF theory. These investigations generally indicated that the RE dopant ions occupy the trivalent yttrium site at the centre of a trigonally coordinated oxygen prism. However, a controversy still remained concerning the point symmetry group at the RE sites, which was taken as D_3 in [8,9,11] and D_{3h} in [10].

Since dopant ions may result in different laser wavelengths, YAB crystals doped with transition metal (TM) ions have also been investigated. Doping chromium into YAB crystal generates safe radiation for eyes (425–675 nm) [15]. It can be reasonably expected that Cr^{3+} ions substitute for Al^{3+} instead of Y^{3+} since no charge compensation is required and the Cr^{3+} ionic size (0.062 nm) is close to that of Al^{3+} (0.054 nm), whereas it is 0.134 nm for Y^{3+} [16–18]. EPR investigations of Cr^{3+} doped YAB single crystal at room temperature were carried out in [19] and recently in [20]. The spin Hamiltonian parameters reported in [19,20] were quite comparable, e.g. the zero-field splitting parameters (ZFSPs): $|D| = 0.52 \pm 0.02\ cm^{-1}$ and $|E| = 0.010 \pm 0.005\ cm^{-1}$ and the g-values: $g_x \approx g_y \approx g_z = 1.978 \pm 0.005$ [20]. The g factors of Cr^{3+} with the ground state $^4A_2$ in YAB were also theoretically calculated [21] and compared with the experimental ones [19,20].

The EPR spectra of Cr^{3+}:YAB were interpreted [19,20] assuming that Cr^{3+} ions locate at octahedral sites with an orthorhombic distortion. As discussed later, a closer analysis of EPR spectra [19,20] indicates, in fact, considerable low symmetry features. Moreover, it turns out that the symmetry apparently observed in EPR spectra does not conform to the crystallographic data. We have recently investigated Mn^{2+} doped YAB [22] and predicted that dopant Mn^{2+}

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ions replace Al^{3+} ions, while substitution increases the local symmetry around Al^{3+} sites from the actual monoclinic C_2 [1,23] to trigonal D_3. These findings indicate an approximated nature of the previous interpretation of EPR spectra [19,20] and necessitate reconsideration of the EPR data taking into account low symmetry aspects [24].

To the best of our knowledge, no theoretical investigations aimed at analysis of the ZFSPs determined by EPR for Cr^{3+} doped into YAB single crystal [19,20] have been carried out as yet. The present paper attempts to fill this gap. To this end, the semi-empirical superposition model (SPM) is applied to carry out theoretical analysis of the ZFSPs as well as the crystal field parameters (CFPs) for Cr^{3+} ions in YAB. The aims are as follows: (i) to estimate the ZFSP values for Cr^{3+} ions at all possible cation sites and clarify the parameter signs, (ii) to estimate the respective CFP values for Cr^{3+} ions and provide additional insight into low symmetry aspects, and (iii) to understand the structural distortion around the substitutional Cr^{3+} centers at various cation sites. The present considerations and the predicted ZFSPs and CFPs may be useful in future studies aimed at technological applications of the Huntite-type borates with the formula $RM_3(BO_3)_4$.

2. Crystallographic data and the axes systems

In order to calculate the ZFSPs (or CFPs) using SPM (see Sections 3 and 4), the ligand bond lengths (R_i) and the angular positions (θ_i and φ_i) of the six (nearest neighbor) O^{2-} ligands around the transition ion in YAB must be determined in a well specified axis system. Our analysis [22] of the crystallographic data [1,23] and the local site symmetry (LSS) indicates that in YAB there exist three Al sites with monoclinic C_2 symmetry. The LSS is trigonal D_3 for Y sites, whereas trigonal D_3 and monoclinic C_2 for B sites. Since the crystallographic axis system (CAS), ($a = b$, c) with the angle between a and b equal to 120° is not Cartesian, instead of the a-axis the a^*-axis is adopted as perpendicular to the b- and c-axis (see Fig. 1). The three Al sites are crystallographically equivalent but magnetically inequivalent, i.e. they are related by symmetry operations. The local symmetry-adapted axis systems (SAAS) are mutually rotated by 120° about the c-axis. Hence, the SAAS adopted for one Al site is suitable only for that particular site. In our calculations we adopt the SAAS for the Al-II site with the monoclinic C_2 axis oriented along the b-axis, i.e. ($x||a^*$, $y||b$, $z||c$). This SAAS with $C_2||b||y$-axis is suitable only for that particular site (and also for the Y sites). Importantly, the adopted orientation of the monoclinic

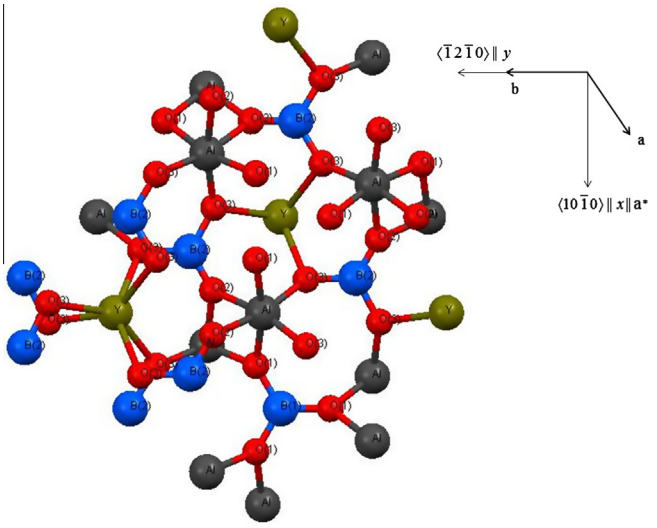

Fig. 1. Crystal structure of YAB along the c-axis. The positions of the ions in the YAB structure are indicated.

C_2 axis w.r.t. the axes (x, y, z) determines the particular form out of the three possible monoclinic forms [25] of the CF [26–28] and ZFS Hamiltonians [29,30] (see Section 3).

A note of caution is pertinent concerning the rhombic symmetry apparently observed in EPR spectra [19,20]. The EPR measurements of Cr^{3+} ion doped YAB crystal [20] indicate that the principal magnetic z-axes of the Cr^{3+} ions at the three Al^{3+} sites are oriented along the crystallographic c-axis, i.e. the ⟨0001⟩-direction, whereas the principal z-, x- and y-axes of the spectra were in the ⟨0001⟩, ⟨10$\bar{1}$0⟩, and ⟨$\bar{1}$2$\bar{1}$0⟩ directions of the crystal, respectively. The crystallographic axes and their relations with other principal magnetic axes are depicted in Fig. 1. In view of the actual monoclinic C_2 symmetry at the Al sites, the rhombic axes, as observed in EPR spectra [20], may be considered only as the principal axis system (PAS) of the 2nd-rank ZFS terms. Likewise, the statement, quote [20]: 'There are three Al^{3+} octahedra in the unit cell, which have trigonal symmetry about the c-axis is not quite true. The local trigonal as well as orthorhombic site symmetry may be considered only as an approximation, moreover since the monoclinic C_2 axis is not parallel to the c-axis. Additionally, according to group theory there is no direct descend in symmetry from trigonal point symmetry groups to an orthorhombic one; such descend is possible only to monoclinic or triclinic point symmetry groups. Implications of taking into account low symmetry aspects [24] for interpretation of the EPR data as well as for SPM calculations are considered in Sections 3 and 4.

Our SPM calculations in see Section 4 were carried out using the axis system (AS) for the Al-II site, and thus the monoclinic axis C_2 is parallel to the axis $y||b$. Hence, if this AS is used for the Al-I and Al-III sites, the apparent triclinic ZSFPs (or CFPs) should appear. However, if we select the AS so that $C_2||a$, i.e. rotation by −30° about the c-axis for the Al-I site, whereas by +30° for the Al-III site, then in the AS ($x||a$, $y||b^*$, $z||c$) again only the monoclinic ZSFPs (or CFPs) should appear. In the AS for the Al-II site the calculated values of the coordinates (R_i, θ_i, φ_i) for the six O^{2-} ligands in the $[Cr–O_6]^{9-}$ octahedral cluster for each cation site in YAB crystal are – for Y sites: (0.23026 nm, 124.812°, −142.089°), (0.23026 nm, 55.188°, −157.911°), (0.23026 nm, 55.188°, −37.911°), (0.23026 nm, 55.188°, 82.089°), (0.23026 nm, 124.812°, 97.911°), (0.23026 nm, 124.812°, −22.089°), whereas for Al sites: (0.19156 nm, 50.982°, 7.535°), (0.19156 nm, 129.018°, 172.465°), (0.19563 nm, 51.942°, 113.940°), (0.19563 nm, 128.058°, 66.060°), (0.18819 nm, 125.673°, −52.491°), (0.18819 nm, 54.327°, −127.509°). For the two structurally different boron sites in the $[Cr–O_3]^{3-}$ clusters we obtain – for B(1) site: (0.139395 nm, 90°, 60°), (0.139395 nm, 90°, 180°), (0.139395 nm, 90°, 300°), whereas for for B(2) site: (0.125455 nm, 90°, 0°), (0.140338 nm, 94.4358°, 178.065°), (0.140338 nm, 85.5642°, 224.048°).

3. Spin Hamiltonian, CF Hamiltonian, and SPM analysis

The EPR spectra [19,20] were analyzed assuming orthorhombic site symmetry for Cr^{3+}($S = 3/2$) centers and using the conventional spin Hamiltonian (SH) involving the ZFSPs: D and E [31,32]. Since the background theory utilized here follows that in our previous papers [24,26–30], we only briefly recap the basic notation. In general, SH form may be expressed in the extended Stevens operators [33,34] as [24,31,32]:

$$H = H_{Ze} + H_{ZFS} = \mu_B \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \sum B_k^q O_k^q(S_x, S_y, S_z)$$
$$= \mu_B \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \sum f_k b_k^q O_k^q(S_x, S_y, S_z), \quad (1)$$

where $\mathbf{g}$ is the spectroscopic splitting factor, μ_B – Bohr magneton, $\mathbf{B}$- the applied magnetic field, $\mathbf{S}$- the effective spin operator, and B_k^q and b_k^q are ZFSPs associated with the extended Stevens operators O_k^q, whereas $f_k = 1/3$, 1/60, and 1/1260 are the scaling factors for $k = 2$,