Studies of the Angular Distortion around Ti^{3+} on the Trigonal (2a) Al^{3+} Site of $LaMgAl_{11}O_{19}$

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The angular distortion around the impurity Ti^{3+} on the trigonal (2a) Al^{3+} site of $LaMgAl_{11}O_{19}$ is theoretically studied from the perturbation formulas of the anisotropic g factors, $g_\parallel$ and $g_\perp$, for a $3d^1$ ion in trigonally distorted octahedra. Based on the studies, the metal-ligand bonding angle is found to increase from θ_H in the host (2a) Al^{3+} site to θ in the impurity center by about 2°, due to the local tightness around the larger Ti^{3+} replacing the smaller Al^{3+}. The theoretical results based on the above angular distortion are in reasonable agreement with the observed values.

Key words: Defect Structure; Gyromagnetic Factors; Crystal- and Ligand-Field Theory; Ti^{3+}; $LaMgAl_{11}O_{19}$.

1. Introduction

$LaMgAl_{11}O_{19}$ (LMA) crystals are currently of interest as laser and phosphor hosts [1 – 6], as good candidates for soft X-ray spectroscopy analysis [7] and substrates for superconductor thin films [8]. These properties, particularly optical properties, are closely related to defect structures of this material doped with transition-metal (or rare-earth) ions. For example, LMA:Ti^{3+} is regarded as a potential tunable laser material due to its strong Ti fluorescence, with a slightly longer lifetime and a substantially broader band than that in Ti doped sapphire [9]. To investigate the impurity energy levels in LMA:Ti^{3+}, electron paramagnetic resonance (EPR) experiments were carried out, and the gyromagnetic factors of various centers were measured [9]. Among them, the dominant (86% or 92% occupancy for Ti in as-grown or reduced samples) trigonal center exhibits significant g anisotropy Δg ($= g_\parallel - g_\perp \approx 0.16$), which was ascribed to the impurity Ti^{3+} occupying the trigonal (2a) Al^{3+} site in LMA [9]. These experimental data were analyzed with formulas for the g factors in trigonally distorted octahedra based on the crystal-field theory [9, 10]. However, in these calculations the local structure of the Ti^{3+} impurity center (or angular distortion) was not involved, and the contributions to the g factors from the cubic field splitting ($= 10Dq$) as well as the spin-orbit (S.O.) coupling coefficient of the ligand O^{2-} (which is comparable to that of Ti^{3+}) were not included. In order to obtain information about the local structure of this center and to explain its g factors more exactly, calculations were carried out with perturbation formulas of the g factors for a $3d^1$ ion in trigonally distorted octahedra based on the cluster approach. In these formulas, the contributions to the g factors from the S.O. coupling and the p orbitals of ligands are considered, and the related parameters are connected with the experimental optical spectra and the local structure of the studied system.

2. Calculations

LMA belongs to the hexagonal magnetoplumbite ($PbFe_{12}O_{19}$) type structure with space group $P6_3/mmc$. The host Al^{3+} site is usually occupied by trivalent transition-metal ions, such as Ti^{3+} and Cr^{3+}. There are three kinds of octahedral Al^{3+} sites for the doped Ti^{3+}, namely (2a), (4f) and (12k) sites, with D_{3d}, C_{3v} and C_s symmetry, respectively. The probabilities of Ti occupancy of these sites are, respectively, 86% (92%), 2% (1%) and 12% (7%) in as-grown (reduced) samples [9]. Obviously, studies on the g factors and local structure for the predominant trigonal (2a) Ti^{3+} center are of great importance.

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For a $3d^1$ (Ti^{3+}) ion in trigonally distorted octahedra, its ground orbital triplet $^2T_{2g}$ of cubic case would be split into an orbital doublet ^2E_g and a singlet $^2A_{1g}$, with the $^2A_1$ lying lowest [10]. Since the S.O. coupling coefficient ($\approx 136\ \text{cm}^{-1}$ [11]) of the ligand O^{2-} is comparable to that ($\approx 154\ \text{cm}^{-1}$ [12]) of Ti^{3+}, the contributions to the g factors from the S.O. coupling and the p orbitals of the ligands may be included, as pointed out in [13 – 17].

The two-S.O.-coupling-coefficient formulas of the g factors, $g_\parallel$ and $g_\perp$, for a $3d^1$ ion under octahedral trigonal symmetry can be derived with the cluster approach, i. e. [18]

$$g_\parallel = g_0 - (g_0 + k)\zeta^2/{D_2}^2, \tag{1}$$

$$g_\perp = g_0 - 2k\zeta/D_2 - 4k'\zeta'/D_1 - (g_s - 2k)\zeta^2/(2{D_2}^2),$$

where g_0 ($= 2.0023$) is the pure spin value, D_1 is the energy difference between the ground state $^2A_{1g}$ and the original ^2E_g state of the cubic case, and D_2 is that between $^2A_{1g}$ and the excited state ^2E_g due to trigonal splitting of the cubic $^2T_{2g}$ state [10, 19]. They can be written in terms of the cubic field parameter Dq and the trigonal field parameter V as $D_1 = 10Dq$ and $D_2 = V$ [19]. The parameter Dq is related to the optical spectral data, and V can be calculated from the local structure of the impurity center. The latter is characteristic of trigonal distortion and related to the impurity-ligand bonding angle of the studied system.

The S.O. coupling coefficients ζ, ζ' and the orbital reduction factors k, k', based on the cluster approach, can be expressed as

$$\begin{aligned}
\zeta &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2),\\
\zeta' &= (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2),\\
k &= N_t(1 + \lambda_t^2/2),\\
k' &= (N_tN_e)^{1/2}(1 - \lambda_t\lambda_e/2),
\end{aligned} \tag{2}$$

where ζ_d^0 and ζ_p^0 are the S.O. coupling coefficients of a free $3d^1$ and a ligand ion, respectively. N_γ and λ_γ ($\gamma = t_{2g}$ or e_g denotes the irreducible representation of an O_h group) are, respectively, the normalization factors and the mixing coefficients, which satisfy the normalization condition [13 – 15]

$$N_\gamma(1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2) = 1. \tag{3}$$

Here $S_{dp}(\gamma)$ is the group overlap integral.

Since there are no Racah parameters for a $3d^1$ ion, the normalization factors of this work are approximately estimated from those of other Ti^{3+} clusters [18], i.e., $N_t \approx N_e \approx 0.767$ for the studied Ti^{3+} center, in consideration of the almost regular octahedral environment around Ti^{3+} [9] and hence little difference between orbital admixtures along various directions.

From the superposition model [20], the trigonal field parameter V is expressed as

$$\begin{aligned}
V = {}&(18/7)\bar{A}_2(3\cos^2\theta - 1)\\
&+ (40/21)\bar{A}_4(35\cos^4\theta - 30\cos^2\theta + 3)\\
&+ (40\sqrt{2}/3)\bar{A}_4\sin^3\theta\cos\theta,
\end{aligned} \tag{4}$$

where θ is the angle between the impurity-ligand bond and the C_3 (or c) axis, $\bar{A}_2$ and $\bar{A}_4$ are the intrinsic parameters (with the reference bonding length R). The relationships $\bar{A}_4 \approx (3/4)Dq$ and $\bar{A}_2/\bar{A}_4 \approx 10.8$ have been proved to be reasonable for many $3d^n$ ions in octahedral environments [20 – 23] and therefore adopted here.

Since the ionic radius r_i (≈ 0.76 Å [24]) of the impurity Ti^{3+} is by about 50% larger than the radius r_h (≈ 0.51 Å [24]) of the host Al^{3+}, the distance R and the angle θ would be different from the host Al^{3+}-O^{2-} bonding length R_H (≈ 1.885 Å [9]) and the angle θ_H ($\approx 51.49°$ [9]) on a (2a) site. Thus we can reasonably estimate R from the empirical formula [25]

$$R \approx R_H + (r_i - r_h)/2. \tag{5}$$

Then the distance $R \approx 2.01$ Å is obtained. From the distance R and the Slater-type SCF functions [26, 27], the group overlap integrals $S_{dp}(t_{2g}) \approx 0.0602$ and $S_{dp}(e_g) \approx 0.1494$ are calculated. Thus the parameters $\zeta \approx 134\ \text{cm}^{-1}$, $\zeta' \approx 84\ \text{cm}^{-1}$, $k \approx 0.890$ and $k' \approx 0.525$ are determined from (2) and (3).

According to the optical absorption spectra of LMA:Ti^{3+} we have $Dq \approx 2000\ \text{cm}^{-1}$ [9]. Substituting these parameters (including the host angle θ_H) into (1) and (4), the g factors are calculated as shown in Table 1.

One finds that the above g factors based on the host angle are larger than the observed values, suggesting that the trigonal distortion obtained from θ_H is too great to be regarded as suitable. Thus, the metal-ligand bonding angle in the impurity center may be expected to change a little by an angular distortion $\Delta\theta$ ($= \theta - \theta_H$), so as to decrease the trigonal distortion

Table 1. The gyromagnetic factors for the trigonal (2a) Ti^{3+} center in LMA at 20 K.

	Cal.[a]	Cal.[b]	Cal.[c]	Expt. [9]
$g_{\parallel}$	1.9606	2.0005	1.9675	1.9623
$g_{\perp}$	1.8165	1.9460	1.7905	1.7962

[a] Calculations based on the formulas in [9, 10] where the contributions from the cubic field splitting 10*Dq* and the S.O. coupling coefficient of the ligands are neglected.

[b] Calculations based on the host bonding angle θ_H and the perturbation formulas of (1) in this work.

[c] Calculations based on the angular distortion $\Delta\theta$ in (6) and the perturbation formulas of (1) in this work.

and hence the calculated g factors. By fitting the theoretical results to the observed values (at 20 K [9]), we have

$$\Delta\theta \approx 2.48^\circ \text{ or } \theta \approx 53.97^\circ. \tag{6}$$

The corresponding calculated g factors are shown in Table 1. For comparisons, the theoretical values based on the formulas of [9, 10] (where the contributions to the g factors from the cubic field splitting 10*Dq* and the S.O. coupling coefficient of ligands were not considered) are also calculated and collected in Table 1.

3. Discussion

Table 1 shows that the theoretical g factors based on the angular distortion $\Delta\theta$ in (6) and the perturbation formulas in (1) agree reasonably with the observed values, while those for absence of the angular distortion obtained in [9, 10] do not. There are several points that may be discussed.

1. The angular distortion $\Delta\theta$ ($\approx 2.48^\circ$) for the dominant trigonal (2a) Ti^{3+} center in LMA obtained in this work reveals that the impurity-ligand bonding angle is increased by about 2° relative to the corresponding host θ_H. This shows that substitution of the smaller Al^{3+} by the larger Ti^{3+} can induce considerable lattice tightness. Thus, the six impurity-ligand bonds are likely to lessen the local tension in this center. This yields an increase $\Delta\theta$ in the bonding angle and a decrease in the trigonal field parameter V (≈ 1260 cm^{-1}, which is comparable to the trigonal splitting (≈ 1200 cm^{-1}) of the $^2T_{2g}$ state obtained from the optical spectrum [9]) and consequently better results of the g factors [see (1) and Table 1]. Therefore, the local structure of this center can be described as the ligand octahedron transforming from significantly elongated ($\theta_H \approx 51.49^\circ$ [9]) in the host (2a) Al^{3+} site to slightly elongated ($\theta \approx 53.97^\circ$) around the impurity Ti^{3+}. Interestingly, similar angular increases ($\Delta\theta \approx 3^\circ \sim 5^\circ$) in D_{3d} impurity centers were also obtained for V^{2+}, Mn^{2+} and Ni^{2+} replacing the smaller Mg^{2+} in CsMgCl$_3$ from EPR analyses [15].

2. The theoretical results based on the angular distortion and the perturbation formulas (1) are by and large better than those based on the formulas in [9, 10]. In fact, the contributions ($-4k'\zeta'/D_1$) to $g_{\perp}$ from the cubic field splitting 10*Dq* are estimated to be about -0.011, while those from the S.O. coupling coefficient of ligands are found to be about 0.011 and 0.048 for $g_{\parallel}$ and $g_{\perp}$, respectively. Compared with those in [9, 10], the improvement of the calculated results in this work can be understood by considering the above contributions. On the other hand, the larger theoretical $g_{\parallel}$ of the present work than that of the experimental result is mainly due to the neglection of the higher (fourth-) order perturbation contributions. In general, the contributions to $g_{\parallel}$ from the fourth-order perturbation terms may be by about one order of magnitude smaller than those from the third-order perturbation ones, i. e., $g_{\parallel}^{(4)} \approx -0.004$. In consideration of this point, one can expect a better value of $g_{\parallel}$.

3. It is noted that the experimental g factors of this center at higher temperature (100 K) are slightly different from those at 20 K [9] cited in this work, i. e., $g_{\parallel}$ and $g_{\perp}$ vary by about 0.0035 and 0.0142, respectively. Based on the above studies, it can be expected that the bonding angle θ would decrease a little at the higher temperature, which leads to a slightly larger V and hence higher g factors. Still the theoretical study in this work can be regarded as valid.

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