Superposition Model for the Zero-field Splitting $b_2$ of Gd$^{3+}$ Ions in $\alpha$-LiIO$_3$ and LiNbO$_3$ Crystals

Wen-Chen Zheng$^{a,b}$ and Shao-Yi Wu$^{a,b}$

Department of Material Science, Sichuan University, Chengdu 610064, P. R. China
International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, P. R. China

Reprint requests for W. C. Z.: E-mail: zhengwenchen@netease.com

Z. Naturforsch. 57a, 749–752 (2002); received February 6, 2002

The zero-field splitting of Gd$^{3+}$ ions in $\alpha$-LiIO$_3$ and LiNbO$_3$ crystals are studied by the superposition model. The zero-field splittings $b_0^2$ for the trigonal Gd$^{3+}$ centers in both crystals are reasonably explained and the defect structures of these Gd$^{3+}$ centers are obtained. These defect structures are consistent with the expectation based on the electrostatic interaction models and agree qualitatively with the corresponding results obtained for similar trivalent paramagnetic (rare-earth and transition-metal) ions in $\alpha$-LiIO$_3$ and LiNbO$_3$ crystals.

Keywords: Electron Paramagnetic Resonance (EPR); Defect Structure; Superposition Model; Gd$^{3+}$; $\alpha$-LiIO$_3$; LiNbO$_3$.

1. Introduction

Crystals of LiNbO$_3$ and $\alpha$-LiIO$_3$, activated with transition metal and rare-earth ions, are of considerable interest because they can be used for optical devices (solid state lasers, holographic data storage, amplifiers, optical waveguides, etc.). Many methods have been used to study these active or impurity centers in the two crystals [1–12]. The EPR zero-field splittings $b_2^2$ for Gd$^{3+}$ ions (or the trigonal Gd$^{3+}$ centers) in $\alpha$-LiIO$_3$ [13] and LiNbO$_3$ [14] crystals were reported, however no theoretical investigations for these EPR data have been made. Since the zero-field splittings $b_2^2$ of paramagnetic impurities are sensitive to the local geometry of these impurity ions in crystals, useful information on the defect structures of the trigonal Gd$^{3+}$ centers in $\alpha$-LiIO$_3$ and LiNbO$_3$ crystals can be obtained by studying these EPR data. So the theoretical investigations of zero-field splittings $b_2^2$ for Gd$^{3+}$ ions in both crystals are of interest and intriguing. In this paper, we explain the zero-field splittings $b_2^2$ and study the defect structures for the trigonal Gd$^{3+}$ centers in $\alpha$-LiIO$_3$ and LiNbO$_3$ crystals with the superposition model. The results are discussed.

2. Superposition Model

The empirical superposition model [15, 16] has been successfully used to explain the zero-field splittings of S-state (4f$^7$, 3d$^5$)-ions in crystals. The model assumes that the zero-field splitting $b_2^m$ is given by a sum of axially symmetry contributions of the $n$ ligands of the MX$_n$ cluster only, i.e. [15, 16]

$$b_2^m = \sum_i b_2(R_i) \left( \frac{R_0}{R_i} \right)^{t_m} K_{2n}^m(\theta_i, \phi_i),$$

(1)

where $K_{2n}^m(\theta_i, \phi_i)$ are the coordination factors [15, 16]. Thus, for S-state ions in the trigonal MX$_s$ cluster, we have

$$b_2^s = \left( \frac{3}{2} \right) b_2(R_{ij}) \left[ \left( \frac{R_0}{R_{ij}} \right)^{t_s} \left( 3 \cos^2 \theta_i - 1 \right) \right. \left. + \left( \frac{R_0}{R_{ij}} \right)^{t_s} \left( 3 \cos^2 \theta_j - 1 \right) \right],$$

(2)

where $R_i$ ($i = 1, 2$) is the metal-ligand distance and $\theta_i$ is the angle between $R_i$ and the $C_3$ axis of the studied trigonal MX$_s$ cluster in the crystal. $t_s$ is the power-law exponent and $b_2(R_{ij})$ is the intrinsic parameter with the reference distance $R_0$. For the Gd$^{3+}$--O$^2$--combination [17] we have $t_s \approx 2.5 \pm 1.5$.
and \( b_0(R_0) \approx -(2000 \pm 500) \cdot 10^{-4} \text{cm}^{-1} \) with \( R_0 \approx 2.699 \) Å.

3. Calculation for \( \alpha\text{-LiIO}_3: \text{Gd}^{3+} \)

Similar to trigonal iron-group ions (e.g. \( \text{Cr}^{3+} \) and \( \text{Fe}^{3+} \) [10, 11, 18]) and \( \text{Er}^{3+} \) [19] in \( \alpha\text{-LiIO}_3 \) crystals, \( \text{Gd}^{3+} \) substitutes for \( \text{Li}^+ \) in this lattice, and the excess charge compensation is performed by two nearest \( \text{Li}^+ \) vacancy (\( V_{\text{Li}} \)) along the \( C_3 \)-axis. Since the effective charge of the cation vacancy \( V_{\text{Li}} \) is negative, the \( \text{Li}^+ \) and \( \text{O}^{2-} \) in the vicinity of \( V_{\text{Li}} \) should be displaced from their equilibrium positions because of the electrostatic interactions between \( V_{\text{Li}} \) and these ions. The radiofrequency discrete saturation (RFDS) studies [13] are suggested that for the \( \text{Gd}^{3+} \) center in \( \alpha\text{-LiIO}_3 \) the two nearest- \( \text{Li}^+ \) ions along the \( C_3 \)-axis are shifted towards the neighbouring vacancy \( V_{\text{Li}} \) by 0.57 and 0.25 Å, respectively, from the equilibrium position owing to the electrostatic attraction between \( \text{Li}^+ \) and \( V_{\text{Li}} \). However, the displacement \( \Delta X \) away from the \( V_{\text{Li}} \) for the six nearest \( \text{O}^{2-} \) ions (i.e., the ions in the planes between \( \text{Gd}^{3+} \) and \( V_{\text{Li}} \)), and hence the defect structure of the trigonal \( \text{Gd}^{3+} \) center in \( \alpha\text{-LiIO}_3 \) were not reported. Considering the \( \text{O}^{2-} \) displacement \( \Delta X \) caused by the electrostatic repulsion between \( \text{O}^{2-} \) and \( V_{\text{Li}} \), the structural parameters \( R_i \) and \( \theta_i \) for the trigonal \( \text{Gd}^{3+} \) center in \( \alpha\text{-LiIO}_3 \) can be calculated from the structural data \( R_{\text{i}} \approx 2.13 \) Å, \( R_{\text{i}} (\approx 2.11 \) Å), \( \theta_{\text{i}} (\approx 52.05^\circ) \) and \( \theta_{\text{i}} (\approx 52.90^\circ) \) of the host \( \text{LiIO}_3 \) cluster in \( \alpha\text{-LiIO}_3 \) [20] and the displacement \( \Delta X \). By fitting the calculated zero-field splitting \( b_0^2 \) from the superposition model to the observed value, we obtain the displacement

\[
\Delta X \approx 0.098 (29) \text{ Å}.
\]

Table 1. Zero-field splittings \( b_0^2 \) (in unit of \( 10^{-4} \text{cm}^{-1} \)) for the trigonal \( \text{Gd}^{3+} \) centers in \( \alpha\text{-LiIO}_3 \) and \( \text{LiNbO}_3 \) crystals.

<table>
<thead>
<tr>
<th></th>
<th>Calculation\textsuperscript{a}</th>
<th>Calculation\textsuperscript{b}</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha\text{-LiIO}_3 )</td>
<td>141.2</td>
<td>141.3</td>
<td>141.6 [23]</td>
</tr>
<tr>
<td>( \text{LiNbO}_3 )</td>
<td>1188</td>
<td>1183</td>
<td>1185 (13)</td>
</tr>
</tbody>
</table>

\( \text{a} \) Calculated by considering the ligand- or \( \text{Gd}^{3+} \)-displacement but neglecting the radial extension of the impurity-ligand distances

\( \text{b} \) Calculated by considering the ligand- or \( \text{Gd}^{3+} \)-displacement and the radial extension of the impurity-ligand distances.

\( \text{Nb}^{5+} \), vacancy, \( \text{Li}^+ \) etc. [21]. So, the impurity ions, such as rare-earth and transition-metal ions, max occupy different sites. Since the impurity ions can influence strongly the properties of \( \text{LiNbO}_3 \) crystals, knowledge of the location of the impurity and the defect structure of the impurity center are of importance. Rutherford backscattering spectrometry (RBS/channeling), X-ray standing wave (XSW), proton-induced x-ray emission (PIXE), extended x-ray absorption fine structure (EXAFS), electron nuclear double resonance (ENDOR) and EPR measurements [1–7, 11] were used to study the lattice locations and defect structures for many rare-earth and transition-metal ions in \( \text{LiNbO}_3 \). It is found that all these divalent, trivalent and tetravalent paramagnetic impurity ions occupy \( \text{Li}^+ \) octahedral sites. So, although the lattice location of \( \text{Gd}^{3+} \) in \( \text{LiNbO}_3 \) was not reported, we can suggest reasonably that \( \text{Gd}^{3+} \), like the other paramagnetic ions, occupies the \( \text{Li}^+ \) octahedral sites. In the \( \text{LiNbO}_3 \) structure, since the electrostatic repulsive forces between \( \text{Li}^+ \) and \( \text{Nb}^{5+} \) pair displace the cations from the centers of symmetry of their oxygen octahedra, the positions of \( \text{Li}^+ \) and \( \text{Nb}^{5+} \) are eccentric and closer to the distinctive neighbouring vacant octahedra [11, 21]. If \( \text{Li}^+ \) is replaced by the impurity ion carrying extra charge, the impurity ion should not occupy exactly the site of \( \text{Li}^+ \), but is further displaced by \( \Delta Z \) away from the center of octahedron along the \( C_3 \)-axis because the electrostatic repulsive force acting on the impurity is greater. This has been confirmed by RBS/channeling, XSW, EXAFS and EPR studies for many rare-earth and transition-metal ions in \( \text{LiNbO}_3 \) crystals [1–4, 11]. For rare-earth impurity ions in \( \text{LiNbO}_3 \), the displacement of the impurity from the \( \text{Li}^+ \) position is also strongly dependent upon the ionic radius of the impurity [1, 2]. For \( \text{Gd}^{3+} \) in \( \text{LiNbO}_3 \), the off-center displacement \( \Delta Z \) was not reported. According to the RBS/
channeling measurements [1], the displacement of the trivalent rare-earth impurity ion from the Li$^+$ position can be approximately regarded as a function of the ionic radius of the impurity. Thus, from the ionic radius of Gd$^{3+}$ [22], we can estimate the displacement to be $\Delta Z \approx 0.4$ Å. The local structural data $R$ and $\theta$ of a trigonal Gd$^{3+}$ center in LiNbO$_3$ can also be calculated from the structural parameters $R_0^b (\approx 2.238$ Å), $R_0^a (\approx 2.068$ Å), $\theta_0^b (\approx 44.57^\circ)$ and $\theta_0^a (\approx 69.74^\circ)$ of the LiO$_6$ octahedron in the host LiNbO$_3$ [21] and the displacement $\Delta Z$. If we apply the parameter $\frac{\theta_0^b}{R_0^b} \approx -2000 \times 10^{-6}$cm$^{-1}$ and $t_2 \approx 1$ (which are within the errors), the zero-field splitting $b_2^0$ for the trigonal Gd$^{3+}$ center in LiNbO$_3$ can be reasonably explained. The comparison of $b_2^0$ between calculation and experiment is also shown in Table 1.

5. Discussions

We have shown that the zero-field splittings $b_2^0$ for the trigonal Gd$^{3+}$ centers in a-LiIO$_3$ and LiNbO$_3$ crystals can be explained by taking into account suitable ligand (O$^-$ ions) displacements for a-LiIO$_3$; Gd$^{3+}$ and Gd$^{3+}$ displacements for LiNbO$_3$:Gd$^{3+}$. These displacements are consistent with expectations based on electrostatic interaction models and results obtained for similar trivalent paramagnetic impurities in the corresponding centers of both crystals [1 – 4, 10, 11, 18]. So, the above displacements and the superposition model parameters $b_2^0(R_0)$ and $t_2$ obtained in [17] can be regarded as reasonable.

It should be pointed out that the radial extension of the metal-ligand distances $R$, caused by the larger ionic radius ($\approx 0.938$ Å [22]) of Gd$^{3+}$ than that ($\approx 0.68$ Å [22]) of the replaced Li$^+$ ion for the Gd$^{3+}$ centers in both crystals are not considered in the above studies. In the previous papers, an approximate relationship [18, 23]

$$ R \approx R_{HI} + (r_i - r_{A2^0})/2 $$

was often used to estimate the impurity-ligand distance $R$ in the doped crystals ($R_{HI}$ is the metal-ligand distance in the host crystal, and $r_i$ and $r_{A2^0}$ are the ionic radius of the impurity and the replaced host ion, respectively). From this relationship, for a-LiIO$_3$; Gd$^{3+}$, we obtain $R_0^a \approx 2.259$ Å and $R_0^b \approx 2.239$ Å by considering the above radial extension. Thus, by fitting the calculated zero-field splitting $b_2^0$ to the observed value, we obtain

$$ \Delta X \approx 0.106 (35)$ Å.

The results is very close to the above value obtained by neglecting the radial extension of the distances $R_i$. Calculated and experimental values of $b_2^0$ are given in Table 1.

For LiNbO$_3$: Gd$^3$, we have $R_0^a \approx 2.367$ Å and $R_0^b \approx 2.197$ Å from (4). By slightly changing the power-law exponent $t_2$ from 1 to 1.2 (the latter is within the error of $t_2$), the calculated splitting $b_2^0$ agrees well with the observed value (see Table 1). Obviously, the consideration of the radial extensions of the metal-ligand distances does not change the above conclusions, and so these conclusions are suitable and rational.